

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 α . The transitions may be considered as candidates for laboratory searches for space-time variation of α .

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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 in Ref. [1]). Indications that the fine-structure constant $\alpha = e^2/\hbar c$ might change over cosmological scales have 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 α along a particular direction in space [8]. This so-called Australian dipole reconciles all existing astrophysical and laboratory (null) measurements [9] (see also Ref. [10]).

Since the solar system (and the Earth within it) moves with respect to the frame of the gradient, the values of α on Earth should change as we move from regions of space with smaller α to regions with larger values. Thus the spatial variation of α may be studied using laboratory experiments that measure the change of α in time [11]. A number of such experiments have already been performed and reported (see, e.g. the review in Ref. [12]). The best current limit $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17} \text{ yr}^{-1}$ comes from a comparison of Hg^+ 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 α over $\sim 10^{10}$ -yr time scales. 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 are significantly more sensitive to the change of α than in the Hg^+ - 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 a variation of α is great. This is exactly what was used in the Hg^+ - Al^+ experiment [13].

A number of other atomic transitions have been found where the 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 nearly degenerate excited states of dysprosium have already been used to place strong limits on terrestrial α variation [20–22].

In present Brief Report 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 that are as good as or even better than that used in Hg^+ . 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, in Sec. II C we consider the Hg^{2+} and Hg^{3+} mercury ions, 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 criterion 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

$$\omega(x) = \omega_0 + qx, \quad (1)$$

where ω_0 is the laboratory value of the frequency, $x = (\alpha/\alpha_0)^2 - 1$, and q is the sensitivity coefficient, which must be found from atomic calculations:

$$q = \left. \frac{d\omega}{dx} \right|_{x=0} \approx \frac{\omega(\delta x) - \omega(-\delta x)}{2\delta x}. \quad (2)$$

Here δx must be small enough to exclude terms non-linear 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. Techniques to include correlations depend on atomic structure and we will discuss them in the relevant sections.

It is worth noting that the Breit interaction is not an important contribution to the relativistic shift for the heavy atoms that we consider. As an example, we have calculated the effect of the Breit interaction on the $5d_{3/2}$ - $5d_{5/2}$ and $5d_{3/2}$ - $6s_{1/2}$ transitions in Ta^{4+} : The q values change by 2% and 0.5%, respectively. This is consistent with previous work in light atoms ($Z \leq 30$) [23,24], where in all cases the effect of Breit interaction is found to contribute less than 10% (and usually much less than this). Extrapolating to heavy atoms, the

TABLE I. Energies and sensitivity coefficients q for the isoelectronic sequence Ta⁴⁺, W⁵⁺, and Re⁶⁺ (cm⁻¹).

Ion	Z	Level	Energy		q
			Experiment	Theory	
Ta ⁴⁺	73	5d _{3/2}	0	0	0
		5d _{5/2}	6608 ^a	5833	5161
		6s _{1/2}	47052 ^a	44812	-30931
W ⁵⁺	74	5d _{3/2}	0	0	0
		5d _{5/2}	8707 ^b	7981	7292
		6s _{1/2}	79433 ^b	77293	-38423
Re ⁶⁺	75	5d _{3/2}	0	0	0
		5d _{5/2}	10996 ^c	10410	9626
		6s _{1/2}	115066 ^c	112575	-46470

^aReference [27].^bReference [28].^cReference [29].

relativistic corrections scale as Z^2 , while the Breit interaction scales more like $\sim Z$. Therefore, the contribution of the Breit interaction to relativistic effects scales as $\sim 1/Z$ and it may be safely neglected in our calculations.

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 [25] in the V^{N-1} approximation to perform the calculations. The 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 the frozen core. Correlations are included with the use of the second-order correlation potential $\hat{\Sigma}$.

We use the B -spline technique [26] to generate a complete set of single-electron states that are needed for the calculation of $\hat{\Sigma}$. These states are the eigenstates of the relativistic Hartree-Fock Hamiltonian \hat{H}_0 with the \hat{V}^{N-1} electron potential. We use 50 B splines of order 9 in a cavity of radius $40a_B$. Energies for the valence states ϵ_v are found by solving the Brueckner orbital equations for external electrons

$$(\hat{H}_0 + \hat{\Sigma} - \epsilon_v)\psi_v = 0. \quad (3)$$

TABLE II. Energy levels and sensitivity coefficients q for Ac²⁺ (cm⁻¹).

Level	Energy		q
	Experiment ^a	Theory	
7s _{1/2}	0	0	0
6d _{3/2}	801	1582	27297
6d _{5/2}	4204	5449	30230
5f _{5/2}	23455	21698	56170
5f _{7/2}	26080	24845	57324
7p _{1/2}	29466	30542	6861
7p _{3/2}	38063	39550	19118

^aReference [30].TABLE III. Calculated energy levels and sensitivity coefficients q for U⁵⁺ (cm⁻¹).

Level	Energy	q
5f _{5/2}	0	0
5f _{7/2}	6960	4687
6d _{3/2}	76173	-52900
6d _{5/2}	84683	-46300
7s _{1/2}	123368	-110355
7p _{1/2}	173761	
7p _{3/2}	195351	

The results for Yb⁺-like tantalum, tungsten, and rhenium and for Fr-like actinium and uranium are presented in Tables I, II, and III. 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 α . One of the most interesting system is U⁵⁺, 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 α . 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 [31]. Table III also shows calculated energies of the 7p_{1/2} and 7p_{3/2} 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 U⁵⁺ 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 α compared to the single-electron s - d transitions.

TABLE IV. Energy levels and sensitivity coefficients q for Zr²⁺ (cm⁻¹).

Level	Energy		q	
	Experiment ^a	Theory		
4d ²	³ F ₂	0	0	0
4d5s	³ D ₁	18399	18554	-6018
	³ D ₂	18803	18988	-5637
	³ D ₃	19533	19764	-4860
4d5s	¹ D ₂	25066	26188	-4025
5s ²	¹ S ₀	48507	49297	-11000

^aReference [37].

TABLE V. Energy levels and sensitivity coefficients q for Hf^{2+} (cm^{-1}).

Leading configurations	Level	Energy		q
		Experiment ^a	Theory	
$5d^2$	3F_2	0	0	0
	3F_3	3558	5200	
	3F_4	6652	7700	
$5d6s$	3D_1	2652	-19600	
	3D_2	3121	-14600	
	3D_3	7112	-15500	
55% $5d6s$	1D_2	6124	-6700	
68% $5d^2$, 30% $6s^2$	3P_0	8775	-13500	
43% $5d^2$, 55% $6s^2$	1S_0	11403	-19800	
$5d^2$	3P_1	11345	5100	
	3P_2	12995	4400	
$5d^2$	1G_4	16151	6200	
	1S_0	33745	400	

For calculations we use the configuration-interaction plus many-body perturbation theory method developed in our previous works [32–36]. Calculations are done in the V^{N-2} approximation with two valence electrons removed from the initial Hartree-Fock procedure. Basis states for valence electrons are calculated in the field of the frozen core. The configuration-interaction technique is used to construct two-electron states of valence electrons. Core-valence correlations are included by means of the many-body perturbation theory. The B -spline technique [26] is used to calculate basis states for valence electrons and to calculate the core-valence correlation operator $\hat{\Sigma}$.

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

TABLE VI. Energy levels and sensitivity coefficients q for Ac^+ (cm^{-1}).

Level	Energy		q
	Experiment ^a	Theory	
$7s^2$	1S_0	0	0
$6d7s$	3D_1	4740	5460
	3D_2	5267	6083
	3D_3	7427	8514
$6d7s$	1D_2	9087	10385
	3F_2	13236	14639
$6d^2$	3F_3	14949	16552
	3F_4	16757	18646
	3P_0	17737	19204
$6d^2$	3P_1	19015	20649
	3P_2	22199	21132

^aReference [30].TABLE VII. Energy levels and sensitivity coefficients q for Hg^{2+} (cm^{-1}).

Level	Energy		q
	Experiment ^a	Theory	
$5d^{10}$	1S_0	0	0
$5d^96s$	3D_3	42850	42191
	3D_2	46029	45920
	3D_1	58405	58500
$5d^96s$	1D_2	61085	61835
	3F_4	97893	97719

^aReference [30].

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. The effective nuclear charge for electrons in almost filled many-electron subshells is higher than for valence electrons outside the closed shells. Therefore, relativistic effects are larger and the q coefficients are larger too [19].

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

TABLE VIII. Energy levels and sensitivity coefficients q for Hg^{3+} (cm^{-1}).

Level	Energy		q
	Experiment ^a	Theory	
$5d^9$	$^2D_{5/2}$	0	0
	$^2D_{3/2}$	15685	16140
$5d^86s$	$^4F_{9/2}$	60138	59370
	$^4F_{7/2}$	66109	66206
	$^4F_{5/2}$	69942	71809
	$^4F_{3/2}$	71763	73365
$5d^86s$	$^2F_{7/2}$	78854	79805
	$^2F_{5/2}$	77675	78337
$5d^86s$	$^4P_{5/2}$	86031	88669
	$^4P_{3/2}$	83916	86568
	$^4P_{1/2}$	82391	86501
$5d^76s^2$	$^4F_{5/2}$	145120	-130300

^aReferences [40,41].

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 the corresponding states are metastable.

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