Ion clock and search for the variation of the fine structure constant using optical transitions in Nd$^{13+}$ and Sm$^{15+}$.

V.A. Dzuba$^{1,2}$, A. Derevianko$^2$, and V. V. Flambaum$^1$

$^1$School of Physics, University of New South Wales, Sydney, NSW 2052, Australia

$^2$Department of Physics, University of Nevada, Reno, Nevada 89557, USA

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We study ultranarrow $5s_{1/2} - 4f_{5/2}$ transitions in Nd$^{13+}$ and Sm$^{15+}$ and demonstrate that they lie in the optical region. The transitions are insensitive to external perturbations. At the same time they are sensitive to the variation of the fine structure constant $\alpha$. The fractional accuracy of the frequency of the transitions can be smaller than $10^{-19}$, which may provide a basis for atomic clocks of superb accuracy. Sensitivity to the variation of $\alpha$ approaches $10^{-20}$ per year.

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Building accurate atomic clocks is important for both technical applications and fundamental physics. 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]. Frequency standards based on optical transitions in neutral atoms trapped in optical lattice aim at fractional accuracy of $10^{-18}$ [2]. Further progress is possible with clocks using nuclear optical transition [3], or clocks using optical transitions in highly charged ions [4–6].

One of the important applications of precise atomic clocks in fundamental physics is the search for time variation of the fine structure constant. The possibility for fundamental constants to change in space or time is suggested by theories unifying gravity with other interactions (see, e.g. [7,8]). The analysis of quasar absorption spectra shows that there might be a direction in space along which the fine structure constant $\alpha$ ($\alpha = e^2/\hbar c$) is changing at constant rate over cosmological distances (alpha-dipole) [9]. Since the Earth moves in the framework of the alpha-dipole, the space variation of $\alpha$ should manifest itself in terrestrial studies as changing of $\alpha$ in time at approximate rate of $\dot{\alpha}/\alpha = 10^{-18}$ yr$^{-1}$ [10]. The best current limit on time-variation of $\alpha$ obtained from comparing Al$^+$ and Hg$^+$ clocks is significantly larger, $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17}$yr$^{-1}$ [11]. At least an order of magnitude improvement is needed to verify the alpha-dipole hypothesis in terrestrial studies. Two or more clocks with different dependence of clock frequencies on the fine structure constant and operating on the same level of accuracy ($10^{-18}$ or better) should be monitored over significant time interval (from few months to few years) to reveal any variation of $\alpha$ in time. If $\alpha$ is changing, then the readings of the clocks would shift in time against each other.

It was suggested in Ref. [4] to use highly charged ions (HCI) for this purpose. HCIs are less sensitive to external perturbations than neutral atoms (or singly-charged ions) due to their more compact size. Notice that many of HCIs have optical transitions where standard laser techniques can be used and where accuracy of the frequency measurements can be possibly even better than in optical standards using neutral or single-ionized atoms. A number atomic transitions in HCI were studied in earlier works [4–14] focusing mostly on their sensitivity to the variation of the fine structure constant. A detailed study of the effect of external perturbations on clock frequencies of some promising HCI systems was recently reported in Ref. [6]. There it was shown that the relative accuracy on the level of $10^{-19}$ might be possible for HCIs with the $4f^{12}$ configurations of valence electrons. These systems are not sensitive to the variation of $\alpha$. However, they can be used as a reference point against which the frequencies of the transitions sensitive to the variation of $\alpha$ are monitored.

In present work we study other promising systems which are immune to external perturbations while being sensitive to the variation of the fine structure constant. This makes them excellent candidates for terrestrial studies of the time variation of $\alpha$. We focus on the $5s - 4f$ transitions in Nd$^{13+}$ and Sm$^{15+}$ ions. Frequencies of these transitions are in the optical region due to the $5s - 4f$ level crossing which happens for the isoelectronic sequence of silver atom near $Z = 61$ (promethium ion) [14]. The first excited states in these ions ($4f_{5/2}$ in Nd$^{13+}$ and the $5s$ in Sm$^{15+}$) are metastable states because they can only decay to the ground state via the E3 transition. The states are not sensitive to external perturbations. On the other hand, the $s - f$ transitions are the transitions which are most sensitive to the variation of the fine structure constant [15]. Due to the inversion of the states from Nd$^{13+}$ to Sm$^{15+}$, corresponding frequencies would move in time in opposite direction if $\alpha$ changes. This further enhances the sensitivity. If the frequencies of the $5s - 4f_{5/2}$ transition in Nd$^{13+}$ and $4f_{5/2} - 5s$ transition in Sm$^{15+}$ are monitored simultaneously for extended period of time the sensitivity of the measurements can be on the level $\delta \alpha / \alpha \sim 10^{-19}$ per year or better.

Note that similar transition in Pm$^{14+}$ is even more sensitive to variation of $\alpha$. However, in this work we consider only isotopes with zero nuclear spin to suppress...
the second-order Zeeman shift. The promethium atom has no stable isotopes and no long-living isotopes with zero nuclear spin. Therefore we limit ourself in this work to the Nd$^{13^{+}}$ and Sm$^{15^{+}}$ ions.

The sensitivity of the atomic transitions to the variation of the fine structure constant can be revealed by varying the value of $\alpha$ in computer codes. We use the correlation potential method [16] to perform the calculations. The Nd$^{13^{+}}$ and Sm$^{15^{+}}$ ions have a single valence electron above the Pd-like closed-shell core. Therefore, it is convenient to use the $VN^{-1}$ approximation in which relativistic Hartree-Fock calculations are first done for the closed-shell core and states of valence electron are calculated in the self-consistent field of the frozen core. Correlations between valence and core electrons are included by constructing the second-order correlations potential $\Sigma$ and solving the Hartree-Fock-like equations with an extra operator $\Sigma$ for the states of external electron

$$ \hat{H}_0 + \Sigma - \varepsilon_v \psi_v = 0. $$

(1)

Here $\hat{H}_0$ is the relativistic Hartree-Fock Hamiltonian and index $v$ labels valence orbitals. Solving (1) gives energies and wave functions for different states of the valence electron which include correlations (the so called Brueckner orbitals). Many-body perturbation theory and B-spline basis states [17] are used to calculate $\Sigma$.

The dependence of the atomic frequencies on the fine structure constant $\alpha$ the frequencies may be presented as

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

(2)

where $x = (\alpha/\alpha_0)^2 - 1$, $\alpha$ is the current value of the fine structure constant, and $\alpha_0$ is the value of the fine structure constant at some fixed moment of time, say the beginning of the observations. Note that we use atomic units which means that the unit of energy is fixed and does not vary with $\alpha$. Therefore, equation (2) gives comprehensive description of the frequency dependence on $\alpha$. In the end, only change of the dimensionless values (e.g., ratio of two frequencies) can be studied. Therefore, the actual choice of units cannot affect the results.

The sensitivity coefficient $q$ in (2) is calculated by running the computer code with different values of $\alpha$ and taking numerical derivative,

$$ q = \frac{\omega(0.01) - \omega(-0.01)}{0.02}. $$

(3)

It follows from (2) that the relative change in frequency is related to the relative change in $\alpha$ by

$$ \frac{\delta \omega}{\omega} = \frac{2q}{\omega} \frac{\delta \alpha}{\alpha}, $$

(4)

where $K = 2q/\omega$ is the enhancement factor.

We chose the Nd$^{13^{+}}$ and Sm$^{13^{+}}$ ions because the 5s - 4f transition for these ions lie in the optical (UV) region. Table I shows calculated energy levels of the 4f and 5s states of the ions together with the sensitivity coefficients $q$ (see [2] and [11]) and the enhancement factor $K$. All other states of these ions lie very high in the spectrum, far outside of the optical region. The 5s - 4f$_{2}/2$ transition is very narrow for both ions. The lowest-order transitions between the 5s and 4f$_{2}/2$ states are the M2 and E3 transitions. The M2 transition is very weak since it vanishes by the 4f$_{2}/2$ - 5s E3 transition for Nd$^{13^{+}}$ and by the 5s - 4f$_{2}/2$ and 5s - 4f$_{7}/2$ E3 transitions for Sm$^{15^{+}}$ ion. The E3 decay rate is given by (we use atomic units: $\hbar = 1$, $m_e = 1$, $|e| = 1$)

$$ \Gamma_b = 0.001693 \alpha \langle E3 \rangle |\langle a||E3||b\rangle|^2 2J_b + 1. $$

(5)

Here $a$ is the ground state and $b$ is the excited metastable state, $\alpha = 1/137.36$ is the fine structure constant, $\omega_{ab}$ is the frequency of the transition. Estimates show that for Nd$^{13^{+}}$ $\Gamma_4f_{5/2} \approx 1.1 \times 10^{-23}$ a.u. = 7.4 $\times$ 10$^{-8}$ Hz, $1/\Gamma_4f_{5/2} \approx 4.8 \times 10^{-23}$ (Q is the quality factor), and for Sm$^{15^{+}}$ $\Gamma_5s \approx 4.3 \times 10^{-23}$ a.u. = 2.8 $\times$ 10$^{-7}$ Hz, $1/\Gamma_5s \approx 1.7 \times 10^{-22}$ (see also Table I).

Note, that the 4f - 5s level crossing [14] happens at about $Z = 61$ (promethium ion) leading to inversion of the levels order in samarium ion. As a results, the $q$-coefficients and enhancement factors have different sign for Nd$^{13^{+}}$ and Sm$^{15^{+}}$. It may be beneficial to measure the frequency of the 4f$_{5/2}$ - 5s transition in Sm$^{15^{+}}$ ($\lambda = 170$ nm) against the frequency of the 5s - 4f$_{5/2}$ transition in Nd$^{13^{+}}$ ($\lambda = 180$ nm). This would bring extra enhancement to the sensitivity of the clock frequencies to the variation of the fine structure constant. Using data from Table I one can get

$$ q_1 - q_2 = 242000 \; \text{cm}^{-1}, $$

$$ \frac{\delta (\omega_1/\omega_2)}{\omega_1/\omega_2} = 8.3 \frac{\delta \alpha}{\alpha}. $$

(6)

Here $\omega_1$ is the clock frequency for Nd$^{13^{+}}$ and $\omega_2$ is the clock frequency for Sm$^{15^{+}}$. Eq. (6) shows that if $\alpha$ drifts, the ratio of the clock frequencies changes about eight times faster. This means that if the ratio is monitored for a year with the accuracy of 10$^{-19}$, the sensitivity of the measurements to the variation of $\alpha$ would be close to 10$^{-20}$ per year.

<table>
<thead>
<tr>
<th>Ion</th>
<th>State</th>
<th>Energy (cm$^{-1}$)</th>
<th>q</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$^{13^{+}}$</td>
<td>5s$_{1/2}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4f$_{5/2}$</td>
<td>58897</td>
<td>106000</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>4f$_{7/2}$</td>
<td>63613</td>
<td>110200</td>
<td>3.5</td>
</tr>
<tr>
<td>Sm$^{15^{+}}$</td>
<td>4f$_{5/2}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4f$_{7/2}$</td>
<td>6806</td>
<td>6300</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>5s$_{1/2}$</td>
<td>55675</td>
<td>-136000</td>
<td>-4.9</td>
</tr>
</tbody>
</table>
Below we consider various systematic effects which affect the clock transition frequency. As discussed in [6], the clock HCl is assumed to be trapped and sympathetically cooled.

a. Black body radiation shift – The frequencies of the clock transitions might be affected by the black body radiation (BBR) shift. The BBR frequency shift at an ambient temperature \( T \) can be expressed as

\[
\frac{\delta \omega}{\omega} = - \left( \frac{T}{T_0} \right)^4 \frac{\Delta \alpha}{2 \omega} \left( \frac{831.9 \text{ V}}{\text{ m}} \right)^2,
\]

where \( T_0 = 300 \text{ K} \), \( \Delta \alpha \) is the difference in the values of the static dipole polarizabilities of the clock states. The polarizability \( \alpha_v(0) \) for the state \( v \) is given by

\[
\alpha_v(0) = \frac{2}{3(2j_v + 1)} \sum_n \langle v|D|n \rangle^2 \varepsilon_n - \varepsilon_v,
\]

where \( D = \sum_i e r_i \) is the electric dipole operator and summation goes over complete set of states. The results of calculations, which include Brueckner-type correlations and core polarization effects, are presented in Table II. Using (7) and the data from the table one can get at room temperature \( \delta \omega/\omega = -3.6 \times 10^{-18} \) for \( \text{Nd}^{13+} \) and \( \delta \omega/\omega = 2.9 \times 10^{-18} \) for \( \text{Sm}^{15+} \). For cryogenic Paul trap operating at the temperature of liquid helium (\( \sim 4 \text{ K} \)) the fractional BBR shift is \( \delta \omega/\omega \sim 10^{-25} \) for both ions.

b. Zeeman shift – Clock frequencies are affected by magnetic fields. The first-order Zeeman shift can be eliminated by averaging the measurements over two virtual clock transitions with opposite g-factors. Uncontrollable second-order AC Zeeman shift arises due to misbalances of currents in ion traps. It can be evaluated as

\[
\delta E_c = - \frac{1}{2j_v + 1} \sum_i \left| \frac{c_i |\mu| |i \rangle}{E_i - E_c} \right| B^2 \equiv \gamma_c B^2,
\]

The second-order Zeeman shift is negligibly small for the \( 5s \) states since there are only strongly forbidden \( M1 \) transitions in \( ^8 \). The shift for the \( 4f_{5/2} \) states is dominated by the \( 4f_{7/2} - 4f_{5/2} \) transition within the fine structure doublet. The calculated values of \( \gamma_c \) for these states are presented in Table II. Using the value of AC magnetic field \( B = 5 \times 10^{-7} \) measured in \( \text{Al}^{+}/\text{Be}^{+} \) trap (7) leads to \( \delta \omega/\omega \sim 10^{-26} \).

c. Electric quadrupole shift – Clock frequencies can be affected by coupling of atomic quadrupole moments to the gradients of trapping electric field. Obviously, this does not affect the \( 5s \) state due its vanishing quadrupole moment, but can shift the \( 4f_{5/2} \) state. It was suggested in [6] to use hyperfine structure (hfs) to suppress the quadrupole shift. However, using isotopes with non-zero nuclear spin leads to enhanced second-order Zeeman shift. This is because small hfs intervals enter energy denominators in (8) increasing the shift by several orders of magnitude compared to isotopes with zero nuclear spin. For this reason in this work we propose a different method to suppress electric quadrupole shift. It uses a linear combination of transition frequencies between states with different projection of total angular momentum \( J \).

The quadrupole shift for a state with total angular momentum \( J \) and its projection \( J_z = M \) is given by

\[
\delta E_{JM} \sim \frac{3M^2 - J(J + 1)}{2J(2J - 1)} Q \frac{\partial E_z}{\partial z} = c_{JM} Q \frac{\partial E_z}{\partial z},
\]

where \( Q \) is the electric quadrupole moment. The dependence of the shift on the projection \( M \) is in the prefactor only. The quadrupole moment \( Q \) of the atomic state is defined as twice the expectation value of the electric quadrupole operator \( (E2) \) in the stretched state

\[
Q = 2\langle nJM = J | E2 | nJM = J \rangle.
\]

Taking two transitions to states with different values of \( M \) and writing the frequencies as \( \omega_M = \omega_0 + c_{JM} Q \frac{\partial E_z}{\partial z} \) one can get

\[
\omega_0 = \frac{\omega_M - \omega_1}{1 - c_{JM} c'_{JM}}.
\]

Here \( \omega_0 \) is the frequency of the transition at zero electric and magnetic fields. The expression (12) does not depend on the quadrupole moment nor the gradient of electric field. For better accuracy it is important to have \( c_{JM} \) and \( c'_{JM} \) as different as possible. Using \( c_{5/2,1/2} = -0.4 \) and \( c_{5/2,5/2} = 0.5 \) leads to

\[
\omega_0 = \frac{\omega_{1/2} + 0.8\omega_{5/2}}{1.8}.
\]

d. Other perturbations – The performance of ion clocks can be affected by many other systematic effects, such as density of the background gases, Doppler (motion-induced) effects, gravity, etc. Consideration similar to what was done in our previous work [6] show that none of the corresponding fractional frequency shift is below the value of \( 10^{-19} \).

| TABLE II: Parameters of the clock transitions for \( \text{Nd}^{13+} \) and \( \text{Sm}^{15+} \). | \( \text{Nd}^{13+} \) | \( \text{Sm}^{15+} \) |
|---|---|---|---|
| | Ground state | Excited state | Ground state | Excited state |
| \( \lambda \) [nm] | 170 | 180 | |
| \( \Gamma \) [Hz] | 0 | 7.4[8] | 0 | 2.8[7] |
| \( \alpha(0) \) [a.u.] | 1.1048 | 0.3701 | 0.144 | 1.344 | 0.8366 |
| \( \gamma_c \) [a.u.] | 0 | 0.144 | 1.344 | 0 | |
| \( A/gI \) [MHz] | 123000 | 1070 | 1400 | 154000 |
To summarize, the Nd$^{13+}$ and Sm$^{15+}$ HCIs may offer an intriguing possibility for developing clockwork of unprecedented accuracy that is highly sensitive to variation of the fine-structure constant. The $10^{-19}$ fractional accuracy matches projected accuracy of the $^{229}$Th nuclear clock [3], but without complications of radioactivity.

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