Transitions in Zr, Hf, Ta, W, Re, Hg, Ac and U ions with high sensitivity to variation of the fine-structure constant

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We study transitions between ground and low-energy excited states of heavy ions corresponding to \( s - d \) single-electron transitions or \( s^2 - d^2 \) double-electron transitions. The large nuclear charge \( Z \) and significant change in angular momentum of electron orbitals make these transitions highly sensitive to a potential variation in the fine-structure constant, \( \alpha \). The transitions may be considered as candidates for laboratory searches for space-time variation of \( \alpha \).

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I. INTRODUCTION

Theories unifying gravity with other interactions suggest that the fundamental constants of nature may vary over space and time (see, e.g., the review \[1\]). Indications that the fine-structure constant, \( \alpha = e^2/\hbar c \), might change over cosmological scales has been found in quasar absorption spectra \[2–7\]. The most recent analysis of around 300 quasar absorption spectra taken from Keck and VLT telescopes is consistent with a smooth spatial gradient in the values of \( \alpha \) along a particular direction in space \[8\]. This “Australian dipole” reconciles all existing astrophysical and laboratory (null) measurements \( \[9\] \), see also \[10\].

Since the solar system (and the Earth within it) moves with respect to the frame of the gradient, the values of \( \alpha \) on Earth should change as we move from regions of space with smaller \( \alpha \) to regions with larger values. Thus the spatial variation of \( \alpha \) may be studied using laboratory experiments that measure the change of \( \alpha \) in time \[11\]. A number of such experiments have already been performed and reported (see, e.g., the review \[12\]). The best current limit, \( \dot{\alpha}/\alpha = (1.6 \pm 2.3) \times 10^{-17} \) year\(^{-1} \), comes from comparison of Hg\(^{2+}\) and Al\(^{+}\) optical clocks over the course of a year \[13\]. This limit is better than that obtained from quasar absorption spectra if one assumes a linear time variation of \( \alpha \) over \( \sim 10^{10} \) year timescales. However, it needs to be further improved by two or three orders-of-magnitude to test the Australian dipole hypothesis \[11\]. One way of achieving this is to find an atomic system where the spectra is significantly more sensitive to the change of \( \alpha \) than in the Hg\(^{2+}\)/Al\(^{+}\) system.

In our first paper on this subject \[14\] we suggested using \( s - d \) optical transitions in heavy atoms and ions. The sensitivity of these transitions to variation of \( \alpha \) is large. This is exactly what was used in the Hg\(^{2+}\)/Al\(^{+}\) experiment \[13\].

A number of other atomic transitions have been found where sensitivity of the frequencies of the transitions to the variation of the fine-structure constant is even higher. These include close, long-lived states of different configurations \[14–16\], fine-structure anomalies \[17\], and optical transitions in highly charged ions \[18, 19\]. The near-degenerate excited states of dysprosium have already been used to place strong limits on terrestrial \( \alpha \)-variation \[20–22\].

In present paper we further study the original idea of using the \( s - d \) and \( s - f \) transitions in heavy ions. We consider a number of ions and find many transitions which are as good as that used in Hg\(^{2+}\), or even better. Results for ions with one valence electron above closed shells are presented in Sec. II A these are Tm-like Ta\(^{4+}\), W\(^{5+}\), and Re\(^{6+}\), and Fr-like Ac\(^{2+}\) and U\(^{5+}\). In Sec. II B we study ions with two electrons above closed shells: Sr-like Zr\(^{2+}\), Yb-like Hf\(^{2+}\), and Ra-like Ac\(^{+}\). Finally we consider the Hg\(^{2+}\) and Hg\(^{3+}\) mercury ions in Sec. II C which have closed shells and single-hole electronic structures, respectively. In all cases we have chosen ions with relatively low-energy transitions, so that they may be within the range of lasers – an important criteria for potential clocks.

II. CALCULATIONS

The dependence of atomic frequencies on the fine-structure constant appears due to relativistic corrections. In the vicinity of its present laboratory value \( \alpha_0 \approx 1/137 \) it is presented in the form

\[
\omega(x) = \omega_0 + qx, \tag{1}
\]

where \( \omega_0 \) is the laboratory value of the frequency and \( x = (\alpha/\alpha_0)^2 - 1 \). \( q \) is the sensitivity coefficient which must be found from atomic calculations:

\[
q = \left. \frac{d \omega}{dx} \right|_{x=0} = \frac{\omega(\delta x) - \omega(-\delta x)}{2 \delta x} \tag{2}
\]

Here \( \delta x \) must be small enough to exclude terms nonlinear in \( \delta(\alpha^2) \), yet should be large enough to ensure numerical stability. In the present calculations we use \( \delta x = 0.01 \).

For all atoms we start the calculations from the relativistic Hartree-Fock method (RHF). Techniques to include correlations depend on atomic structure and we will discuss them in the relevant sections.
Ac
tronic sequence Ta$^{4+}$, W$^{5+}$ and Re$^{6+}$ (cm$^{-1}$).

| Ion   | Z  | Level | Energy (Exp) | Energy (Thy) |
|-------|----|-------|--------------|--------------|
| Ta$^{4+}$ | 73 | 5d$^{5/2}$ | 0            | 0            |
|       |    | 5d$^{3/2}$ | 6608$^a$     | 5161         |
|       |    | 6s$^{1/2}$ | 47052$^a$    | -30931       |
| W$^{5+}$ | 74 | 5d$^{5/2}$ | 0            | 0            |
|       |    | 5d$^{3/2}$ | 8707$^b$     | 7981         |
|       |    | 6s$^{1/2}$ | 79433$^b$    | -38423       |
| Re$^{6+}$ | 75 | 5d$^{5/2}$ | 0            | 0            |
|       |    | 5d$^{3/2}$ | 10996$^c$    | 10410        |
|       |    | 6s$^{1/2}$ | 115066$^c$   | -46470       |

$^a$Reference 22
$^b$Reference 28
$^c$Reference 23

TABLE II: Energy levels and sensitivity coefficients (q) for Ac$^{2+}$ (cm$^{-1}$).

| Level | Energy | $q$ |
|-------|--------|-----|
| 7s$^{1/2}$ | 0      | 0   |
| 6d$^{3/2}$ | 801    | 1582| 27297|
| 6d$^{5/2}$ | 4204   | 5449| 30230|
| 5f$^{3/2}$ | 23455  | 21688| 56170|
| 5f$^{5/2}$ | 26080  | 24845| 57324|
| 7p$^{3/2}$ | 29466  | 30542| 6861 |
| 7p$^{5/2}$ | 38063  | 39550| 19118|

$^a$Reference 28

A. Ta V, W VI, Re VII, Ac III, and U VI

These ions have one external electron above closed shells. We use the correlation potential method [23] in the $V^{N-1}$ approximation to perform the calculations. Initial Hartree-Fock procedure is done for a closed-shell ion, with the external electron removed. States of the external electron are calculated in the field of frozen core. Correlations are included with the use of the second-order correlation potential $\Sigma$.

We use the $B$-spline technique [24] to generate a complete set of single-electron states which are needed for the calculation of $\Sigma$. These states are the eigenstates of the RHF Hamiltonian $\hat{H}_0$ with the $V^{N-1}$ electron potential. We use 50 $B$-splines of order 9 in a cavity of radius 40$a_B$.

Energies for the valence states ($\epsilon_v$) are found by solving the Brueckner orbital equations for external electron

$$ (\hat{H}_0 + \Sigma - \epsilon_v) \psi_v = 0. $$

The results for Yb$^+$-like tantalum, tungsten and rhenium and for Fr-like actinium and uranium are presented in Tables II, III and IV. All these ions have $s-d$ or $s-f$ transitions with large $q$ coefficients. Most of the states with large $q$-coefficients are metastable states. Large $q$-coefficients can be either positive or negative which can be used to further improve the sensitivity of the frequency shift measurements to the time-variation of $\alpha$.

One of the most interesting system is U$^{5+}$, where the $q$-coefficient for the frequency of the transition from the ground 5f$^{5/2}$ state to the metastable 7s state is very large ($q \sim -10^5$) and negative. The ratio of this frequency to the fine structure interval in the ground state (where $q$ is positive) is very sensitive to the variation of $\alpha$. While such high energies are outside the range of normal optical lasers, they can potentially be reached using high-UV lasers, such as those that employ high-harmonic generation [25]. Table IV also shows calculated energies of the 7p$^{3/2}$ and 7p$^{5/2}$ states. It is useful to know their positions to make sure that the 6d and 7s states are metastable. To the best of our knowledge the experimental data on the energy levels of U$^{5+}$ is absent.

B. Zr III, Hf III, and Ac II

These ions have two external electrons above closed shells. Energies of the $s$ and $d$ valence states are close to each other which means that states of the $s^2$ and $d^2$ configurations should be close as well. Frequencies of the transitions between states of these configurations are expected to be more sensitive to the variation of $\alpha$ compared to the single-electron $s-d$ transitions.

For calculations we use the CI+MBPT method developed in our previous works [30–34]. Calculations are done in the $V^{N-2}$ approximation with two valence

TABLE III: Calculated energy levels and sensitivity coefficients (q) for U$^{5+}$ (cm$^{-1}$).

| Level | Energy | $q$ |
|-------|--------|-----|
| 5f$^{5/2}$ | 0      | 0   |
| 5f$^{7/2}$ | 6960   | 4687|
| 6d$^{3/2}$ | 76173  | -5200|
| 6d$^{5/2}$ | 84683  | -46300|
| 7s$^{1/2}$ | 123368 | -110355|
| 7p$^{1/2}$ | 173761 |     |
| 7p$^{3/2}$ | 195351 |     |
The means of the many-body perturbation theory (MBPT).

The results are presented in Tables IV, V and VI. The results for Zr$^{2+}$ and Ac$^+$ show that the $q$-coefficients for the $d^2 - s^2$ transition are indeed about two times larger than for the $d - s$ transitions. It is natural to expect larger values of $q$ for Hf$^{2+}$ than for Zr$^{2+}$ due to larger Z. It turns out however, that Hf$^{2+}$ has no states of pure 6s$^2$ configuration: there is strong mixing between the 6s$^2$ and 5d$^2$ configurations, and the weight of the 6s$^2$ configuration does not exceed 55% (see Table V). This affects the values of $q$. They are not as large as they would be for the pure 6s$^2$ case. Note also that there is no experimental data on the spectrum of Hf$^{2+}$.

The largest $q$-coefficients among these three ions are for the Ac$^+$ (Table VI). This ion has excited metastable states of the 6d$^2$ configuration while the ground state is practically pure 7s$^2$ configuration.

**C. Hg III and Hg IV**

Finally, we consider the Hg$^{2+}$ and Hg$^{3+}$ ions. Here additional enhancement is expected due to excitations of the electrons from the (almost) filled 5d subshell. Effective nuclear charge for electrons in almost filled many-electron subshells are higher than for valence electrons outside of the closed shells. Therefore, relativistic effects are larger and the $q$-coefficients are larger too.

These ions have ten (Hg$^{2+}$) and nine (Hg$^{3+}$) external electrons. For the calculations we use the method especially developed for the many-electron cases in Refs. [38, 39]. The results are presented in Tables VII and VIII.

Here again we see that the value of the $q$-coefficient for double $d - s$ transition is about two times larger than for single $d - s$ transition. The value of $q$ for these transitions is very large, $q \sim -10^5$ and corresponding states are metastable.
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