Atomic clocks highly sensitive to the variation of the fine-structure constant based on Hf II, Hf IV, and W VI ions

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We demonstrate that several metastable excited states in Hf II, Hf IV, and W VI ions may be good clock states since they are sufficiently long-living and are not sensitive to the perturbations. The cooling electric dipole ($E1$) transition is available for Hf II, while sympathetic cooling is possible for Hf IV and W VI using Ca^+ or Sr^+ ions. Energy levels; Landé g factors; transition amplitudes for electric dipole ($E1$), electric quadrupole ($E2$), and magnetic dipole ($M1$) transitions; lifetimes; and electric quadrupole moments for Hf II, Hf IV, and W VI ions are investigated using a combination of several methods of relativistic many-body calculations including the configuration interaction (CI), linearized coupled-cluster single-doubles (SD), and many-body perturbation theory (CI + SD), and also the configuration interaction with perturbation theory (CIPT). Scalar polarizabilities of the ground states and the clock states have been calculated to determine the blackbody radiation (BBR) shifts. We have found that the relative BBR shifts for these transitions range between 10^{-16} and 10^{-18}. A linear combination of two clock transition frequencies allows one to further suppress BBR. Several $5d$-$6s$ single-electron clock transitions ensure high sensitivity of the transition frequencies to the variation of the fine-structure constant α and may be used to search for dark matter producing this variation of α. The enhancement coefficient for the α variation reaches $K = 8.3$. Six stable isotopes of Hf and five stable isotopes in W allow one to make King plots and study its nonlinearities in order to put limits on the new interactions mediated by scalar particles or other mechanisms.

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I. INTRODUCTION

Atomic clocks possess a high degree of accuracy, allowing them to be used for a wide variety of scientific and industrial applications. In recent years, the optical lattice atomic clock and the ion clock both have been significantly enhanced to achieve uncertainties or stabilities of 10^{-18} [1–8].

Due to the high accuracy of the frequency measurement of optical clock transitions, these transitions can be used not only to ensure timekeeping but also to search for new physics, such as local Lorentz invariance violation, time variation of the fundamental constants ($\alpha = e^2/\hbar c$), and other phenomena which go beyond the standard model (see, e.g., Refs. [1,3,6,7,9–14]).

Most of operating optical clocks use the $^1S_0$ to $^3P_0$ transition between states of the $ns^2_{1/2}$ and $ns_{1/2}np_{1/2}$ configurations. These transitions have low sensitivity to variation of the fine-structure constant [15,16]. It was shown in Refs. [12,13] that maximum sensitivity to the α variation corresponds to the maximum change in the total angular momentum j of the equivalent single-electron transitions. However, the above-mentioned transitions are the $ns_{1/2}$ to $np_{1/2}$ transitions with $\Delta j = 0$. It was suggested in Refs. [12,13,17] to use transitions between states of different configurations. The most prominent example of this kind among operating optical clocks is the clock based on the Yb^+ ion, in which the $4f_{7/2}$-$6s_{1/2}$ and $6s_{1/2}$-$5d_{5/2}$ transitions are used for timekeeping and constraining of the time variation of the fine-structure constant [18–20]. A number of the promising transitions were studied in earlier works [17,21–23]. In the present paper we continue the search for promising candidates and study the s-d and $d_{3/2}$-$d_{5/2}$ clock transitions in Hf II, Hf IV, and W VI. An important advantage of these systems is the existence of a sufficiently large number of stable isotopes of Hf and W. Hf has six stable isotopes, including four isotopes with zero nuclear spin (this includes a long-living ^{174}Hf isotope with a lifetime of $\sim 2 \times 10^{15}$ years and a natural abundance of 0.16%). W has five stable isotopes with three zero nuclear spin isotopes. This allows the use of the isotopes in the search for nonlinearities of the King plot. The minimal requirements for this include having four stable isotopes and two transitions where high accuracy of the measurements is possible. This is the case for both Hf and W. The study of the nonlinearity may help to obtain information on nuclear structure and put constraints on new interactions mediated by scalar particles [24,25]. In addition, the Hf II ion has three metastable states, making it possible to construct two independent combinations of the frequencies of the clock transitions with suppressed blackbody radiation shift. Measuring one such combined frequency against the other over a long period of time is a highly sensitive tool for the search of the time variation of the fine-structure constant.

We provide a detailed analysis of the electronic characteristics of certain low-lying states of these systems. We use the CI + SD (configuration interaction with single-double coupled-cluster [26]) and the CIPT (configuration interaction

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with perturbation theory [27]) methods for our calculations. Our studies investigate the energy levels; Landé g factors; transition amplitudes; $E1$, $M1$, and $E2$ transitions for the low-lying states; lifetimes; and quadrupole moments. Using the technique described in Ref. [28], we also calculate the scalar polarizabilities of the ground and excited clock states in order to determine the blackbody radiation (BBR) shifts. The sensitivity to the variation of the fine-structure constant is estimated by calculating excitation energies with different values of α in the computer codes. We demonstrate that the considered clocks are good candidates for very accurate time-keeping and are sensitive to new physics.

II. METHOD OF CALCULATION

A. Calculation of energy levels

The Hf II, Hf IV, W VI ions have similar electron structure with the $[1s^2, \ldots, 5s^2 5p^6 4f^{14}]$ closed-shell core and three valence electrons in Hf II and one valence electron in Hf IV and W VI. The calculations are performed by combining the configuration interaction (CI) technique with the linearized single-double coupled-cluster (SD) method, as described in Ref. [26]. We start with the relativistic Hartree-Fock (RHF) calculations for the closed-shell core, which corresponds to the V^{N-M} approximation [29]. Here N is the total number of electrons in an atom or ion, and M is the number of valence electrons ($M = 3$ for Hf II and $M = 1$ for Hf IV and W VI). The RHF Hamiltonian has the following form:

$$\hat{H}^{\rm RHF} = c\boldsymbol{\alpha}\cdot\boldsymbol{p} + (\beta - 1)mc^2 + V_{\rm nuc}(r) + V_{\rm core}(r), \qquad (1)$$

where c is the speed of light, $\boldsymbol{\alpha}$ and β are the Dirac matrices, $\boldsymbol{p}$ is the electron momentum, m is the electron mass, $V_{\rm nuc}$ is the nuclear potential obtained by integrating the Fermi distribution of nuclear charge density, and $V_{\rm core}(r)$ is the self-consistent RHF potential created by the electrons of the closed-shell core.

The B-spline method is used to construct the set of single-electron basis states [30,31]. The states are defined as linear combinations of B-splines which are eigenstates of the RHF Hamiltonian (1). Forty B-splines of the order 9 are calculated within a box of radius $R_{\rm max} = 40a_B$ (where a_B represents Bohr's radius) and an orbital angular momentum of $0 \leqslant l \leqslant 6$. It was found that this choice of parameters leads to the basis which is sufficiently saturated for the low-lying states of interest. Further increase in the values of $l_{\rm max}$ and $R_{\rm max}$ and the number of B-splines leads to negligible change in the results. The basis states are used for solving the linearized SD equations and for generating the many-electron states for CI calculations.

The SD equations for the core have the following form [26,32]:

$$\begin{aligned}
&(\epsilon_a - \epsilon_m)\rho_{ma} \\
&\quad = \sum_{bn} \tilde{g}_{mban}\rho_{nb} + \sum_{bnr} g_{mbnr}\tilde{\rho}_{nrab} - \sum_{bcn} g_{bcan}\tilde{\rho}_{mnbc}, \\
&(\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n)\rho_{mnab} \\
&\quad = g_{mnab} + \sum_{cd} g_{cdab}\rho_{mncd} + \sum_{rs} g_{mnrs}\rho_{rsab} \\
&\qquad + \sum_{r} g_{mnrb}\rho_{ra} - \sum_{c} g_{cnab}\rho_{mc} + \sum_{rc} \tilde{g}_{cnrb}\tilde{\rho}_{mrac} \\
&\qquad + \sum_{r} g_{nmra}\rho_{rb} - \sum_{c} g_{cmba}\rho_{nc} + \sum_{rc} \tilde{g}_{cmra}\tilde{\rho}_{nrbc}. \qquad (2)
\end{aligned}$$

Here parameters g are Coulomb integrals,

$$g_{mnab} = \iint \psi_m^\dagger(r_1)\psi_n^\dagger(r_2)\frac{e^2}{r_{12}}\psi_a(r_1)\psi_b(r_2)d\mathbf{r}_1 d\mathbf{r}_2,$$

and parameters ϵ are the single-electron Hartree-Fock energies. The coefficients ρ_{ma} and ρ_{mnab} are the expansion coefficients for the atomic wave function which are to be found by solving the equations iteratively.

The tilde above g or ρ means the sum of direct and exchange terms, e.g.,

$$\tilde{\rho}_{nrbc} = \rho_{nrbc} - \rho_{nrcb}.$$

Indexes a, b, and c numerate states in the atomic core; indexes m, n, r, and s numerate states above the core; and indexes i and j numerate any state.

The SD equations for valence states are obtained from Eq. (2) by replacing the core index a by the valence index v, removing the term $\sum_r g_{mnrb}\rho_{rv}$ which has only valence excitations, and replacing ϵ_a by ϵ_0. The energy parameter ϵ_0 is fixed and relates to the valence state of interest. It is convenient to introduce the correlation operators $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$, which describe the correlation interaction of external electrons with the core. Using the SD equations for valence states one can write

$$\langle v|\hat{\Sigma}_1|m\rangle = (\epsilon_0 - \epsilon_m)\rho_{mv} \qquad (3)$$

and

$$\begin{aligned}
q_{mnvw} &= g_{mnvw} \\
&\quad + \sum_{cd} g_{cdvw}\rho_{mncd} - \sum_{c}(g_{cnvw}\rho_{mc} + g_{cmwv}\rho_{nc}) \\
&\quad + \sum_{rc}(g_{cnrw}\tilde{\rho}_{mrvc} + g_{cmrv}\tilde{\rho}_{nrwc} + g_{cnwr}\rho_{mrvc} \\
&\quad + g_{cmvr}\rho_{nrwc} - g_{cmwr}\rho_{nrcv} - g_{cnvr}\rho_{mrcw}) \\
&\equiv g_{mnvw} + \langle mn|\hat{\Sigma}_2|vw\rangle. \qquad (4)
\end{aligned}$$

The one-electron Σ_1 operator represents the correlation interaction between valence electrons and electrons in the core [33]. The two-electron Σ_2 operator is interpreted as the screening of Coulomb interaction between valence electrons by core electrons [34].

The CI Hamiltonian with the Σ_1 and Σ_2 operators included is

$$\hat{H}^{\rm eff} = \sum_{i=1}^{M}(\hat{H}^{\rm RHF} + \Sigma_1)_i + \sum_{i<j}^{M}\left(\frac{e^2}{|r_i - r_j|} + \Sigma_{2ij}\right). \qquad (5)$$

Here summation goes over valance electrons, i and j numerate valence electrons, and e is the electron charge. The size of the CI matrix is huge if the number of valence electrons is large ($M \geqslant 3$). In calculations for Hf II we use the CIPT technique [27] for dramatic increase of the efficiency of the calculations at the cost of very little sacrifice in the accuracy of the results. This is achieved by constructing the CI matrix for the $N_{\rm eff}$'s

lowest (on the energy scale) many-electron basis state and treating the other states perturbatively. The CI matrix in the CIPT method has the form

$$\langle i|H^{\rm CI}|j\rangle \to \langle i|H^{\rm CI}|j\rangle + \sum_k \frac{\langle i|H^{\rm CI}|k\rangle\langle k|H^{\rm CI}|j\rangle}{E-E_k}. \quad (6)$$

Here $i, j \leqslant N_{\rm eff}$, $N_{\rm eff} < k \leqslant N_{\rm total}$, $E_k = \langle k|H^{\rm CI}|k\rangle$, and E is the energy of the state of interest. Since $N_{\rm eff} \ll N_{\rm total}$ the task of matrix diagonalization is significantly simplified (see Ref. [27] for details).

The Landé g factors for low-lying states are investigated in all systems. These factors are calculated as expectation values of the magnetic dipole ($M1$) operator and are compared with the nonrelativistic expression

$$g(J,L,S) = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}, \quad (7)$$

where S is the total spin and L is the total angular momentum for the valence electrons, and J is the corresponding total momentum ($J = L + S$). This comparison of g factors helps in the level identification.

B. Calculation of transition amplitudes and lifetimes

The time-dependent Hartree-Fock (TDHF) method [which corresponds to the well-known random-phase approximation (RPA)] is used to compute transition amplitudes. The RPA equation for the core can be written as

$$(\hat{H}^{\rm RHF} - \epsilon_c)\delta\psi_c = -\left(\hat{f} + \delta V^f_{\rm core}\right)\psi_c. \quad (8)$$

The operator $\hat{f}$ refers to an external field. The index c denotes single-electron states in the core, ψ_c is a single-electron wave function, $\delta\psi_c$ is a correction to the state c due to an external field, and $\delta V^f_{\rm core}$ is the correction to the self-consistent RHF potential caused by the change of all core states in the external field (see, e.g., Ref. [33]). The RPA equation (8) is solved self-consistently for all states in the core. The transition amplitudes are found by calculating matrix elements between states a and b by the formula

$$A_{ab} = \langle b|\hat{f} + \delta V^f_{\rm core}|a\rangle. \quad (9)$$

Here, $|a\rangle$ and $|b\rangle$ are the many-electron wave functions calculated with the CI method described above.

In this study, electric dipole ($E1$), electric quadrupole ($E2$), and magnetic dipole ($M1$) rates are taken into account, and they are calculated according to the following equations (in atomic units):

$$(T_{ab})_{E1,M1} = \frac{4}{3}(\alpha\omega)^3 \frac{\left(A^2_{ab}\right)_{E1,M1}}{2J_b+1}, \quad (10)$$

$$(T_{ab})_{E2} = \frac{1}{15}(\alpha\omega)^5 \frac{\left(A^2_{ab}\right)_{E2}}{2J_b+1}. \quad (11)$$

Here α is the fine-structure constant ($\alpha \approx \frac{1}{137}$), ω_{ab} is the frequency of the transition, A_{ab} is the transition amplitude (9), and J_b is the total angular momentum of the upper state b. Note that magnetic amplitudes $(A_{ab})_{M1}$ contain the Bohr magneton μ_B ($\mu_B = \alpha/2 \approx 3.65 \times 10^{-3}$ in atomic units).

The lifetimes τ_b of each excited state b, expressed in seconds, can be found as follows:

$$\tau_b = 2.41 \times 10^{-17} \Big/ \sum_a T_{ab}, \quad (12)$$

where the summation goes over all possible transitions to lower states a.

III. RESULTS

A. Energy levels, Landé g factors, transition amplitudes, and lifetimes

The results for energy levels, g factors, and lifetimes of low-lying states of Hf II, Hf IV, and W VI are presented in Table I and compared with available experimental data. The data in the table indicate excellent agreement between theory and experiment. In most states, the deviations of the calculated energies from the observed values are within 1000 cm^{-1}. The agreement is also good between calculated and experimental g factors of Hf II, where experimental data are available. This is important for correct identification of the states. One noticeable exemption refers to states 12 and 13 where the difference between theory and experiment is significant. These states have the same parity and total momentum J, and the energy interval between them is small ($\sim$1000 cm^{-1}). This means that the states are strongly mixed. Note that the sums of the theoretical and experimental g factors of these states are very close. This indicates that the two-level mixing approximation works very well for this pair of states. In principle, mixing coefficients can be corrected using experimental g factors. See the discussion of the sensitivity of the clock states to the variation of the fine-structure constant (Sec. III D).

Table I presents one odd state for each ion. These are the lowest odd states which are connected to the ground state by the electric dipole ($E1$) transition. These transitions can be used for cooling, at least in principle. However, the only transition in the Hf II ion is in the ultraviolet region (wavelength is 356 nm), where lasers are available. A more realistic option for Hf IV and W VI ions is to use sympathetic cooling [36,37]. It is done by co-trapping the ions with other ions (which are called "logic" ions) with a close charge-to-mass ratio for which laser cooling is possible. The Ca^+ ion seems to be a good logic ion for W VI, while either Ca^+ or Sr^+ can be used for Hf IV.

Our results for transition amplitudes and transition probabilities, together with experimental data and earlier calculated results, where available, are shown in Table II. We consider only those low-lying states which are connected to clock or cooling states through electric dipole ($E1$), magnetic dipole ($M1$), or electric quadrupole ($E2$) transitions. Comparing our results on the transition rates with those from previous studies, we find good agreement. Note that experimental values of the frequencies from the NIST database have been used to calculate transition probabilities.

Based on the transition rates displayed in Table II, we derived the lifetimes of the excited states (clock and cooling states) of all the atomic systems using Eq. (12) and we present them in Table I. The lifetimes of the states presented in the table were calculated with taking into account all possible

TABLE I. Excitation energies (E), Landé g factors, and lifetimes (τ) for the first excited states of Hf II, Hf IV, and W VI. Possible clock states are indicated by bold state numbers. Odd states can be used for cooling.

				E (cm^{-1})		g factor		τ	
No.	Conf.	Term	J	Present	Expt.	Present	NIST [35]	Present	Ref.
		Hf II			[35]				[39]$_{\text{Expt.}}$
1	$5d6s^2$	^2D	3/2	0	0	0.793	0.787		
2	$5d6s^2$	^2D	5/2	3054	3050.88	1.175	1.173	3.23 s	
3	$5d^26s$	^4F	3/2	3578	3644.65	0.415	0.425	66.6 s	
4	$5d^26s$	^4F	5/2	4312	4904.85	1.055	1.052	9.7 s	
5	$5d^26s$	^4P	1/2	11675	11951.70	2.653	2.598		
6	$5d^26s$	^2F	5/2	11783	12070.46	0.901	0.964		
7	$5d^26s$	^4P	3/2	11781	12920.94	1.694	1.664		
8	$5d^26s$	^4P	5/2	12581	13485.56	1.467	1.410		
9	$5d^26s$	^2D	3/2	13836	14359.42	1.075	1.034		
10	$5d^26s$	^2P	1/2	13995	15254.29	0.690	0.737		
11	$5d^26s$	^2D	5/2	17352	17368.87	1.200	1.273		
12	$5d^26s$	^2P	3/2	17199	17830.34	0.670	1.122		
13	$5d^3$	^4F	3/2	18528	18897.64	0.839	0.446		
14	$5d^3$	^4F	5/2	18284	20134.94	1.118	1.030		
15	$5d^3$	^4P	1/2	24773	26996.51	2.610	2.58		
16	$5d^3$	^4P	3/2	25797	27285.13	1.697	1.643		
17	$5d6s6p$	$^4F^{\text{o}}$	3/2	28580	28068.79	0.516	0.512	40.3 ns	39.4 ± 0.2 ns
		Hf IV			[38]				
1	$5d$	^2D	3/2	0	0	0.800			
2	$5d$	^2D	5/2	4721	4692	1.200		0.90 s	
3	$6s$	^2S	1/2	17530	18380	2.000		0.321 s	
4	$6p$	$^2P^{\text{o}}$	1/2	66611	67039	0.667		0.78 ns	
		W VI			[35]				[40]$_{\text{Theo.}}$
1	$5d$	^2D	3/2	0	0	0.800			
2	$5d$	^2D	5/2	8726	8709.3	1.200		0.14 s	0.14 s
3	$6s$	^2S	1/2	78316	79431.3	2.000			
4	$6p$	$^2P^{\text{o}}$	1/2	146912	147553.1	0.667		0.18 ns	0.184 ns

transitions to lower states. The results show consistency with previous studies.

B. Polarizabilities and blackbody radiation shifts

Scalar polarizability is one of the key properties of atoms that sets their chemical characteristics. For establishing optical clocks, the values of the static and dynamic scalar polarizabilities should be taken into account. Scalar polarizabilities provide the value of the blackbody radiation (BBR) shift of the clock state frequency, which is a primary source of uncertainty for a clock.

The scalar polarizability α_{0v} of an atomic system in state v can be expressed as a sum over a complete set of states n (these states are constructed using the B-spline technique described above; the use of the B-splines ensures the completeness of the basis):

$$\alpha_{0v} = \frac{2}{3(2J_v+1)} \sum_n \frac{A_{vn}^2}{E_n - E_v}. \tag{13}$$

Here J_v is the total angular momentum of state v, and A_{vn} is the electric dipole transition amplitude (reduced matrix element). Notations v and n refer to the many-electron atomic states. It is convenient to present the polarizability as a sum of two terms, the polarizability of the closed-shell core and the contribution from the valence electrons. The polarizability of the core is given in the RPA approximation by

$$\alpha_{0\text{core}} = \frac{2}{3} \sum_{cn} \frac{\langle c||\hat{d} + \delta V_{\text{core}}^d||n\rangle\langle n||\hat{d}||c\rangle}{E_n - E_c}. \tag{14}$$

Here summation over c goes over core states, summation over n is over a complete set of single-electron basis states, $\hat{d} = -er$ is the $E1$ operator in the length form, δV_{core}^d is the core polarization correction to the $E1$ operator [see Eq. (9)]. Note that the RPA correction goes only into one of the two reduced matrix elements in Eq. (14) [41].

For the calculation of the valence contribution to the polarizabilities of the ground and clock states of Hf II we apply the technique developed in Ref. [28] for atoms or ions with open shells. The method relies on Eq. (13) and the Dalgarno-Lewis approach [42], which reduces the summation in Eq. (13) to the solving of the matrix equation (see Refs. [28,42] for more details). For Hf IV and W VI, which both have only one external electron above closed shells, we use direct summation in Eq. (13) over the complete set of single-electron basis states.

There is also a core-valence contribution to the polarizabilities which comes from the fact that calculation of the

TABLE II. Transition amplitudes (A, in a.u.) and transition probabilities (T, in s^{-1}) evaluated with NIST frequencies for some low states. 5.67[−3] means 5.67×10^{-3}, etc.

		ω, NIST [35]		Present		Ref.
Transition	Type	(cm^{-1})	(a.u.)	A (a.u.)	T (s^{-1})	T (s^{-1})
		Hf II				[39]$_{\text{Expt.}}$
2-1	$M1$	3050.88	0.0139	5.67[−3]	0.309	
2-1	$E2$	3050.88	0.0139	−0.309	4.697[−7]	
3-1	$M1$	3644.65	0.0166	−7.49[−4]	1.375[−2]	
3-1	$E2$	3644.65	0.0166	0.265	1.259[−6]	
3-2	$M1$	593.7	0.0027	3.53[−3]	1.318[−3]	
3-2	$E2$	593.7	0.0027	0.341	0.241[−9]	
4-1	$M1$	4904.85	0.0223	−7.54[−4]	2.261[−2]	
4-1	$E2$	4904.85	0.0223	−0.420	9.325[−6]	
4-2	$M1$	1853.97	0.0084	−1.63[−3]	5.743[−3]	
4-2	$E2$	1853.97	0.0084	−0.259	2.734[−8]	
4-3	$M1$	1260.2	0.0057	1.05[−2]	7.497[−2]	
4-3	$E2$	1260.2	0.0057	1.56	1.439[−7]	
17-1	$E1$	28068.79	0.1279	1.200	16.11[6]	17.6[6] ± 0.9
17-2	$E1$	25017.91	0.1140	−0.068	3.674[4]	
17-3	$E1$	24424.14	0.1113	1.024	7.728[6]	7.0[6] ± 0.4
17-4	$E1$	23163.94	0.1055	0.016	1.660[3]	
17-5	$E1$	16117.09	0.0734	0.068	9.712[3]	2.1[4] ± 0.003
17-6	$E1$	15998.33	0.0729	0.522	0.565[6]	0.50[6] ± 0.09
17-7	$E1$	15147.85	0.0690	0.110	0.021[6]	
17-8	$E1$	14583.23	0.0664	0.128	0.026[6]	0.060[6] ± 0.011
17-9	$E1$	13709.37	0.0625	0.030	0.012[5]	
17-10	$E1$	12814.5	0.0584	−0.301	0.096[6]	0.054[6] ± 0.011
17-11	$E1$	10699.92	0.0488	0.224	0.031[6]	
17-12	$E1$	10238.45	0.0466	0.517	0.145[6]	
17-13	$E1$	9171.15	0.0418	0.342	0.046[6]	0.081[6] ± 0.019
17-14	$E1$	7933.85	0.0361	−0.265	0.018[6]	
17-15	$E1$	1072.28	0.0049	−0.069	2.964	
17-16	$E1$	783.66	0.0036	0.023	0.127	
		Hf IV				
2-1	$M1$	4692	0.0214	−5.66[−3]	1.115	
2-1	$E2$	4692	0.0214	−2.43	2.501[−4]	
3-1	$M1$	18380	0.0837	2.22[−6]	3.091[−5]	
3-1	$E2$	18380	0.0837	4.40	2.267	
3-2	$E2$	13688	0.0624	−5.62	0.850	
4-1	E1	67039	0.3055	1.62	7.996[8]	
4-3	E1	48659	0.2217	2.04	4.860[8]	
		W VI				[40]$_{\text{Theo.}}$
2-1	$M1$	8709.3	0.0397	−5.65[−3]	7.126	7.12
2-1	$E2$	8709.3	0.0397	−1.60	2.400[−3]	2.54[−3]
4-1	$E1$	147553.1	0.6723	1.18	4.529[9]	
4-3	$E1$	68121.8	0.3104	1.70	9.218[8]	

core polarizabilities is affected by valence electrons via Pauli blocking. We include this contribution by omitting in the summation over n in Eq. (14) states occupied by valence electrons.

The present results for the polarizabilities of the ground states and clock states for all considered atomic systems are shown in Table III. According to the calculations, clock states of all atomic systems have polarizabilities similar to those of their ground states, with the notable exception of the Hf IV third excited state, where this difference is approximately 14 a_b^3. This is because of the difference in the electronic configurations. The external electron in the ground state is in the $5d_{3/2}$ state, while in the clock state it is in the $6s_{1/2}$ state.

By using the values of scalar polarizability, we can figure out the BBR shift of a clock state at 300 K. The BBR shift in Hz is determined by the following expression (see, e.g., Ref. [8]):

$$\delta\omega_{\text{BBR}} = -8.611 \times 10^{-3}\left(\frac{T}{300\ K}\right)^4 \Delta\alpha_0, \qquad (15)$$

TABLE III. Scalar static polarizabilities of the ground states, α_0(GS), and clock states, α_0(CS), and BBR frequency shifts for the clock transition. $\delta\omega_{\rm BBR}/\omega$ is the fractional contribution of the BBR shift; where ω is the clock transition frequency. Total means total scalar polarizability (core + valence).

Clock	α_0(GS) (units of a_B^3)			α_0(CS) (units of a_B^3)				BBR ($T = 300$ K)		
transition	Core	Valence	Total	Core	Valence	Total	$\Delta\alpha_0$	$\delta\omega_{\rm BBR}$ (Hz)	ω (Hz)	$\delta\omega_{\rm BBR}/\omega$
					Hf II					
2-1	2.72	48.04	50.76	2.72	43.22	45.94	−4.93	0.043	1.093[14]	3.9[−16]
3-1	2.72	48.04	50.76	2.61	40.10	42.71	−8.05	0.070	1.093[14]	6.4[−16]
4-1	2.72	48.04	50.76	2.61	42.84	45.45	−5.31	0.046	1.470[14]	3.2[−16]
					Hf IV					
2-1	3.06	2.86	5.92	2.98	2.86	5.85	−0.07	0.60[−3]	1.404[14]	4.3[−18]
3-1	3.06	2.86	5.92	3.13	16.84	19.97	14.05	−0.12	5.510[14]	−2.2[-16]
					W VI					
2-1	1.96	0.76	2.73	1.92	0.75	2.66	−0.07	0.60[−3]	2.611[14]	2.3[−18]

where T is a temperature in K (e.g., room-temperature $T = 300$ K), $\Delta\alpha_0 = \alpha_0(\mathrm{CS}) - \alpha_0(\mathrm{GS})$ is the difference between the clock state and the ground-state polarizabilities presented in atomic units. The BBR shifts for clock states investigated in this paper are presented in Table III. The relative BBR shifts in the 2-1 transition in Hf IV and the 2-1 transition in W VI are among the smallest considered so far, they are 4.3×10^{-18} and 2.3×10^{-18} respectively, while BBR shifts in other transitions are $\sim 10^{-16}$, similar to BBR shifts in other atomic clocks (see, e.g., Refs. [23,43–46]). A linear combination of two clock transition frequencies allows one to cancel BBR shifts [47].

C. Electric quadrupole moments

As is discussed above, the search for clock transitions sensitive to the variation of the fine-structure constant leads us to transitions with large changes of the total momentum of the equivalent singe-electron transitions. As a consequence, at least one of the states may have a relatively large value of the total momentum J (e.g., $J > 1$). This means that the state is sensitive to the electric quadrupole shift. Therefore, it is important to know the value of this shift. The corresponding term in the Hamiltonian is (see, e.g., Ref. [48])

$$H_{\mathcal{Q}} = \sum_{q=1}^{-1} (-1)^q \nabla \mathcal{E}_q^{(2)} \hat{\Theta}_{-q}. \tag{16}$$

The tensor $\nabla \mathcal{E}_q^{(2)}$ is the external electric field gradient at the position of the system, Θ_q describes the electric-quadrupole operator, and $\hat{\Theta}_q = |e| r^2 C_q^{(2)}$, the same as for $E2$ transitions.

The electric quadrupole moment Θ is defined as the expectation value of Θ_0 for the extended state:

$$\Theta = \langle nJJ|\hat{\Theta}_0|nJJ\rangle \equiv \langle J\|\hat{\Theta}\|J\rangle \sqrt{\frac{J(2J-1)}{(2J+3)(2J+1)(J+1)}}, \tag{17}$$

where $\langle J\|\hat{\Theta}\|J\rangle$ is the reduced matrix element (ME) of the electric quadrupole operator. We compute the values of Θ using the CI + SD and RPA methods described in the previous section.

In Table IV we display the reduced ME of the electric quadrupole operator and the quadrupole moment Θ values for all considered states. The quadrupole momentum of the ground state of Hf II is anomalously small. This is due to the mixing between states of the $6s^2 5d$ and $6s5d^2$ configurations leading to strong cancellation between terms proportional to the $\langle 5d_{3/2}||\hat{\Theta}||5d_{3/2}\rangle$ ME and terms proportional to the $\langle 6s_{1/2}||\hat{\Theta}||5d_{3/2}\rangle$ ME. Strong cancellation is probably accidental, which means that the result is likely to be not very stable and may vary significantly under variation of the computation procedure. In states where the $6s5d^2$ configuration dominates, the value of the quadrupole moment is not suppressed and stable. This means that the uncertainty of the calculated values of the quadrupole moment is of the order of the quadrupole moment itself in cases when it is small (first two lines of Table IV). For larger values of Θ the absolute uncertainty might be similar while the relative uncertainty is much smaller. The values of the quadrupole moments for both excited clock states are almost the same. In the case of the

TABLE IV. Quadrupole moment (Θ, in a.u.) of the ground state and the considered optical clock states.

No.	Conf.	Term	J	E (cm^{-1})	ME (a.u.) $\langle J\|\hat{\Theta}\|J\rangle$	Θ
				Hf II		
1	$5d6s^2$	^2D	3/2	0	−2.910[−2]	−6.507[−3]
2	$5d6s^2$	^2D	5/2	3050.88	−5.806[−1]	−1.415[−1]
3	$5d^26s$	^4F	3/2	3644.65	−1.797	−0.401
4	$5d^26s$	^4F	5/2	4904.85	−1.621	−0.395
				Hf IV		
1	$5d$	^2D	3/2	0	−3.608	−0.807
2	$5d$	^2D	5/2	4692	−4.956	−1.210
				W VI		
1	$5d$	^2D	3/2	0	−2.381	−0.532
2	$5d$	^2D	5/2	8709.3	−3.263	−0.796

Hf IV ion, the difference between the values in the ground state and in the excited state is much smaller than that in the Hf^+ ion. The quadrupole moment in the ground state is about 1.5 times larger than that in the first excited state. This is because both states (the ground and the excited) have the same electron configuration. Note that the quadrupole moment of the second excited state ($6s\ ^2S_{1/2}$) is zero because the total angular momentum J is 1/2. The W VI ion has differences similar to those in the Hf IV ion.

It is worth noting that the quadrupole shift in odd isotopes of Hf II and Hf IV (^{177}Hf, $I = 7/2$, and ^{179}Hf, $I = 9/2$) can be totally avoided when working with specific hyperfine components of the states, namely, substates with $F = 3$ and $F_z = 2$, since $\Delta E \sim 3F_z^2 - F(F+1)$. Such substates exist for both ground and clock states in both isotopes. Another way of suppressing the quadrupole shift is by averaging over transitions between different hyperfine or Zeeman components [21,48]. Averaging over Zeeman components should work for even isotopes too.

D. Sensitivity of the clock transitions to the variation of the fine-structure constant

It has been shown that optical atomic clock transitions can be used to search for the time variation of the fine-structure constant α [12,13,16]. The frequencies of these transitions depend differently on α. By comparing the ratio of two clock frequencies over long periods of time, one can link any possible change in the ratio of frequencies to the time variation of α. The ratio of frequencies does not depend on the units one uses. In atomic units, dependence of the optical transition frequencies appears to be due to the relativistic corrections proportional to α^2. Therefore, we present the frequency as

$$\omega = \omega_0 + q\left[\left(\frac{\alpha}{\alpha_0}\right)^2 - 1\right], \tag{18}$$

where α_0 and ω_0 are the present-day values of the fine-structure constant and the frequency of the transition, and q is the sensitivity coefficient which comes from the atomic calculations [12,13,16]. The rate of the variation of ω_1/ω_2 is

$$\frac{\dot{\omega}_1}{\omega_1} - \frac{\dot{\omega}_2}{\omega_2} = (K_1 - K_2)\frac{\dot{\alpha}}{\alpha}. \tag{19}$$

The dimensionless value $K = 2q/\omega$ is often called the enhancement factor. We use the computer codes to calculate q and K by performing calculations of the frequencies with different values of α and calculating the derivative numerically as

$$q = \frac{\omega(\delta) - \omega(-\delta)}{2\delta}, \tag{20}$$

where $\delta = (\alpha/\alpha_0)^2 - 1$ [see Eq. (18)]. In order to achieve linear behavior, the value of δ must be small; however, it must be large enough to suppress numerical noise. Most accurate results can be obtained by using $\delta = 0.01$. The calculated values of q and K for all considered clock transitions are summarized in Table V. We see that all values of the enhancement coefficient K are significantly bigger than 1. The enhancement factor for the 2-1 interval is 3.65. This is the fine-structure interval and under normal circumstances the interval $\propto (Z\alpha)^2$ and $K = 2$. Here the factor is significantly larger due to strong mixing of the upper state with the states of the $5d^26s$ configuration. Note that values of K are positive, with only one negative K factor for the $5d_{3/2}$-$6s_{1/2}$ transition in the Hf IV ion. Indeed, the simple analytical estimate performed in Refs. [12,13] indicates that the transition from a lower j orbital in the ground state to a higher j orbital gives a positive K while the transition from a higher j orbital to a lower j orbital gives a negative K.

TABLE V. Sensitivity of clock transitions to variation of the fine-structure constant (q, K).

No.	Conf.	Term	J	ω (cm^{-1})	q (cm^{-1})	K
			Hf II			
2	$5d6s^2$	^2D	5/2	3050.88	5631	3.65
3	$5d^26s$	^4F	3/2	3644.65	15060	8.30
4	$5d^26s$	^4F	5/2	4904.85	15002	6.16
			Hf IV			
2	$5d$	^2D	5/2	4692	4342	1.85
3	$6s$	^2S	1/2	18380	−24268	−2.64
			W VI			
2	$5d$	^2D	5/2	8709.3	8609	1.98

It was shown in Ref. [47] that having two clock transitions in one atom or ion allows one to construct a "synthetic" frequency which is not sensitive to the BBR shift. They also proposed a realization of the method with the use of an optical frequency comb generator stabilized to both clock frequencies. The synthetic frequency is generated as one of the components of the comb spectrum (see Ref. [47] for details).

Using such frequencies may benefit the search for the time variation of the fine-structure constant. The Hf II ion has three clock transitions. This means that one can contract two independent "synthetic" frequencies nonsensitive to the BBR shift. Measuring one such frequency against the other over a long period of time allows highly sensitive search for the variation of the fine-structure constant. Following Ref. [47] we write a synthetic frequency as

$$\omega_{ij} = \omega_i - \epsilon_{ij}\omega_j, \tag{21}$$

where $\epsilon_{ij} = \Delta\alpha_{0i}/\Delta\alpha_{0j}$. Since BBR shift $\propto \Delta\alpha_0$ [see Eq. (15)], the synthetic frequency (21) is not sensitive to it. If the fine-structure constant α varies in time, then the synthetic frequency varies as

$$\frac{\dot{\omega}_{ij}}{\omega_{ij}} = \frac{K_i\omega_i - \epsilon_{ij}K_j\omega_j}{\omega_i - \epsilon_{ij}\omega_j}\frac{\dot{\alpha}}{\alpha} \equiv K_{ij}\frac{\dot{\alpha}}{\alpha}. \tag{22}$$

Table VI shows three possible synthetic frequencies for Hf II. Any two of these frequencies can be used for searching of the time variation of the fine-structure constant. For example, if the ω_{32} and ω_{42} frequencies are used, then

$$\frac{\dot{\omega}_{32}}{\omega_{32}} - \frac{\dot{\omega}_{42}}{\omega_{42}} = -20\frac{\dot{\alpha}}{\alpha}. \tag{23}$$

TABLE VI. Synthetic frequencies of Hf II clock transitions and their sensitivity to variation of the fine-structure constant. Indexes i and j correspond to the clock transitions from state number i or j (see Table I) to the ground state.

i	j	ϵ_{ij}	ω_{ij} (cm^{-1})	K_{ij}
3	2	1.633	1336.86	−9.03
4	2	1.077	1618.83	11.26
4	3	0.660	2500.66	4.10

The combinations of frequencies which are not sensitive to the BBR shift turn out to be very sensitive to the time variation of the fine-structure constant.

IV. CONCLUSIONS

Metastable states of Hf II, Hf IV, and W VI ions are studied as candidates for high-accuracy optical clocks which are highly sensitive to the variation of the fine-structure constant α. Slow drift and oscillating variation of α may be due to the interaction between the scalar dark matter field and electromagnetic field [49–52]. The Yukawa-type scalar field affecting α may also be produced by massive bodies [53]. Transient α variation may be produced by the passing of macroscopic forms of dark matter such as Bose stars and topological defects [54].

Six stable isotopes of Hf and five stable isotopes of W, as well as several clock transitions in Hf and W ions, make it possible to make King plots and study their nonlinearities in order to put limits on the new interactions mediated by scalar particles or other mechanisms [24,25].

Energy levels, lifetimes, transition rates, scalar polarizabilities of the clock and ground states, and BBR shifts have been calculated, and the possibility for high accuracy of the timekeeping has been demonstrated. The studied transitions correspond to the s-d or d-s transitions between single-electron states.

The sensitivity coefficients K to α variation have been calculated and found to be among the highest compared to other operating or prospective atomic optical clocks. We found that constructing synthetic frequencies with suppressed sensitivity to the BBR shift leads to further increase in sensitivity to the variation of the fine-structure constant.

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