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High-precision atomic clocks with highly charged ions: Nuclear-spin-zero f^{12}-shell ions

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Optical atomic clocks using highly charged ions hold an intriguing promise of metrology at the 19th significant figure. Here we study transitions within the $4f^{12}$ ground-state electronic configuration of highly charged ions. We consider isotopes lacking hyperfine structure and show that the detrimental effects of coupling of electronic quadrupole moments to the gradients of a trapping electric field can be effectively reduced by using specially chosen virtual clock transitions. The estimated systematic fractional clock accuracy is shown to be below 10^{-19}.

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Developing accurate atomic clocks is important for both technological and fundamental reasons. The cesium primary frequency standard which is currently used to define the SI units of time and length has fractional accuracy of the order of 10^{-16} [1]. State-of-the-art clocks using trapped singly charged ions have demonstrated fractional accuracies at the level of 10^{-17} [2]. Frequency standards based on neutral atoms trapped in an optical lattice aim at a fractional accuracy of 10^{-18} [3]. Further progress is possible with clocks using a nuclear optical transition [4] or clocks using optical transitions in highly charged ions [5–9].

In our previous paper [8] we proposed ion clocks based on optical transitions in trapped highly charged ions (HCIs). A clock HCI is cotrapped with a lighter singly charged ion (e.g., Be^+) which is used for sympathetic cooling of the HCI and quantum-logic clock readout and initialization. We identified HCIs with the $4f^{12}$ ground-state configuration to be especially promising for precision timekeeping. It was demonstrated that such ions can serve as a basis of a clockwork of exceptional accuracy, with fractional uncertainty of about 10^{-19}. One of the most important systematic effects was determined to be the frequency shift due to interaction of ionic quadrupole moments with gradients of the trapping electric field. It was suggested to use combinations of different hyperfine transitions to suppress this shift.

Here we analyze similar $4f^{12}$ HCIs but propose another approach to suppressing the quadrupole shift. Instead of using different hyperfine transitions we combine transitions between states of different projections of the total angular momentum. We focus on isotopes with zero nuclear spin. Since these lack a complicated hyperfine structure, the processes of initializing the clock becomes easier. Also the detrimental second-order ac Zeeman shift becomes substantially suppressed. In the end, compared to the original proposal [8], our current scheme can be easier to implement and can have higher accuracy.

The electronic states arising from the $4f^{12}$ configuration have some unique features which make them convenient when building very accurate atomic clocks. First, transitions within these configuration are always in the optical or near-IR region practically for any ionization degree. Second, there is always a metastable state in this configuration with long enough life time to be used as a clock state. The latter can be understood using simple arguments. The fine structure of the $4f$ states in the highly charged ions is large and the lowest states of the $4f^{12}$ configuration can be considered as the states of the two-hole states of the $4f^2_{7/2}$ relativistic configuration. The states of this configuration can have the total angular momentum $J = 6,4,2,0$. According to Hund's rules, the $J = 6$ state is the ground state and $J = 4$ state is the first excited state. The excited state can only decay to the ground state via electric quadrupole transition which is suppressed due to the small size of the HCI and relatively small frequency. This makes it a very long living state, suitable for an atomic clock.

Similar consideration holds for any ions with the nl^2 ($l = 1,2,3$) two-electron or two-hole ground-state configuration, e.g., $4f^2$, nd^8, and nd^2 ($n = 3,4,5$), and np^4 ($n = 2,3,4,5,6$). However, the radiative width of the states tends to increase with the decreasing value of the total angular momentum. For example, the width of the states of the $4f^2$ configuration ($4f^2_{5/2}$ electron states) is roughly one order of magnitude larger than the width of the states of the $4f^{12}$ configuration ($4f^2_{7/2}$ hole states). The width of the states of the $4d^8$ configuration ($4d^2_{5/2}$ hole states) is close to those of the $4f^2$ configuration. But the width of the states of the $4d^2$ configuration ($4d^2_{3/2}$ electron states) is larger again. For this reason in the present paper we only consider the states of the $4f^{12}$ configuration which can be used to build the most accurate HCI optical clocks.

In this paper, we study ions which have the electron configuration of palladium or cadmium plus twelve $4f$ electrons: $[\mathrm{Pd}]5s^2 4f^{12}$ or $[\mathrm{Pd}]4f^{12}$. The $[\mathrm{Pd}]4f^{12}$ configuration is the ground-state configuration for all ions starting from Re^{17+} which have nuclear charge $Z \geqslant 75$ and degree of ionization $Z_i = Z - 58$. These are not the only ions which have the $4f^{12}$ configuration in the ground state. For example, neutral erbium has the $[\mathrm{Xe}]4f^{12}6s^2$ ground-state configuration, Er III ions has the $[\mathrm{Xe}]4f^{12}$ ground-state configuration, etc. Many properties of these ions and neutral erbium are very similar to those of the HCIs. However, HCIs are naturally more suitable for accurate timekeeping because of their smaller electronic-cloud size and thereby suppressed couplings and lower sensitivity to external perturbations.

Table I lists relevant properties of the most abundant stable even-even isotopes of the HCIs which have the $4f^{12}$ configuration of the ground state. All enumerated isotopes have a vanishing nuclear spin. Numerical calculations were carried out with the version of the configuration interaction (CI) method described in [10,11].

In the present paper we consider ions qualitatively, without trying to achieve high accuracy of the calculations. Therefore,

TABLE I. Properties of clock transitions in even-even isotopes (nuclear spin $I = 0$) of highly charged ions with the $4f^{12}$ ground-state configuration of valence electrons. The complete ground-state configuration is $[\mathrm{Pd}]5s^2 4f^{12}$ for Hf^{12+} and W^{14+} and $[\mathrm{Pd}]4f^{12}$ for other ions. ΔE is the energy interval between the ground and the excited clock states, λ is the corresponding wavelength, Γ is the radiative width of the clock state, τ is its lifetime, and $\mathcal{Q}$ is the quality factor ($\mathcal{Q} = \omega/\Gamma$). Numbers in square brackets represent powers of 10.

Z	Ion	ΔE (cm^{-1})	λ (nm)	Γ (μHz)	τ (days)	$1/\mathcal{Q}$
72	$^{180}\mathrm{Hf}^{12+}$	8555	1168	9.5	4.6	3.7[−20]
74	$^{184}\mathrm{W}^{14+}$	9199	1087	9.6	4.6	3.5[−20]
76	$^{192}\mathrm{Os}^{18+}$	9918	1008	13.6	3.2	4.6[−20]
78	$^{194}\mathrm{Pt}^{20+}$	10411	960	13.5	3.3	4.3[−20]
80	$^{202}\mathrm{Hg}^{22+}$	10844	922	13.2	3.4	4.1[−20]
82	$^{208}\mathrm{Pb}^{24+}$	11257	888	12.8	3.4	3.8[−20]
84	$^{208}\mathrm{Po}^{26+}$	11624	860	12.3	3.6	3.5[−20]
88	$^{226}\mathrm{Ra}^{30+}$	12275	814	11.2	3.9	3.1[−20]
90	$^{232}\mathrm{Th}^{32+}$	12567	795	10.7	4.1	2.8[−20]
92	$^{238}\mathrm{U}^{34+}$	12841	778	10.2	4.4	2.6[−20]

we consider only the mixing of all relativistic configurations corresponding to a single nonrelativistic $4f^{12}$ configuration. These are the $4f^6_{5/2}4f^6_{7/2}$, $4f^5_{5/2}4f^7_{7/2}$, and $4f^4_{5/2}4f^8_{7/2}$ configurations. the standard CI technique is used to construct the states of definite value of the total angular momentum J. In this paper we are interested only in ionic parameters which are determined by matrix elements of the electric quadrupole operator for the states of the $4f^{12}$ configuration. From our previous similar calculations [8] we know that mixing with configurations involving excitations from the $4f$ subshell have little effect on these matrix elements.

To check the accuracy of such approach we performed test calculations for the Er I atom and Er III ion which have the $6s^2 4f^{12}$ and $4f^{12}$ configurations of their ground states. The calculated frequency for the clock transition in these systems turned out to be about 20% larger than the experimental one [12]. A better accuracy should be expected for the ions considered in present paper since the central field for valence electrons in ions is stronger. The 20% uncertainty for the frequency translates to the factor 2.5 uncertainty for the width, lifetime, and quality factor [see formula (1)]. Note that if like for Er I and Er III, the calculated frequency is larger than the real one, then the parameters of the clock transitions are even better than those presented in Table I.

There is also some uncertainty in the transition probability due to uncertainty in the calculated $E2$ transition amplitude. However, this uncertainty is relatively small. If we use nonrelativistic notations, as for Er I and Er III, the clock transition is between the $^3\mathrm{H}_6$ and $^3\mathrm{F}_4$ states. The change in approximate quantum numbers $\Delta S = 0$ and $\Delta L = 2$ is consistent with the selection rules for the electric quadrupole transition. Therefore, there is no reason for the amplitude to be small. Numerical calculations show that the amplitude is of the same order as diagonal matrix elements of the $E2$ operator (quadrupole moments). The accuracy for nonsuppressed amplitudes is about 10% [13]. This corresponds to the 20% uncertainty in the transition probability.

TABLE II. Electric quadrupole moments of the ground ($J = 6$) and excited ($J = 4$) clock states for ions from Hf^{12+} to U^{34+} and the amplitude of the $E2$ transition between the states. The numbers are in atomic units.

Ion	Q_6	Q_4	Q_6/Q_4	$\langle 6\|\|E2\|\|4\rangle$
Hf^{12+}	0.2276	−0.0132	−17.2	0.3240
W^{14+}	0.1879	−0.0137	−13.7	0.2715
Os^{18+}	0.1837	−0.0151	−12.1	0.2680
Pt^{20+}	0.1611	−0.0141	−11.4	0.2364
Hg^{22+}	0.1430	−0.0130	−11.0	0.2106
Pb^{24+}	0.1282	−0.0120	−10.7	0.1892
Po^{26+}	0.1158	−0.0110	−10.5	0.1712
Ra^{30+}	0.0965	−0.0093	−10.4	0.1427
Th^{32+}	0.0888	−0.0086	−10.3	0.1312
U^{34+}	0.0821	−0.0080	−10.3	0.1212

The probability of the electric quadrupole ($E2$) transition is given by (we use atomic units: $\hbar = 1$, $m_e = 1$, $|e| = 1$)

$$\Gamma_e = \frac{1}{15}\alpha^5 \omega_{eg}^5 \frac{\langle e||E2||g\rangle^2}{2J_e + 1}. \tag{1}$$

Here g is the ground state and e is the excited metastable state, $\alpha \approx 1/137.036$ is the fine structure constant, and ω_{eg} is the frequency of the clock transition. The electric quadrupole operator is defined in length form as $E2_m = r^2 Y_{2m}(\theta,\phi)$. A typical value of frequency for the considered transitions is $\omega_{eg} \sim 0.1$ a.u., the amplitude of the $E2$ transition $\langle e||E2||g\rangle \ll 1$ a.u., $J_e = 4$. This leads to $\Gamma_e \sim 10^{-21}$ a.u. ($\sim$10 μHz) and $\mathcal{Q} = \omega_{eg}/\Gamma_e \sim 10^{20}$ (see Table I).

The main factors which may affect the performance of the clocks are quadrupolar shift, blackbody radiation (BBR), static and dynamic Stark shifts, Zeeman shift, and the effect of micromotion. All these and additional effects were considered in detail in our previous paper [8]. Here we focus on the electric quadrupole shift using an alternative approach.

Electric quadrupole shift. One of the most important systematic effects is the clock frequency shift due to the interaction of ionic quadrupole moments with the gradients of a trapping electric field. In our previous paper [8] we suggested using the hyperfine structure of the clock states to suppress the shift. Here we explore a different approach based on combining transition frequencies between states of different projections of the total angular momentum J.

The coupling of the Q moment to the E field gradient $\partial E_z/\partial z$ reads (z is the quantization axis determined by externally applied B field)

$$H_Q = -\frac{1}{2}Q\frac{\partial \mathcal{E}_z}{\partial z}. \tag{2}$$

The quadrupole moment Q of the atomic state is defined conventionally as twice the expectation value in the stretched state

$$Q_J = 2\langle nJM = J|Q_0|nJM = J\rangle. \tag{3}$$

Calculated values of Q for the ground Q_6 and excited Q_4 states are compiled in Table II. The uncertainty for their values is

TABLE III. Transitions convenient for use to suppress the electric quadrupole shift. J_1, M_1 are the total angular momentum and its projection for the ground state, J_2, M_2 are the total angular momentum and its projection for the clock state, A is given by Eq. (8), $c_1 = 1/(1-A)$, $c_2 = A/(A-1)$ ($\omega_0 = c_1\omega_1 + c_2\omega_2$). We consider extreme values of Q_6/Q_4 from Table II.

		$Q_6/Q_4 = -17$			$Q_6/Q_4 = -10$		
J_1,M_1–J_2,M_2	J_1,M_1'–J_2,M_2'	A	c_1	c_2	A	c_1	c_2
6,2–4,0	6,5–4,4	−0.9351	0.5168	0.4832	−0.9578	0.5108	0.4892
6,2–4,1	6,5–4,4	−0.9494	0.5130	0.4870	−0.9846	0.5039	0.4961
6,2–4,2	6,5–4,4	−0.9922	0.5020	0.4980	−1.0649	0.4843	0.5157
6,2–4,3	6,5–4,3	−0.9669	0.5084	0.4916	−1.0096	0.4976	0.5024

expected to be on the same level as for the energies (<20%). Note that we actually need only the ratio Q_6/Q_4 (see below). The uncertainty for the ratio is likely to be significantly smaller than those for each of the moments Q_6 and Q_4 [14].

Typical values of the gradient $\partial\mathcal{E}_z/\partial z \approx 10^8\ \mathrm{V/m^2}$ and Q moments from Table II one can get, e.g., for Os^{18+}

$$\left(\frac{\Delta\nu}{\nu}\right) \sim 10^{-16}, \tag{4}$$

which is well above the sought fractional accuracy level.

The Q-induced energy shift for a state with total angular momentum J and its projection $J_z = M$ reads

$$\delta E_{JM} \sim \frac{3M^2 - J(J+1)}{3J^2 - J(J+1)} Q_J \frac{\partial E_z}{\partial z} \equiv C_{JM} Q_J \frac{\partial E_z}{\partial z}. \tag{5}$$

The clock frequency of the transition between two states J_1, M_1 and J_2, M_2 can be expressed as

$$\omega = \omega_0 + \left(C_{J_1,M_1} Q_{J_1} + C_{J_2,M_2} Q_{J_2}\right) \frac{\partial E_z}{\partial z}, \tag{6}$$

where ω_0 is the unperturbed clock frequency. The uncertainty due to the electric quadrupole shift can be eliminated if two transitions between states with different projections M are considered. Indeed, using the expression (6) for two transitions J_1,M_1–J_2,M_2 with frequency ω_1 and J_1,M_1'–J_2,M_2' with frequency ω_2 one can find the unperturbed frequency ω_0:

$$\omega_0 = \frac{\omega_1 - A\omega_2}{1 - A}, \tag{7}$$

where

$$A = \frac{C_{J_1,M_1}(Q_{J_1}/Q_{J_2}) + C_{J_2,M_2}}{C_{J_1,M_1'}(Q_{J_1}/Q_{J_2}) + C_{J_2,M_2'}}. \tag{8}$$

Expressions (7) and (8) do not depend on the E-field gradient.

The uncertainty due to the quadrupole shift can be eliminated if quadrupole moments of both states are known. To be precise, we only need to know their ratio. In the approximation of pure two-hole configuration $4f_{7/2}^2$ this ratio can be found analytically. The quadrupole moment for a state with total angular momentum J is given by

$$Q_J = -(2J+1)\begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix}\begin{Bmatrix} J & 2 & J \\ j & j & j \end{Bmatrix}\langle j||E2||j\rangle. \tag{9}$$

Here $J = 6$ or 4 and $j = 7/2$, where j is the total angular momentum of the hole state $4f_{7/2}$. It follows from Eq. (9) that $Q_6/Q_4 = -11$. For this value of the ratio, the quadrupole shift is canceled out by simple averaging of the frequencies of the two transitions $M_1 = 2, M_2 = 3$ and $M_1' = 5, M_2' = 3$:

$$\omega_0 = (\omega_1 + \omega_2)/2, \tag{10}$$

where

$$\begin{aligned} \omega_1 &= E(J=4, M=3) - E(J=6, M=2), \\ \omega_2 &= E(J=4, M=3) - E(J=6, M=5). \end{aligned} \tag{11}$$

The true value of the Q_6/Q_4 ratio may differ from the approximate value of −11 (see Table II) mostly due to the admixture of the $4f_{7/2}4f_{5/2}$ configuration. If this ratio is known (from calculations or measurements), the use of Eqs. (7) and (8) ensures accurate cancellation of the quadrupole shift. Table III lists some convenient $E2$-allowed transitions.

Note that the computed ratio Q_6/Q_4 varies relatively little from ion to ion. For all ions with the $[\mathrm{Pd}]4f^{12}$ configuration of the ground state (from Os^{18+} to U^{34+}), it is within 10% of the analytical value of −11. For all these values the use of simplest case [Eqs. (10) and (11)] leads to at least two orders of magnitude suppression of the quadrupole shift.

Other systematics. Systematic effects which can affect the performance of the ionic clocks with the $4f^{12}$ configuration of the ground state were studied in detail in our previous work [8]. In addition to electric quadrupole shift considered above, they include the frequency shift due to black-body radiation (BBR), Zeeman shift, Doppler effect, and gravity. Actual estimations were done for the Os^{18+}, Bi^{25+}, and U^{34+} ions and discussed in detail for the Bi^{25+} ion. It was clear from the analysis that parameters of the ions vary relatively little from one ion to another and the analysis performed in [8] is valid for all ions considered in the present paper.

Compared to Ref. [8], the absence of a hyperfine structure in the presently considered isotopes modifies analysis of second-order Zeeman shifts. The second-order ac Zeeman shift was

TABLE IV. Other frequency shifts reestimated from Ref. [8].

Effect	Shift	Condition
BBR	1.8×10^{-21}– 6.6×10^{-20}	$T = 300$ K
Quadratic Zeeman	$<10^{-24}$	$B_{\mathrm{ac}} < 10^{-7}$ T
Micromotion	10^{-19}	Mass scaling from Al^{+}[a]
Gravity	10^{-19}	$\Delta h = 1$ mm[b]

[a] Reference [15].

[b] Change of height.

estimated in [8] assuming the value of the magnetic field $B_{\mathrm{ac}} = 5 \times 10^{-8}$ T measured in the $\mathrm{Al}^+ + \mathrm{Be}^+$ trap [15] and found to be 4×10^{-20}. Note, however, that the second-order Zeeman shift is strongly enhanced in ions considered in [8] due to small energy intervals between states of the hyperfine structure multiplet. In the present paper we focused on ions lacking a hyperfine structure. This means that the second-order Zeeman shift is further suppressed for these ions by several orders of magnitude. This is an important advantage for using these ions. The estimated values for important frequency shifts are summarized in Table IV.

It was shown in [8] that all other systematic effects produce a fractional frequency shift which is below the value of 10^{-19}. We anticipate that due to the simplified level structure of nuclear-spin-zero isotopes, the present work may provide a simpler and potentially more accurate route to HCI-based clocks that can carry out metrology to the 19th significant figure.

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