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

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(Dated: May 2, 2014)

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 gradients of 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 $10^{-19}$.

PACS numbers: 11.30.Er, 31.15.A-}

Developing accurate atomic clocks is important for both technological and fundamental reasons. Cesium primary frequency standard which is currently used to define the SI units of time and length has fractional accuracy of the order $10^{-16}$[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 optical lattice aim at fractional accuracy of $10^{-18}$[3]. Further progress is possible with clocks using nuclear optical transition[4], or clocks using optical transitions in highly charged ions[5–12].

In our previous paper[8] we proposed ion clocks based on optical transitions in trapped highly charged ions (HCI). Clock HCI is co-trapped with 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 time-keeping. 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 effect was determined to be the frequency shift due to interaction of ionic quadrupole moments with gradients of 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 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/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 $4f^{7/2}_{5/2}$ relativistic configuration. The states of this configuration can have the total angular momentum $J = 6, 4, 2, 0$. According to the 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. This makes it a very long living state, suitable for 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 ($4f^2_{5/2}$ 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 ($4d^2_{5/2}$ electron states) is larger again. For this reason in 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 electron configuration of palladium or cadmium plus twelve $4f$ electrons: [Pd]5s$^24f^{12}$ or [Pd]4f$^{12}$. The [Pd]4f$^{12}$ configuration is the ground state configuration for all ions starting from Re$^{17+}$ which have nuclear charge $Z \geq 75$ 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 [Xe]4f$^{12}6s^2$
interaction of ionic quadrupole moments with the gradients of trapping electric field. In our previous paper \[8\] we suggested using 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 Q-moment to the E-field gradient \(\partial E_z/\partial z\) reads \((z\) is the quantization axis determined by externally applied B-field\)

\[
H_Q = \frac{1}{2} \frac{\partial E_z}{\partial z}.
\]

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

\[
Q_J = 2\langle nJM | J | Q_0 | nJM \rangle = J.
\]

Calculated values of \(Q\) for the ground \(Q_6\) and excited \(Q_4\) states are compiled in Table II. Typical values of the gradient \(\partial E_z/\partial z \approx 10^8 \text{ V/m}^2\) and Q-moments from Table II one can get e.g., for Os\(^{18+}\)

\[
\left(\frac{\Delta \nu}{\nu}\right) \sim 10^{-16},
\]

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

\[
\delta E_{JM} \sim \frac{3M^2 - J(J + 1)}{3J^2 - J(J + 1)} Q J_z \frac{\partial E_z}{\partial z} \equiv C_{JM} Q J_z \frac{\partial E_z}{\partial z}.
\]

Clock frequency of the transition between two states \(J_1, M_1\) and \(J_2, M_2\) can be expressed as

\[
\omega = \omega_0 + (C_{J_1, M_1} Q J_1 + C_{J_2, M_2} Q J_2) \frac{\partial E_z}{\partial z},
\]

where \(\omega_0\) 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

\[
\Delta \omega = (C_{J_1, M_1} Q J_1 + C_{J_2, M_2} Q J_2) \frac{\partial E_z}{\partial z}.
\]
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 (10), (11) leads to at least two orders of magnitude suppression of the quadrupole shift.

b. 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 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 hyperfine structure in presently considered isotopes modifies analysis of second-order Zeeman shifts. The second-order AC Zeeman shift was estimated in [8] assuming the value of the magnetic field $B_{AC} = 5 \times 10^{-8}$ T measured in the Al$^+/Be^+$ trap [12] and found to be $4 \times 10^{-20}$. 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 present paper we focused on ions lacking hyperfine structure. This means that the second-order Zeeman shift is further suppressed for these ions by several orders of magnitude. This is important advantage for using these ions.

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

Acknowledgments

The authors are grateful to G. Gribakin for useful discussions. The work was supported in part by the Australian Research Council and the U.S. National Science Foundation.
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