

# Highly charged $W^{13+}$ , $Ir^{16+}$ , and $Pt^{17+}$ ions as promising optical clock candidates for probing variations of the fine-structure constant

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Transitions among the first three low-lying states in the highly charged  $W^{13+}$ ,  $Ir^{16+}$ , and  $Pt^{17+}$  ions are found to be strongly forbidden with wavelengths in the optical regime. By determining their energy levels, lifetimes, and other spectroscopic properties that are decisive quantities for estimating dominant systematics due to stray electromagnetic interactions in an experiment, we demonstrate that it can be possible to measure frequencies of the lowest forbidden transitions below a  $10^{-19}$  precision level in the above ions, and hence, they seem to be suitable for frequency standards. We employ a sophisticated relativistic coupled cluster method to carry out calculations of these properties of the above states involving  $4f$ - and  $5s$ -core orbitals. We also found, by estimating their relativistic sensitivity coefficients, that these clock transitions can be highly sensitive to the tiny drift in the fine-structure constant  $\alpha_e$ . Consequently, a clock based on one of these ions, particularly  $Pt^{17+}$ , could be used for corroborating the hypothesis of temporal and spatial variation in  $\alpha_e$ .

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## I. INTRODUCTION

The present frequency standard is based on the ground state hyperfine transition in  $^{133}\text{Cs}$ , but it operates in the microwave regime with an uncertainty of one part in  $10^{15}$  [1]. Several areas of science and technology, such as navigation systems [2,3], telecommunications [4], telescopes [5], testing fundamental physics [6], etc., demand more precise, accurate clocks, especially operating in the optical regime. This entails a search for new candidates that can offer atomic clocks with unprecedented accuracy. On the basis of ionic charges, the present optical clocks can be classified as either neutral atoms trapped in optical lattice dispositions or a singly charged ion confined in a Paul trap. The optical lattice based clocks thrive as the most stable clocks, because of their contrived line widths that can be manipulated to yield optimum stability by suitably choosing the strengths of the applied magnetic fields [7]. On the other hand, a singly charged ion can be isolated from the environmental perturbations using the developed sophisticated ion-trap techniques. Thereby, accuracies in the transition frequency measurements can be efficiently controlled in these ions making them expedient contenders for the atomic clocks. Today a single trapped  $\text{Al}^+$  ion is the most accurate atomic clock with a fractional uncertainty below  $10^{-17}$ . In fact, many experiments using other singly charged ions, such as  $\text{Hg}^+$ ,  $\text{Ca}^+$ ,  $\text{Sr}^+$ ,  $\text{Yb}^+$ , etc., are also in progress to surpass its limit [8,9]. However, it would be strenuous to suppress uncertainties below  $10^{-18}$  in the currently working atomic clocks due to practical limitations in controlling certain systematics during the measurements. This advocates a search for other suitable candidates where the systematic effects could be minuscule. In this context, a nuclear transition between the isomeric states of  $^{229}\text{Th}$  resonating with an atomic transition having a similar energy range has been suggested to build an ultimate clock with a precision less than  $10^{-19}$  [10]. It has

also been argued by Schiller *et al.* to consider ro-vibrational transitions in the one-electron molecular  $\text{H}_2^+$  and  $\text{HD}^+$  ions for making molecular clocks [11]. Several other molecules have also been theoretically investigated for their suitability to be considered for molecular clocks [12]. But, it has been realized from the estimated light shifts induced by the probe lasers that it would be challenging to surpass systematic uncertainties below  $10^{-16}$  precision in these molecular systems [11,12]. Fairly recently, highly charged ions (HCIs) are being suggested as alternative candidates for atomic clocks with the projection of exceptionally small uncertainty of below  $10^{-20}$  [13–17]. Since the atomic orbitals are greatly shrunk in HCIs, these systems are expected to be the least perturbed by the external electric and magnetic fields compared to their counter neutral and singly charged ions. Though a technique to trap a HCI is not developed yet, strategies to laser trap a multinumner of HCIs and to perform high precision measurements using them have already been demonstrated [18,19]. It may also be ideal to adopt a sympathetic cooling mechanism instead of laser cooling, as adopted in the  $\text{Al}^+$  clock [20], for HCIs. Thus, it seems with the advent of new technologies, one of the HCIs can be considered for developing an ultimate atomic clock. In this perspective it would of immense interest to search for suitable HCIs for clocks by analyzing various systematics in these ions. In the present study, we have analyzed the energy levels of the first three low-lying states and their other relevant spectroscopic properties of the heavy Pm-like highly charged  $W^{13+}$ ,  $Ir^{16+}$ , and  $Pt^{17+}$  ions to find out their aptness for being considered as atomic clocks. These results along with the properties of the other states in these ions reported in Refs. [17,21] would be very useful for the experimentalists to assess these ions as possible potential candidates for atomic clocks.

As an important application, atomic clocks are competent for establishing the constancy of certain dimensionless fundamental constants, such as the fine-structure constant  $\alpha_e$ , with time and space [6,8]. Since atomic transition frequencies are functions of  $\alpha_e$ , high precision measurements of clock frequencies at different times and various locations can yield

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signatures to ascertain such a hypothetical conjecture. Electrons in HCIs experience unusually enhanced relativistic effects and can be gauged by evaluating relativistic sensitivity coefficients  $q$  of their atomic transitions [22–25]. For unambiguous detection of subtle changes in transition frequencies due to  $\alpha_e$  variation, it would be judicious to contemplate transitions for which  $q$  are very large. Our evaluation demonstrates large  $q$  values in the proposed clock transitions, especially in  $\text{Pt}^{17+}$ . Hence, we suggest the considered ions are the pertinent candidates for probing plausible variation in  $\alpha_e$ .

To carry out calculations of the interested atomic properties precisely in the considered ions, we employ an all order perturbative method in the relativistic coupled cluster (RCC) theory framework using the Fock-space formalism that has been developed by us recently [23,24]. In contrast to the earlier studies on HCIs, where electron correlation effects are incorporated through either a hybrid method like configuration-interaction and many-body perturbation theory (CI + MBPT) or other variants of many-body methods [13–17], our RCC method treats correlation effects seen by all the electrons on an equal footing and obeys size extensivity behavior. We start our calculations using a Dirac-Hartree-Fock (DHF) method and incorporate electron-electron ( $e-e$ ) correlation effects over the DHF wave functions through the RCC method. Results at the intermediate level approximated methods, such as second order relativistic many-body perturbation theory [RMBPT(2) method], that have also been presented in order to investigate the propagation of correlation effects from the lower to the higher order method. It is, however, arduous to determine polarizabilities using the RCC method in the considered ions. We, therefore, employ an *ab initio* method in the third order relativistic many-body perturbation theory [RMBPT(3) method] approximation to calculate electric dipole  $\alpha_d^{E1}$  and magnetic dipole  $\alpha_d^{M1}$  polarizabilities in these systems. We discuss these methods very briefly in the next section.

## II. ONE ELECTRON DETACHMENT THEORY

Our intention in this work is to identify the first three low-lying energy levels of the heavy Pm-like highly charged  $\text{W}^{13+}$ ,  $\text{Ir}^{16+}$ , and  $\text{Pt}^{17+}$  ions reliably. Configurations of atomic states in these ions have one orbital less than the closed-core  $[4f^{14}]5s^2$ . Thus, the first three configurations with the lowest ionization potentials (IPs) from the above closed core can be obviously obtained by removing an electron from one of the outer  $4f_{5/2}$ ,  $4f_{7/2}$ , and  $5s$  orbitals resulting in  $4f^{13}5s^2\ ^2F_{5/2}$ ,  $4f^{13}5s^2\ ^2F_{7/2}$ , and  $[4f^{14}]5s\ ^2S_{1/2}$  configurations, respectively. These configurations can correspond to either the ground or the first two excited states of these ions depending on their energy values. Owing to the open-shell electronic structure of the above ions it is strenuous to calculate their energy levels. Moreover, HCIs generally manifest strong energy level crossings among their isoelectronic sequence.

For determining one of the above states, say  $|\Psi_a\rangle$ , in the Fock-space formalism, we express it as

$$|\Psi_a\rangle = \Omega_a |\Phi_a\rangle = (1 + \Omega_c + \Omega_a^v) |\Phi_a\rangle, \quad (1)$$

where the reference function  $|\Phi_a\rangle$  is constructed by  $|\Phi_a\rangle = a_a |\Phi_0\rangle$  with the DHF wave function  $|\Phi_0\rangle$  of the closed-core  $[4f^{14}]5s^2$ . Here  $\Omega_a$  is known as a wave operator, responsible

for creating configuration state functions by carrying out excitations from  $|\Phi_a\rangle$ . Conveniently, excitations from  $|\Phi_0\rangle$  are described by  $\Omega_c$ , setting aside  $a_a$  as a mute spectator. Then, the superfluous correlation effect that was appended through  $\Omega_c$  due to consideration of the removed electron in the closed core is redressed by  $\Omega_a^v$  acting upon  $|\Phi_a\rangle$ . The above DHF wave function is evaluated using the Dirac-Coulomb-Breit (DCB) Hamiltonian given by

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

with  $\boldsymbol{\alpha}$  and  $\beta$  are the usual Dirac matrices,  $V_n(r_i)$  is the nuclear potential seen by an electron at the position  $r_i$  that is calculated using the Fermi-charge distribution approximation,  $r_{ij}$  is the inter-electronic distance between the electrons present at  $r_i$  and  $r_j$  and  $\hat{\mathbf{r}}_{ij}$  is the unit vector along the inter electronic distance.

In a perturbative series expansion, the above defined wave operators can be written in a form

$$\Omega_c = \sum_{k>0} \Omega_c^{(k)} \quad \text{and} \quad \Omega_a^v = \sum_{k>0} \Omega_a^{v(k)}, \quad (3)$$

where the superscript  $k$  refers to the number of times residual interaction ( $V_r = H - H_0$ ) is accounted for in the calculations, for the DHF Hamiltonian  $H_0$  used to obtain  $|\Phi_0\rangle$  and  $|\Phi_a\rangle$ . In the RMBPT(2) method, we restrict  $k = 2$ . The  $k$ th order amplitudes for the  $\Omega_c$  and  $\Omega_a^v$  operators are obtained by solving the equations

$$[\Omega_c^{(k)}, H_0] P_0 = Q_0 V_r (1 + \Omega_c^{(k-1)}) P_0 \quad (4)$$

and

$$\begin{aligned} [\Omega_a^{v(k)}, H_0] P_a &= Q_a V_r (1 + \Omega_c^{(k-1)} + \Omega_a^{v(k-1)}) P_a - \sum_{m=2}^{k-1} \\ &\times \Omega_a^{v(k-m)} P_a V_r (1 + \Omega_c^{(m-1)} + \Omega_a^{v(m-1)}) P_a, \end{aligned} \quad (5)$$

where the projection operators  $P_0 = |\Phi_0\rangle\langle\Phi_0|$  and  $P_a = |\Phi_a\rangle\langle\Phi_a|$  represent the model space and  $Q_0 = 1 - P_0$  and  $Q_a = 1 - P_a$  describe the orthogonal space of the DHF Hamiltonian  $H_0$  for the closed core and without the electron  $a$  of the closed core, respectively. The above equation follows  $\Omega_c^0 = 0$  and  $\Omega_a^{v(0)} = 0$ . The energy of the state  $|\Psi_a\rangle$  is evaluated by using an effective Hamiltonian

$$H_a^{\text{eff}} = P_a H \Omega_a P_a = \sum_k H_{\text{eff}}^{(k)}, \quad (6)$$

with  $k$  in superscript is representing the order of  $V_r$  involved in the expansion of  $\Omega_a$ .

To evaluate polarizabilities, we use the expression

$$\alpha_d^O = -2 \frac{\langle\Psi_a|O|\Psi_a^{(1)}\rangle}{\langle\Psi_a|\Psi_a\rangle}, \quad (7)$$

where  $|\Psi_a^{(1)}\rangle$  is the first-order perturbed state wave function for the state  $|\Psi_a\rangle$  due to the corresponding electric or magnetic dipole operator  $O$ . Following Eq. (1),  $|\Psi_a^{(1)}\rangle$  is also expressed

as

$$|\Psi_a^{(1)}\rangle = (\Omega_c^{(1)} + \Omega_a^{v(1)})|\Phi_a\rangle, \quad (8)$$

where  $\Omega_a^{c(1)}$  and  $\Omega_a^{v(1)}$  are the first order perturbed wave operators to  $\Omega_a^c$  and  $\Omega_a^v$ , respectively. Similar to Eq. (3), we express in the perturbation analysis as

$$\Omega_c^{(1)} = \sum_{k>0} \Omega_c^{(k,1)} \quad \text{and} \quad \Omega_a^{v(1)} = \sum_{k>0} \Omega_a^{v(k,1)}, \quad (9)$$

with  $k$  representing the number of  $V_r$  involved.

We obtain amplitudes of the  $\Omega_c^{(1)}$  and  $\Omega_a^{v(1)}$  operators using the following equations

$$\begin{aligned} [\Omega_c^{(k,1)}, H_0]P_0 &= Q_0 O(1 + \Omega_c^{(k)})P_0 + Q_0 V_r \Omega_c^{(k-1,1)}P_0 \\ &\quad - \sum_{m=2}^{k-1} (H_{\text{eff}}^{(m)} \Omega_c^{(k-m,1)} - \Omega_c^{(k-m)} P_0 O \Omega_c^{(m)} P_0), \end{aligned} \quad (10)$$

and

$$\begin{aligned} [\Omega_a^{v(k,1)}, H_0]P_a &= Q_a O(1 + \Omega_c^{(k)} + \Omega_a^{v(k)})P_a \\ &\quad + Q_a V_r (\Omega_c^{(k-1,1)} + \Omega_a^{v(k-1,1)})P_a \\ &\quad - \sum_{m=2}^{k-1} [H_{\text{eff}}^{(m)} \Omega_a^{v(k-m,1)} - \Omega_a^{v(k-m,1)} \\ &\quad \times P_a O (\Omega_c^{(m)} + \Omega_a^{v(m)})P_a], \end{aligned} \quad (11)$$

respectively, where  $\Omega$  operators with a single superscript index correspond to an unperturbed wave operator. Now using the above wave operators, we evaluate Eq. (7) for  $\alpha_d^{E1}$  and  $\alpha_d^{M1}$  by considering up to two orders in  $V_r$  along with one  $O$  operator in the RMBPT(3) method approximation.

Recently, we have developed an all order RCC method to describe one electron detachment process in the Fock space framework. This method is apt to determine the aforementioned states adequately to carry out the intended analysis for atomic clocks [23,24]. In the RCC theory ansatz, the wave functions of the considered states are expressed as

$$|\Psi_a\rangle = e^T \{1 + R_a\} |\Phi_a\rangle \quad (12)$$

with  $\Omega_c = e^T - 1$  and  $\Omega_a^v = e^T R_a - 1$ , where  $T$  and  $R_a$  are the RCC excitation operators that are responsible for exciting electrons from the core  $[4f^{14}]5s^2$  and removing the correlation effect due to the extra electron that is being annihilated from the core, respectively. In this work, we have considered only the single and double excitations (known as the CCSD method in the literature), denoted by the subscripts 1 and 2, respectively, in the CCSD method approximation by expressing

$$T = T_1 + T_2 \quad \text{and} \quad R_a = R_{1a} + R_{2a}. \quad (13)$$

The amplitudes of these operators are evaluated using the equations

$$\langle \Phi_0^* | \bar{H}_N | \Phi_0 \rangle = 0 \quad (14)$$

and

$$\langle \Phi_a^* | (\bar{H}_N - \Delta E_a) R_a | \Phi_a \rangle = -\langle \Phi_a^* | \bar{H}_N | \Phi_a \rangle, \quad (15)$$

where  $|\Phi_0^*\rangle$  and  $|\Phi_a^*\rangle$  are the excited state configurations, here up to doubles, with respect to the DHF states  $|\Phi_0\rangle$  and  $|\Phi_a\rangle$ , respectively, and  $\bar{H}_N = (H_N e^T)_l$  with the normal order Hamiltonian  $H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle$  and subscript  $l$  representing for the linked terms only. Here  $\Delta E_a = H_c^{\text{eff}} - H_a^{\text{eff}}$  is the IP of the electron  $a$  that is being removed from  $H_c^{\text{eff}} = P_0 H (1 + \Omega_c) P_0$ . Following Eq. (6), the expression for  $\Delta E_a$  is given by

$$\Delta E_a = \langle \Phi_a | \bar{H}_N \{1 + R_a\} | \Phi_a \rangle. \quad (16)$$

We also include contributions from the important triply excited configurations by defining a perturbative operator as

$$R_{3a}^{\text{pert}} = \frac{1}{4} \sum_{pr,bdg} \frac{(H_N T_2 + H_N R_{2a})_{dga}^{prb}}{\varepsilon_b + \varepsilon_d + \varepsilon_g - \varepsilon_a - \varepsilon_p - \varepsilon_r}, \quad (17)$$

where  $\{b,d,g\}$  and  $\{p,r\}$  indices represent the occupied and virtual orbitals, respectively, and  $\varepsilon$ 's are their corresponding orbital energies. We account for its contributions considering it as a part of the  $R_a$  operator in Eq. (16) in the evaluation of  $\Delta E_a$  self-consistently along with the solution of Eq. (15). This approach is usually referred to as the CCSD(T) method in the literature.

Once any two given  $|\Psi_f\rangle$  and  $|\Psi_i\rangle$  states are obtained in the above procedure, the matrix element of an operator  $O$  between these two states is evaluated using the expression

$$\begin{aligned} &\frac{\langle \Psi_f | O | \Psi_i \rangle}{\sqrt{\langle \Psi_f | \Psi_f \rangle \langle \Psi_i | \Psi_i \rangle}} \\ &= \frac{\langle \Phi_f | \tilde{O}_{fi} | \Phi_i \rangle}{\sqrt{\langle \Phi_f | \{1 + \tilde{N}_f\} | \Phi_f \rangle \langle \Phi_i | \{1 + \tilde{N}_i\} | \Phi_i \rangle}}, \end{aligned} \quad (18)$$

where  $\tilde{O}_{fi} = \{1 + R_f^\dagger\} e^{T^\dagger} O e^T \{1 + R_i\}$  and  $\tilde{N}_{k=f,i} = \{1 + R_k^\dagger\} e^{T^\dagger} e^T \{1 + R_k\}$ . As can be seen, this expression contains two nontruncative series such as  $e^{T^\dagger} O e^T$  and  $e^{T^\dagger} e^T$  in the numerator and denominator, respectively. We evaluate these terms in several steps adopting the similar procedures as described in Refs. [23–28]. Instinctively, the expectation value of the operator  $O$  with respect to a state, say  $|\Psi_k\rangle$ , is evaluated by considering  $k = f = i$  in the above expression.

### III. RESULTS AND DISCUSSION

Energy level schemes of the highly charged W<sup>13+</sup>, Ir<sup>16+</sup>, and Pt<sup>17+</sup> ions have not been observed yet. Using our DHF, RMBPT(2), CCSD, and CCSD(T) methods, we have determined IPs of an electron from the  $4f_{7/2}$ ,  $4f_{5/2}$ , and  $5s$  orbitals in the  $[4f^{14}5s^2]$  configuration and given them in Table I. We also compare these results with the values listed in the National Institute of Science and Technology (NIST) database [29]. This shows the DHF method predicts larger values while the RMBPT(2) method lower values significantly. The CCSD method brings back the result closer to the NIST data, and the CCSD(T) method further improves the result almost agreeing with the available NIST data. The large differences in the calculations by all these methods indicate the electron correlation effects are very strong in these ions. Though our calculations are not reliable up to all the digits of the values specified in the above table, we present them

TABLE I. Calculated IPs of  $W^{13+}$ ,  $Ir^{16+}$ , and  $Pt^{17+}$  in  $\text{cm}^{-1}$  from the DHF, RMBPT(2), CCSD, and CCSD(T) methods by removing electrons from the  $4f_{5/2,7/2}$  and  $5s_{1/2}$  orbitals of  $[4f^{14}5s^2]$ . They are compared with the available NIST data [29]. More likely our CCSD(T) values are reliable only up to third significant digits.

State	DHF	RMBPT(2)	CCSD	CCSD(T)	NIST
$W^{13+}$					
$4f^{13}5s^2\ ^2F_{7/2}$	2099218	2052209	2077306	2089766	2083000(10000)
$4f^{13}5s^2\ ^2F_{5/2}$	2117989	2069023	2094944	2107732	
$4f^{14}5s\ ^2S_{1/2}$	2253835	2272836	2274550	2279044	
$Ir^{16+}$					
$4f^{13}5s^2\ ^2F_{7/2}$	3042208	2998093	3018285	3016205	2870000(140000)
$4f^{13}5s^2\ ^2F_{5/2}$	3068270	3022290	3043255	3041228	
$4f^{14}5s\ ^2S_{1/2}$	3033685	3053120	3054119	3054196	
$Pt^{17+}$					
$4f^{14}5s\ ^2S_{1/2}$	3315899	3335450	3336302	3336274	3160000(160000)
$4f^{13}5s^2\ ^2F_{7/2}$	3387653	3344199	3363318	3361134	
$4f^{13}5s^2\ ^2F_{5/2}$	3416518	3371212	3391070	3388933	

up to seven digits keeping in mind that NIST data have large uncertainties. Again, these values are very sensitive for the *ab initio* evaluation of various properties that are discussed later. We consider results obtained from the CCSD(T) method for an other required analysis as discussed below. Based on these data, we present the schematic energy level orderings among the  $4f^{13}5s^2\ ^2F_{5/2}$ ,  $4f^{13}5s^2\ ^2F_{7/2}$ , and  $[4f^{14}]5s\ ^2S_{1/2}$  states in Fig. 1 for the  $W^{13+}$ ,  $Ir^{16+}$ , and  $Pt^{17+}$  ions. We have also mentioned transition wavelengths  $\lambda$  among these levels from the excitation energies which are nothing but the differences between the IPs of the above states. As seen, these  $\lambda$ 's are lying either in the optical or near optical region where it is expected the lasers to be available for accessing the energy levels. Since transitions among the above states are highly forbidden and it also seems that they can be accessible by lasers, we consider this as one of the compelling reasons for endorsing the considered HCIs for optical clocks.

To establish further that the investigated ions have an edge over the other proposed HCIs for developing high precision atomic clocks, we also present here many crucial properties of these ions. We find the ground and the first excited states of  $W^{13+}$  and  $Ir^{16+}$  are  $4f^{13}5s^2\ ^2F_{7/2}$  and  $4f^{13}5s^2\ ^2F_{5/2}$ , respectively, while the ground and the first excited states of  $Pt^{17+}$  are  $4f^{14}5s\ ^2S_{1/2}$  and  $4f^{13}5s^2\ ^2F_{7/2}$ , respectively. Thus, they correspond to highly forbidden transitions and are anticipated to have very narrow natural line widths  $\delta\nu_{\text{nat}}$ . For a quantitative estimate of  $\delta\nu_{\text{nat}}$ , we determine lifetimes  $\tau$  of their first excited states by calculating transition amplitudes of the above clock transitions due to magnetic dipole  $M1$ , electric quadrupole  $E2$ , and electric octupole  $E3$  channels employing our CCSD(T) method.

In Table II, we present the estimated  $\lambda$ 's and line strengths  $S$  that are equal to the square of the transition amplitudes, due to various channels from our CCSD(T) method for the proposed

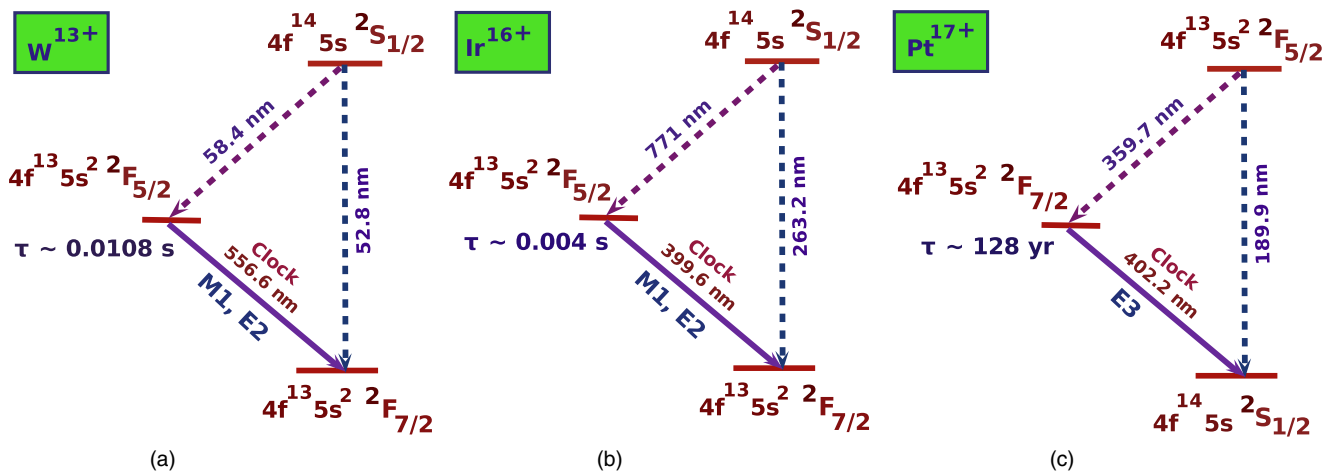


FIG. 1. Predicted first three low-lying energy levels in the Pm-like (a) W, (b) Ir, and (c) Pt ions. Lines with solid arrows represent the proposed clock transitions in the respective ions. These transitions are found to be almost in the optical region, where lasers are available for accessing them, and lifetimes of their first excited states are sufficiently large to carry out high precision measurements, especially on the  $Pt^{17+}$  ion.



TABLE II. Important properties of clock transitions in the considered HCIs, such as wavelengths  $\lambda$  in nm, line strengths  $S^O$  in a.u. for a respective operator  $O$ , and transition rates ( $A^O$  in  $s^{-1}$ ) evaluated using the CCSD(T) method. The derived lifetimes of the first excited states ( $\tau$ ), natural line width  $\delta\nu_{\text{nat}}$ , and quality factors  $Q$  of the respective clock transitions in W<sup>13+</sup>, Ir<sup>16+</sup>, and Pt<sup>17+</sup> are given at the end. Numbers given in the square brackets denote powers of 10.

Transition	$\lambda$	$O$	$S^O$	$A^O$
<b>W<sup>13+</sup></b>				
$4f^{13}5s^2\ ^2F_{5/2} \rightarrow 4f^{13}5s^2\ ^2F_{7/2}$	556.60	E2	0.024	8.61[−4]
		M1	3.549	92.53
<b>Ir<sup>16+</sup></b>				
$4f^{13}5s^2\ ^2F_{5/2} \rightarrow 4f^{13}5s^2\ ^2F_{7/2}$	399.6	E2	0.015	0.003
		M1	3.524	248.14
<b>Pt<sup>17+</sup></b>				
$4f^{13}5s^2\ ^2F_{7/2} \rightarrow 4f^{14}5s\ ^2S_{1/2}$	402.2	E3	0.107	2.47[−10]
	W <sup>13+</sup>	Ir <sup>16+</sup>	Pt <sup>17+</sup>	
$\tau$	0.0108 s	0.004 s	128.57 yr	
$\delta\nu_{\text{nat}}$	92.59 Hz	250 Hz	2.48[−9] Hz	
$Q$	3.652[14]	1.885[13]	1.891[25]	

clock transitions. In fact,  $\lambda$  of only the  $4f^{13}5s^2\ ^2F_{5/2} \rightarrow 4f^{13}5s^2\ ^2F_{7/2}$  transition in W<sup>13+</sup> has been recently measured by Zhao *et al.* as 549.95(6) nm [30], while Kobayashi *et al.* have reported its value as close to 560.25 nm [31]. Similarly, our theoretical value agrees quite well with these results, asserting the validity of our calculations. We also find a good agreement of the excitation energy and  $\lambda$  between our result with the other available relativistic many-body calculation [17] for the  $4f^{13}5s^2\ ^2F_{5/2} \rightarrow 4f^{13}5s^2\ ^2F_{7/2}$  transition in Ir<sup>16+</sup>. Based on this investigation, we assume that the predicted  $\lambda$  in other transitions are accurate within 1%. Combining the calculated  $\lambda$  and  $S$  values, we give the *ab initio* values of the transition probabilities  $A$  due to various channels in the above table. As has been observed,  $A$  due to the  $M1$  channel dominates in W<sup>13+</sup> and Ir<sup>16+</sup> ions and  $A$  due to the  $E3$  channel in Pt<sup>17+</sup> is extremely small ( $\sim 10^{-10}$ ). These values correspond to  $\tau$  of the first excited states to be about 0.01 s, 0.004 s, and 128 yr in W<sup>13+</sup>, Ir<sup>16+</sup>, and Pt<sup>17+</sup>, respectively. From these estimates, we find  $\delta\nu_{\text{nat}}$  as 92.59, 250, and  $2.48 \times 10^{-9}$  Hz with the quality factors ( $Q = \frac{\nu_{\text{clock}}}{\delta\nu_{\text{nat}}}$ , for the clock frequency  $\nu_{\text{clock}}$ ) of the order of  $3.652 \times 10^{14}$ ,  $1.885 \times 10^{13}$ , and  $1.891 \times 10^{25}$  for the respective clock transitions in W<sup>13+</sup>, Ir<sup>16+</sup>, and Pt<sup>17+</sup> ions. These values are quoted towards the bottom of Table II for comparative analysis. It is worth noting here that the above proposed  $E3$  clock transition in Pt<sup>17+</sup> has an extremely smaller  $\delta\nu_{\text{nat}}$  value than the currently available  $E3$  clock transition in <sup>171</sup>Yb<sup>+</sup>, which has about  $\delta\nu_{\text{nat}} = 3.02$  Hz and a relative systematic uncertainty of  $3 \times 10^{-18}$  [32].

Having said and done with the fact that the first low-lying transitions in the investigated ions are suitable enough for the frequency standards owing to their optical frequencies, narrow  $\delta\nu_{\text{nat}}$ , and relatively large  $Q$  values, it is imperative now to learn about how large the systematic shifts would be to measure their  $\nu_{\text{clock}}$ . The major systematics that these ions would experience are the electric quadrupole, quadratic

TABLE III. Calculated values of the magnetic hyperfine constant  $A_{\text{hyp}}$  in MHz, electric quadrupole hyperfine constant  $B_{\text{hyp}}$  in MHz, atomic quadrupole moment  $\Theta$  in a.u., and Lande  $g_J$  factor  $g_J$  of the states involved with the clock transitions in W<sup>13+</sup>, Ir<sup>16+</sup>, and Pt<sup>17+</sup> from the CCSD(T) method. Electric dipole polarizability  $\alpha_d^{E1}$  and magnetic dipole polarizability  $\alpha_d^{M1}$  are also given in a.u. by employing the described RMBPT(3) method.

	<sup>183</sup> W <sup>13+</sup>		<sup>191</sup> Ir <sup>16+</sup>		<sup>195</sup> Pt <sup>17+</sup>	
	Ground	Excited	Ground	Excited	Ground	Excited
$A_{\text{hyp}}$	360	654	193	352	508540	2623
$B_{\text{hyp}}$	0.0	0.0	3496	3962	0.0	0.0
$\Theta$	−0.110	−0.093	−0.087	−0.073	0.0	−0.081
$g_J$	0.85496	1.14124	0.85454	1.17967	2.00049	1.14067
$\alpha_d^{E1}$	0.905	0.881	0.600	0.590	0.349	0.531
$\alpha_d^{M1}$	3.614	−4.816	2.576	−3.432	0.002	−2.585

Zeeman, quadratic Stark, black-body radiation (BBR), etc. shifts due to a stray electromagnetic field [8,9,13,17,33,34]. For estimating the order of magnitudes of these shifts due to an arbitrary electric field, we evaluate the quadrupole moments  $\Theta$ , magnetic dipole  $A_{\text{hyp}}$ , and electric quadrupole  $B_{\text{hyp}}$  hyperfine-structure constants, electric  $\alpha_d^{E1}$  and magnetic  $\alpha_d^{M1}$  dipole polarizabilities, and Lande  $g_J$  factors of the associated states of the clock transitions. We determine  $\Theta$ ,  $A_{\text{hyp}}$ ,  $B_{\text{hyp}}$ , and  $g_J$  values of the interested states by evaluating expectation values of the respective operators using the CCSD(T) method. These values for the corresponding stable isotopes are given in Table III by considering nuclear spin  $I = 1/2$  and nuclear magnetic moment  $\mu_I = 0.117784\mu_N$  of <sup>183</sup>W;  $I = 3/2$ ,  $\mu_I = 0.1461(6)\mu_N$ , and nuclear quadrupole moment  $Q_I = 0.816(9)$  b of <sup>191</sup>Ir; and  $I = 1/2$  and  $\mu_I = 0.60952(6)\mu_N$  of <sup>195</sup>Pt from Ref. [35]. By employing our described RMBPT(3) method, we also present our calculated  $\alpha_d^{E1}$  and  $\alpha_d^{M1}$  values in Table III. Now using the above theoretically evaluated quantities listed in Table III and expressions to estimate various dominant systematics given in Refs. [8,33,34], we present below the order of magnitudes of these shifts for  $\nu_{\text{clock}}$  one by one assuming that the ions will experience, say, a magnetic field about  $|\mathcal{B}| = 5 \times 10^{-8}$  T, an electric field about  $|\mathcal{E}| = 10$  V/m, and its gradient  $|\nabla\mathcal{E}| = 10^8$  V/m<sup>2</sup> as, for example, being considered in the Al<sup>+</sup> clock experiment [13,20].

The quadratic Stark shifts of the energy levels can be found out by [8,33]

$$E_{\text{Stark}} = -\frac{1}{4}\alpha_d^{E1}|\mathcal{E}|^2. \quad (19)$$

The differential Stark shifts  $\delta E_{\text{Stark}}$  of the clock transitions, which is the difference between the Stark shifts of the associated states, are estimated to be about  $2.241 \times 10^{-24}$ ,  $9.455 \times 10^{-25}$ , and  $1.726 \times 10^{-23}$  in atomic units (a.u.) corresponding to the relative shifts ( $\delta\nu_{\text{Stark}}/\nu_{\text{clock}}$ ) with respect to  $\nu_{\text{clock}}$  of the order of  $2.736 \times 10^{-23}$ ,  $8.294 \times 10^{-24}$ , and  $1.523 \times 10^{-24}$  in the W<sup>13+</sup>, Ir<sup>16+</sup>, and Pt<sup>17+</sup> ions, respectively.

Similarly using the expressions for BBR shifts [36]

$$E_{\text{BBR}}^{E1} = -\frac{1}{2}(831.9 \text{ V/m})^2 \left[ \frac{\text{T(K)}}{300} \right]^4 \alpha_d^{E1} \quad (20)$$

and

$$E_{\text{BBR}}^{M1} = -\frac{1}{2}(2.77 \times 10^{-6} \text{ T})^2 \left[ \frac{T(\text{K})}{300} \right]^4 \alpha_d^{M1}, \quad (21)$$

we estimate the BBR shifts due to the dominant E1 and M1 channels at the room temperature  $T = 300^\circ\text{K}$ . After substituting the respective polarizability values, we obtain the total differential BBR shifts  $\delta E_{\text{BBR}}$  to be about  $2.040 \times 10^{-4}$ ,  $8.611 \times 10^{-5}$ , and  $1.600 \times 10^{-3}$  in Hz for the clock transitions in  $\text{W}^{13+}$ ,  $\text{Ir}^{16+}$ , and  $\text{Pt}^{17+}$ , respectively. This gives the relative shifts ( $\delta \nu_{\text{BBR}}/\nu_{\text{clock}}$ ) as  $3.878 \times 10^{-19}$ ,  $1.148 \times 10^{-19}$ , and  $2.145 \times 10^{-18}$  in the  $\text{W}^{13+}$ ,  $\text{Ir}^{16+}$ , and  $\text{Pt}^{17+}$  ions, respectively. Most of these contributions are coming due to the E1 multipole. Errors in the calculations of these quantities are expected to be within 1%. These results can be improved further by developing a RCC method similar to those that have been reported in Refs. [37,38]. Therefore it is assumed that the corresponding relative uncertainties can also be estimated below  $10^{-18}$  in these ions.

The quadrupole shifts (QSs) in the energy levels can be estimated using the formula [8,33,39]

$$E_{QS} = -\langle \nabla \mathcal{E} \cdot \Theta \rangle, \quad (22)$$

and the differential QSs ( $\delta E_{QS}$ ) can be obtained by taking difference between QSs of the states of the clock transitions. By substituting the respective values, we find  $\delta E_{QS}$  are about  $8.643 \times 10^{-17}$ ,  $6.946 \times 10^{-17}$ , and  $4.152 \times 10^{-16}$  in a.u. leading to relative uncertainties as  $1.055 \times 10^{-15}$ ,  $6.092 \times 10^{-16}$ , and  $3.664 \times 10^{-15}$  in the clock transitions of  $\text{W}^{13+}$ ,  $\text{Ir}^{16+}$ , and  $\text{Pt}^{17+}$ , respectively. These are on par with the other HCIs proposed atomic clocks [13,14]. Though this uncertainty appears to be quite significant, it can be brought down by a factor larger than 200 using the sympathetic cooling techniques as discussed in Refs. [13,20]. Moreover, we anticipate that these quantities are calculated within 1% accuracy, and also, it is possible that they can be nullified by averaging out measurements for all possible magnetic sublevels as has been done in the  $\text{Ca}^+$  ion clock [40].

The Zeeman shifts can be estimated by [34]

$$\delta E_{\text{Zeeman}} = \gamma_c |\mathcal{B}|^2, \quad (23)$$

where, for the Bohr magneton  $\mu_B$ ,  $\gamma_c$  is given by

$$\gamma_c = \frac{(\mu_B g_J)^2}{(2F+1)} \sum_{F'} \frac{|\langle F || \mathbf{J} || F' \rangle|^2}{E_F - E_{F'}}, \quad (24)$$

$$\text{or } \gamma_c \approx -\frac{3}{2} \alpha_d^{M1}, \quad (25)$$

for the respective hyperfine state  $F$  with energy  $E_F$ . Hyperfine energy levels can be estimated using  $A_{\text{hyp}}$  and  $B_{\text{hyp}}$  values given in Table III. We find both the expressions given by Eqs. (24) and (25) estimate almost similar results among all combinations of hyperfine levels for the proposed clock transitions. Using Eq. (25), we obtain differential Zeeman shifts  $\delta E_{\text{Zeeman}}$  that are about  $5.768 \times 10^{-25}$ ,  $4.079 \times 10^{-25}$ , and  $1.756 \times 10^{-25}$  in a.u. for the clock transitions in  $\text{W}^{13+}$ ,  $\text{Ir}^{16+}$ , and  $\text{Pt}^{17+}$ , respectively. This leads to relative uncertainties about  $7.042 \times 10^{-24}$ ,  $3.578 \times 10^{-24}$ , and  $1.550 \times 10^{-24}$  in the clock transitions of  $\text{W}^{13+}$ ,  $\text{Ir}^{16+}$ , and  $\text{Pt}^{17+}$ , respectively, which are negligibly small.

TABLE IV. Estimated absolute values of differential Stark shifts  $\delta E_{\text{Stark}}$ , BBR shifts  $\delta E_{\text{BBR}}$ , quadrupole shifts  $\delta E_{QS}$ , and Zeeman shifts  $\delta E_{\text{Zeeman}}$  of the clock transitions in  $\text{W}^{13+}$ ,  $\text{Ir}^{16+}$ , and  $\text{Pt}^{17+}$ . Corresponding fractional shifts with respect to clock frequencies  $\nu_{\text{clock}}$ , i.e.,  $\delta \nu_{\text{Stark}}/\nu_{\text{clock}}$ ,  $\delta \nu_{\text{BBR}}/\nu_{\text{clock}}$ ,  $\delta \nu_{QS}/\nu_{\text{clock}}$ , and  $\delta \nu_{\text{Zeeman}}/\nu_{\text{clock}}$  are given towards the bottom of the table. Relativistic sensitivity coefficients  $q$  with proper signs are also quoted in  $\text{cm}^{-1}$ . Numbers given in the square brackets are to be read as powers of 10.

	$^{184}\text{W}^{13+}$	$^{191}\text{Ir}^{16+}$	$^{195}\text{Pt}^{17+}$
$\delta E_{\text{Stark}}$ (a.u.)	2.241[−24]	9.455[−25]	1.726[−23]
$\delta E_{\text{BBR}}$ (Hz)	2.040[−4]	8.611[−5]	1.600[−3]
$\delta E_{QS}$ (a.u.)	8.643[−17]	6.946[−17]	4.152[−16]
$\delta E_{\text{Zeeman}}$ (a.u.)	5.768[−25]	4.079[−25]	1.756[−25]
$\delta \nu_{\text{Stark}}/\nu_{\text{clock}}$	2.736[−23]	8.294[−24]	1.523[−22]
$\delta \nu_{\text{BBR}}/\nu_{\text{clock}}$	3.787[−19]	1.148[−19]	2.145[−18]
$\delta \nu_{QS}/\nu_{\text{clock}}$	1.055[−15]	6.092[−16]	3.664[−15]
$\delta \nu_{\text{Zeeman}}/\nu_{\text{clock}}$	7.042[−24]	3.578[−24]	1.550[−24]
$q$ ( $\text{cm}^{-1}$ )	17200	23900	−407600

We have listed the above estimated systematics and their relative values to  $\nu_{\text{clock}}$  of all the ions in Table IV. From these estimates, we anticipate to achieve the net relative uncertainty,  $\delta \nu/\nu_{\text{clock}}$ , below  $10^{-19}$  and are in the same order with the other HCIs proposed for clocks. Again for sympathetic cooling, the considered HCIs need to be cooled by another ion having almost similar charge to mass ratio, through transferring momentum due to intraspecies binary collisions. The charge to mass ratios for the undertaken HCIs are about 0.081 and comparable with the  $\text{Be}^+$  ion. Therefore, these ions are conducive for sympathetic cooling to carry out precise spectroscopy measurements including their clock frequencies  $\nu_{\text{clock}}$ .

As was mentioned before, HCIs exhibit large relativistic effects and hence, clocks based on HCIs have advantages to probe for possible variations in  $\alpha_e$ . To find out how large are the  $q$  parameters in the proposed clock transitions, we evaluate them as

$$q = \left. \frac{d\nu_{\text{clock}}(x)}{dx} \right|_{\alpha_e(t)=\alpha_e(0)} \approx \frac{\nu(+x) - \nu(-x)}{2x} \quad (26)$$

by considering the present value of  $\alpha_e(0)$  and for another value of  $\alpha_e(x)$  corresponding to an arbitrary instant of time  $t$  such that  $x = (\frac{\alpha_e(t)}{\alpha_e(0)})^2 - 1$ . For the numerical evaluation, we use  $x = 0.005$  and present the obtained  $q$  values at the end of Table IV. We perceive very large  $q$  values from our calculations of the proposed clock transitions, especially in  $\text{Pt}^{17+}$ , having opposite signs by employing the CCSD(T) method. Thus, if the clock frequencies are measured very precisely in these ions for a reasonable period of time or at two different times, it is possible to provide the signature of the plausible temporal variation in  $\alpha_e$  from the comparison of these frequencies.

#### IV. CONCLUSION

In summary, we have examined three highly charged ions, namely,  $\text{W}^{13+}$ ,  $\text{Ir}^{16+}$ , and  $\text{Pt}^{17+}$  to verify their aptness to be undertaken for optical clocks. After analyzing some of the dominant fractional systematic uncertainties, we demonstrate

that it is possible to measure clock frequencies in these ions to a level of  $10^{-19}$  accuracy. The advantages of considering these ions over the other proposed ions can be subdued to their easy access by optical lasers, development of sophisticated methods to carry out high precision calculations of various properties, suppressed systematic effects, and exhibition of large relativistic sensitivity coefficients. Moreover, the relativistic coefficients are found to have opposite signs in these ions that are, in fact, advantageous for probing temporal variation of the fine-structure constant if the ratio of clock frequencies can

be measured to ultrahigh precision accuracy at two different times.

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