Optical clock sensitive to variation of the fine structure constant based on the Ho\textsuperscript{14+} ion

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We study the Ho\textsuperscript{14+} ion as a candidate for extremely accurate and stable optical atomic clock which is sensitive to the time variation of the fine structure constant. We demonstrate that the proposed system has all desired features including relatively strong optical electric dipole and magnetic dipole transitions which can be used for cooling and detection. Zero quadrupole moments for the relevant states in the clock transition allows interrogating multiple ions to improve the clock stability.

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Theories unifying gravity with other fundamental interactions suggest a possibility for fundamental constants to vary in space or time (see, e.g. \cite{1}). Searching for variation of the fundamental constants is an important way of testing these theories and finding new physics beyond standard model. Laboratory measurements limit the rate at which the fine structure constant may vary on astronomical scale along a certain direction in space forming the so-called alpha-dipole \cite{4}. Earth movement in the frame-atical scale along a certain direction in space forming the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Ion & Ground state & Clock state & Energy (cm\textsuperscript{-1}) \\
\hline
Er\textsuperscript{14+} & 4f\textsuperscript{5}5s & J = 4 & 4f\textsuperscript{5}5s\textsuperscript{2} & J = 0 & 18555 \\
Dy\textsuperscript{10+} & 4f\textsuperscript{5}5p & J = 3 & 4f\textsuperscript{5}5p\textsuperscript{2} & J = 0 & 20835 \\
Ho\textsuperscript{14+} & 4f\textsuperscript{6}5s & J = 0.5 & 4f\textsuperscript{5}5s\textsuperscript{2} & J = 2.5 & 23800 \\
\hline
\end{tabular}
\caption{Highly charged ions with optical clock transitions sensitive to variation of \(\alpha\) satisfying the criteria discussed in the text.}
\end{table}

would lead to the local time variation of \(\alpha\) on the scale of \(10^{-19}\) per year \cite{2}. To test the alpha-dipole hypothesis in terrestrial studies one needs a better accuracy in the laboratory measurements. The current best limit on the local time variation of \(\alpha\) has been obtained by comparing Al\textsuperscript{+} and Hg\textsuperscript{+} optical clocks \cite{2}. The result of this comparison limits time variation of alpha to \((\partial \alpha/\partial t)/\alpha = (-1.6 \pm 2.3) \times 10^{-17} \text{yr}^{-1}\) \cite{2}, i.e. about two orders of magnitude improvement in accuracy is needed to test the alpha-dipole hypothesis.

Current-best optical-clocks approach fractional uncertainty of \(\sim 10^{-18}\) \cite{2}. However, the transitions used in these clocks are not sufficiently sensitive to the variation of \(\alpha\) \cite{2}. If \(\alpha\) does change in time, the relative change \(\delta\omega/\omega\) of the clock frequencies in any given period of time would be about an order of magnitude smaller than relative change in \(\delta\alpha/\alpha\).

It has been suggested in \cite{10} to use highly-charged ions (HCI) as extremely accurate atomic clocks to probe possible variation of \(\alpha\). While HCIs are less sensitive to external perturbations due to their compact size, their sensitivity to variation of \(\alpha\) is enhanced due to larger relativistic effects. In spite of the general trend of increasing energy intervals in HCIs, it is still possible to find clock transitions which are in optical range. This is due to electron energy level crossing while moving from the Modelung to the Coulomb level ordering with increasing

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Low-lying energy levels of Ho\textsuperscript{14+}. Numbers in parentheses correspond to those in Table II and IV to denote electronic states.}
\end{figure}
of the ionization degree [11]. A number of optical clock transitions sensitive to variation of \( \alpha \) were found and examined in Refs. [10–17].

Proposals for HCl clocks so far focused on their high accuracy aspects, such as the reduced sensitivity to blackbody radiation shift due to lack of infrared and optical transitions [14]. These proposals, therefore, naturally assume to use quantum logic spectroscopy (QLS) [18] by co-trapping optically accessible ions. From an experimental viewpoint, however, increase of number of ions is a pressing need in order to improve clock stability, which is limited by the quantum projection noise (QPN) [19]. Clock stability at QPN limit is given by

\[
\sigma_y \approx \frac{1}{\sqrt{\lambda N \tau_c}},
\]

where \( Q = \omega/\Delta \omega \) is the effective quality-factor for the interrogated transition and \( N \) is the number of ions measured in a clock cycle time \( \tau_c \). Assuming \( Q \approx 10^{15} \) and \( \tau_c = 1 \) s that are achievable with the-state-of-the-art lasers [20], a goal uncertainty of e.g., \( 1 \times 10^{-18} \) determines necessary averaging time of \( \tau = 10^6 N^{-1} \) s. In order to achieve this goal within a realistic experimental run time of \( \tau \sim 10^4 \) s (\( \sim 3 \) hours), \( N \approx 10^5 \) ions need to be interrogated simultaneously. Regrettably, QLS is not applicable to such number of ions because of difficulties in controlling degrees of motional states of the ions; therefore electron shelving detection [21] needs to be adopted. Moreover, with \( N > 1 \) ions present, spatially inhomogeneous quadrupole-shift originating from coulomb interactions between ions becomes a major concern.

For these reasons we relax the condition of having simple electron structure and search for ions which have relatively strong electric dipole (E1) or magnetic dipole (M1) optical transitions from both ground and clock states. The criteria for a suitable system are formulated as following:

- Clock transition has high sensitivity to the variation of \( \alpha \) (e.g. it is a 5s to 4f or 5p to 4f transition).
- It is optical transition (230 nm < \( \lambda \) < 2000 nm or 5000 cm\(^{-1} \) < \( h\omega \) < 43000 cm\(^{-1} \)) for existing narrow-linewidth lasers to access.
- It is a transition between long-lived states with lifetime between 100 and 10\(^4 \) seconds.
- There are other relatively strong optical transitions (equivalent lifetime \( \tau \leq 1 \) ms).
- Clock transition is not sensitive to the gradients of electric field (e.g., there is no electric quadrupole moment in both states).

Note that blackbody radiation shift is not a limiting factor for HCl clocks since trapping of HCl for more than an hour requires ultrahigh vacuum environment that is achievable with cryogenic pumps, which naturally cool environmental temperature to \( \sim 10 \) K.

Clock transitions for some HClIs that satisfy all these criteria are presented in Table II. All these ions have complicated electronic structure with six to eight electrons in open 4f, 5s and 5p shells. The analysis is done by the many-electron version of the configuration interaction (CI) method developed in Ref. [22]. Breit and quantum radiative corrections are also included as has been described in Ref. [23, 24]. The precision of this analysis is limited, which means that the clock frequencies calculated in Table II may differ from real ones by up to estimated value of 10000 cm\(^{-1} \). Even with this shift most of the presented transitions remain in the optical range.

We now discuss in more detail the Ho\(^{14+} \) ion which currently appears as the best candidate for an optical clock. Its level structure is shown in Fig. I. Table II shows low-lying energy levels of Ho\(^{14+} \). For the 4f\(^{5}5s^{2} \) \( ^{8}\)F\(_{1/2} \) ground state, the 4f\(^{5}5s^{2} \) \( ^{6}\)H\(_{9/2} \) state can be taken as the clock state. Only levels which are connected to the ground or clock state by electric dipole (E1) or magnetic dipole (M1) transitions are shown in Table II. The total number of states in the considered energy interval is much larger. For each fine structure multiplet, \( N_s = \min(2S + 1, 2L + 1) \) gives the number of states, where \( S \) is total spin and \( L \) is total orbital angular momentum. The values of \( S \) and \( L \) and corresponding names of the multiplets are found from the values of the \( g \)-factors (see Table II). For example, the ground state is the lowest state of the \( ^{8}\)F multiplet which has seven levels with total angular momentum \( J \) ranging from \( J = 1/2 \) to \( J = 13/2 \). Corresponding non-relativistic value of the \( g \)-factor [11] is

\[
g = 4.0 \quad \text{while the value obtained in the CI calculations is} \quad g = 3.94.
\]

The clock transition can go as a magnetic quadrupole (M2) or electric octupole (E3) transition. Corresponding rates are \( 8 \times 10^{-14} \) s\(^{-1} \) and \( 4 \times 10^{-12} \) s\(^{-1} \). However, tran-
sition rate is dominated by the electric dipole (E1) transition mediated by the magnetic-dipole hyperfine-structure (hfs) interaction. Holmium atom has single stable isotope $^{165}$Ho with nuclear spin $I = 7/2$, the nuclear magnetic moment $\mu = 4.173 \mu_N$ [23] and the nuclear electric quadrupole moment $Q = 3.58 b$ [20] ($1b = 10^{-28} m^2$). Calculated hfs constants $A$ and $B$ are presented in Table III.

The largest contribution to the hfs-mediated E1 clock transition moment is given by

$$d_{\text{hfs-E1}} = \frac{\langle 4f^65s^88F_{1/2}|\hat{H}_{\text{hfs}}|4f^65s^88F_{3/2}\rangle}{\Delta E} \times \langle 4f^65s^88F_{3/2}|E1|4f^55s^2^2H_{5/2}^o \rangle,$$

where $\hat{H}_{\text{hfs}}$ is magnetic-dipole hfs Hamiltonian, $E1$ is the electric-dipole operator, and $\Delta E = 1013 \text{ cm}^{-1}$ is the energy interval between ground and dominating intermediate state. This term dominates due to small energy denominator. The hfs matrix element is equal to $1.94 \times 10^{-5}$ a.u. The E1 matrix element is related to the electric dipole transition amplitude between $n = 2$ and 5 states (see Table IV) by an angular coefficient. Its value ($10^{-5}$ a.u.) is small due to absence of the single-electron electric dipole transition between leading configurations (the 5s - 4f transition cannot go as E1). The amplitude is not zero due to configuration mixing.

Spontaneous emission rate corresponding to the hfs-E1 transition-moment [see Eq. (2)] is the same as that for the usual E1 transition (we use atomic units)

$$A_{\text{hfs-E1}} = \frac{4}{3} (\omega \alpha)^3 d_{\text{hfs-E1}}^2 F_c^2 + 1,$$

where $\omega = 0.092$ a.u. is the frequency of the clock transition, $d_{\text{hfs-E1}}$ is reduced matrix element, and $F_c$ is the total angular momentum of the clock state ($F = I + J$). The emission rate from the clock state with $F_c = 3$ is $7.5 \times 10^{-7} \text{ s}^{-1}$. Note that this transition rate gives negligible contribution to the clock state lifetime, which is dominated by the E1 transitions to three first excited states of the ground state configuration.

Rabi frequency $\Omega = d_{\text{hfs-E1}} E$ for the $4f^65s^88F_{1/2} \rightarrow 4f^55s^2^2H_{5/2}^o$ clock transition is estimated from Eq. (2) and laser electric field $E$. For laser intensity of 16 mW/cm$^2$, the Rabi frequency is estimated to be 1 Hz. Corresponding frequency shift of the clock transition is about $10^{-3}$ Hz.

The $^4H_{5/2}$ clock state is split by the hfs interaction into six levels with $F_c = 1, \ldots, 6$. Similarly, the $^8F_{1/2}$ ground state is split to $F_g = 3, 4$. We consider $F_c = F_g = 3$ with $M = 2$ states as a clock transition, because it is insensitive to the electric-field gradients that couple to the atomic quadrupole moment and cause quadrupole shift. Since the quadrupole moment is proportional to $3M^2 - F(F+1)$ ($M$ is projection of $F$), choosing $F = 3$ and $M = \pm 2$ eliminates quadrupole frequency shift. Note that the ground state has no quadrupole moment because of the total electron angular momentum $J = 1/2$.

Optical pumping to the desired $M$ states can be performed by employing strong E1 transitions from the ground state as given in Table IV. In a presence of a bias magnetic field, applying $\sigma^+$ polarization light resonant to the $4f^65s^2^2F_{3/2}^o/4f^55s^2^2H_{5/2}^o$ pump state (denoted by $n = 9$), ions are spin-polarized in the $F_g = M = 3$ state, which is then transferred to the $F_g = 3, M = 2$ state by a stimulated Raman adiabatic passage via the pump state. The same E1 line can be used for the electron-shelving detection [21]. With $\sigma^+$ polarization light resonant to this pump transition, the ground state population is swept into the $F_g = M = 3 \rightarrow F_p = M = 4$ quasi-cyclic transition, where four recycling lasers may depopulate the $F_g = 4$ state as well as $F = 3, 4, 5$ states in the $^8F_{3/2}^o$ manifold. The same scheme as above can be conveniently used to sideband-cool a chain of ions. Here we assume Ho$^{14+}$ ions are initially cooperatively-cooled by coolant ions such as Be$^+$ whose mass-charge ratio $(A/q = 9)$ is similar to that of Ho$^{14+}$ $(A/q \approx 11.8)$.

Lifetime of the clock state is about 37 s. It is mainly due to electric dipole transitions to the first three excited states in the ground state configurations (see Table IV).
The table also lists E1 and M1 transitions that can be used for electronic state manipulation as well as laser-cooling ions’ motion. In particular, the $^6\text{H}_{3/2} \rightarrow ^6\text{F}_{3/2}$ (M1) transition followed by an E1 decay to the ground state may be conveniently used to depopulate the clock state. The amplitudes are given by reduced matrix elements of the electric dipole ($\mathbf{e} \cdot \mathbf{E}$) and magnetic dipole ($\mu \cdot \mathbf{H}$) operators. The M1 amplitudes include electron magnetic moment $\mu$ which in atomic units is equal to $\alpha/2 = 3.65 \times 10^{-3}$ (Gaussian-based atomic units). Spontaneous emission rates for both E1 and M1 transitions are given by Eq. (3) with $F_c$ replaced by $J$.

The clock transition is sensitive to variation of the fine structure constant since it is a 4f to 5s transition [11]. It is convenient to present frequency dependence on $\alpha$ in the form

$$\omega(x) = \omega_0 + qx,$$

where $x = \left[\left(\frac{\alpha}{\alpha_0}\right)^2 - 1\right]$. (4)

The sensitivity coefficient $q$ is found in atomic calculations by varying the value of $\alpha$ in computer codes. In our calculations $q = -186000 \text{ cm}^{-1}$ and variation of the clock frequency is related to the variation of the fine structure constant by

$$\frac{\delta \omega}{\omega} = -18 \frac{\delta \alpha}{\alpha}$$

(5)

As it has been mentioned above the precision of present calculations based on the version of the CI method developed in Ref. [22] is limited. The main problem is the energy interval between states of different configurations. Precision for energy intervals within one configuration is better and is on the level of 10 to 20%. Therefore, to start with, it is important to spectroscopically investigate transitions between different configurations. The best candidates are the E1 transitions from the ground state to the $^6\text{F}_{3/2}$ states located at $\sim 4 \times 10^4 \text{ cm}^{-1}$. Once this frequency is measured, it helps to adjust the calculations and improves significantly all other predictions. Note that even significant change in the frequency of the clock transition of Ho$^{14+}$ leaves it in optical range making the ion an attractive candidate for experimental study.

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