


Highly charged ions of heavy actinides as sensitive probes for time variation of the fine-structure constant

V. A. Dzuba  and V. V. Flambaum 

School of Physics, University of New South Wales, Sydney 2052, Australia

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Highly charged ions of heavy actinides from uranium to einsteinium are studied theoretically to find optical transitions sensitive to the variation of the fine-structure constant. A number of promising transitions have been found in ions with ionization degree ~ 10 . All these transitions correspond in single-electron approximation to the $6p - 5f$ transitions. Many of the transitions are between ground and excited metastable states of the ions, which means that they can probably be used as optical clock transitions. Some of the ions have more than one clock transition with different sensitivity to the variation of the fine-structure constant α . The most promising systems include the Np^{10+} , Np^{9+} , Pu^{11+} , Pu^{10+} , Pu^{9+} , Pu^{8+} , Bk^{15+} , Cm^{12+} , and Es^{15+} ions.

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I. INTRODUCTION

The laboratory search for manifestations of new physics beyond the standard model requires extremely high accuracy of measurements. The highest accuracy has been achieved for the frequencies of optical atomic clocks. Fractional uncertainty of the frequency measurements gets to the level of $\sim 10^{-18}$ with the prospects of further improvements (see, e.g., reviews [1,2]).

Variation of the fine-structure constant α may be caused by interaction of scalar or axion dark matter fields with electromagnetic field [3–5]. Therefore, measurements of α variation are a method to search for dark matter. Variation of α leads to variation of atomic transition frequencies.

Therefore, one of the most promising options in the search for new physics is monitoring a possible drift of the frequencies of optical clock transitions over a long period of time or search for their oscillating variation. Unfortunately, most of operating optical clocks have low sensitivity to the variation of α [6] (with an exception of Yb^+ and Hg^+ clocks). It was suggested in Ref. [7] to use highly charged ions (HCIs) in the search for sensitive transitions. The sensitivity is proportional to $Z^2(Z_i + 1)^2$ where Z is nuclear charge and Z_i is ionization degree. In single-electron approximation it is also proportional to Δj , where j is total angular momentum of a single-electron state [8]

$$\Delta_n = \frac{E_n(Z\alpha)^2}{\nu} \left[\frac{1}{j+1/2} - C(j, l) \right], \quad (1)$$

where Δ_n is relativistic energy shift of a single-electron state, n is principal quantum number E_n is ionization energy from this state, ν is effective principal quantum number ($E_n = -1/(2\nu^2)$), and $C(j, l) \approx 0.6$ is a constant which imitates the many-body effects.

Therefore, the highest sensitivity can be found in $s - f$ or $p - f$ transitions in HCIs of heavy atoms (e.g., $\Delta j = 3$ for the $s_{1/2} - f_{7/2}$ or $p_{1/2} - f_{7/2}$ transition), i.e., these must be transitions between states of different configurations. As

a rule, the frequencies of such transitions in HCIs are well outside of the optical region. To find optical transitions we use the idea of *level crossing* [9]. The energy ordering of the states is different in neutral atoms and hydrogen-like ions. Therefore, if energies are considered as functions of ionization degree Z_i , there must be crossing points at some Z_i for energies of different states. If one of the corresponding states is the ground state and another is the excited metastable state, then the transition between them is likely to be optical transition with features of clock transition with high sensitivity to the variation of the fine-structure constant.

A number of promising transitions were suggested in earlier works. Experimental measurements are also in progress (see, e.g., reviews [10,11]). The highest sensitivities were found for heavy HCI of actinides Cf^{16+} , Cf^{17+} [12], Cf^{15+} , Es^{16+} , Es^{17+} [13], Cm^{15+} , and Bk^{16+} [14]. There should be many other HCI of actinides with optical transitions sensitive to variation of α . The aim of the present work is to conduct a comprehensive analysis of HCIs of heavy actinides from U to Es to find possibly all optical transitions between states of different configurations and identify promising systems which deserve further consideration. We use advanced calculation techniques to study ions with the configuration of external electrons $6s^2 6p^m 5f^n$, $1 \leq n + m \leq 6$. The number of external electrons varies from three to eight. The transitions between states of different configurations correspond to the $6p - 5f$ single-electron transition. The majority of found transitions are $6p_{3/2} - 5f_{5/2}$ or $6p_{3/2} - 5f_{7/2}$ transitions. They are less sensitive to the variation of α than transitions $6p_{1/2} - 5f_{5/2}$ and $6p_{1/2} - 5f_{7/2}$ transitions in ions considered before [12–14]. However, there are some interesting systems which deserve further consideration.

II. METHOD OF CALCULATION

To perform calculations for all ions we use a combination of the linearized single-double coupled cluster (SD) and the configuration interaction methods [15]. The electronic

configuration of the ions is $1s^2 \dots 5d^{10}6s^26p^m5f^n$, where $0 \leq n \leq 6$, $0 \leq m \leq 3$ and $1 \leq n + m \leq 6$. We consider each ion as a closed-shell core of 78 electrons [$1s^2 \dots 5d^{10}$] plus three to eight external electrons distributed over the $6s$, $6p$, and $5f$ states. The calculations are performed using the V^{N-M} approximation [16], where N is the total number of electrons and M is the number of valence electrons ($M = 2 + m + n$, $N = 78 + M$ in our case). The initial relativistic Hartree-Fock (RHF) procedure is done for the closed-shell core of 78 electrons. The RHF Hamiltonian includes the Breit interaction and quantum electrodynamic (QED) corrections,

$$\hat{H}^{\text{RHF}} = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)mc^2 + V_{\text{nuc}}(r) + V_{\text{core}}(r) + V_{\text{Breit}}(r) + V_{\text{QED}}(r), \quad (2)$$

where c is the speed of light, $\boldsymbol{\alpha}$ and β are the Dirac matrices, \mathbf{p} is the electron momentum, m is the electron mass, V_{nuc} is the nuclear potential obtained by integrating the Fermi distribution of the nuclear charge density, $V_{\text{core}}(r)$ is the self-consistent RHF potential created by the electrons of the closed-shell core, $V_{\text{Breit}}(r)$ is Breit potential [17], and $V_{\text{QED}}(r)$ is the radiative QED potential [18].

After completing the self-consistent procedure for the core, the B-spline technique [19] is used to create a complete set of single-electron wave functions. The functions are constructed as linear combinations of B-splines, which are eigenstates of the RHF Hamiltonian. We use 40 B-splines of order 9 in a box with a radius of $R_{\text{max}} = 40a_B$; the orbital angular momentum is $0 \leq l \leq 6$. These basis states are used to solve the SD equations for the core and for the valence states [15] and for constructing the many-electron basis states for the CI calculations.

Solving the SD equations gives us two correlation operators, Σ_1 and Σ_2 . Σ_1 describes the correlation interaction between a particular valence electron and the core, whereas Σ_2 describes the Coulomb interaction screening between a pair of valence electrons [15,20].

The effective CI+SD Hamiltonian has the form

$$\hat{H}^{\text{CI}} = \sum_{i=1}^M (\hat{H}^{\text{RHF}} + \Sigma_1)_i + \sum_{i < j}^M \left(\frac{e^2}{|r_i - r_j|} + \Sigma_{2ij} \right). \quad (3)$$

Here i and j enumerate valence electrons, the summation goes over valence electrons, e is the electron charge, and r is the position operator of the electrons.

It is well known that increasing the number of valence electrons exponentially increases the size of the CI matrix. We have up to eight valence electrons, resulting in a matrix with an exceptionally large size. It will require considerable computational power to handle such a matrix. In exchange for a very small loss of accuracy, the size of the CI matrix can be reduced by orders of magnitude using the CIPT (configuration interaction with perturbation theory) method suggested in [21]. By dividing many-electron basis states into two large groups, low-energy states and high-energy states, and ignoring the off-diagonal matrix elements between high-energy states, the effective CI Hamiltonian is constructed:

$$\langle i | H^{\text{eff}} | j \rangle = \langle i | H^{\text{CI}} | j \rangle + \sum_k \frac{\langle i | H^{\text{CI}} | k \rangle \langle k | H^{\text{CI}} | j \rangle}{E - E_k}. \quad (4)$$

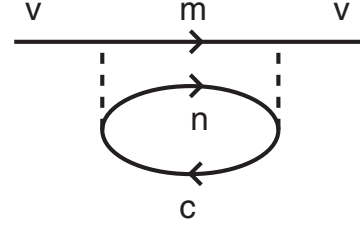


FIG. 1. Diagram representing dominating contribution to the Σ_1 operator. Index v stands for valence state, c is core state, and m, n are virtual states.

Here H^{CI} is given by (3), $i, j \leq N_{\text{eff}}$, $N_{\text{eff}} < k \leq N_{\text{total}}$, N_{eff} is the number of low-energy states, and N_{total} is the total number of many-electron basis states. Note that the choice of N_{eff} is arbitrary. One can increase it until the results become stable. Parameter E in (5) is the energy of the state of interest, and E_k denotes the diagonal matrix element for high-energy states, $E_k = \langle k | H^{\text{CI}} | k \rangle$. The summation in (4) runs over all high-energy states.

The energies and wave functions are found by solving the matrix eigenvalue problem,

$$(\mathbf{H}^{\text{eff}} - E)\mathbf{X} = 0, \quad (5)$$

where \mathbf{X} is the vector of expansion for the many-electron wave function of valence electrons over single-determinant basis states. Note that the parameter E in the denominator of (4) is the same as the energy of the state of interest, which is to be obtained from solving the charged ion equations (5). Since this energy is not known in advance, iterations over E are needed to find it. More detailed explanations of the technique can be found in Ref. [21]. For ions with seven or eight external electrons we also use a modification of the method in which the $6s$ electrons are attributed to the core. This allows us to reduce significantly the demand for computer power while having little effect on the CI calculations. When there are many $6p$ and $5f$ electrons, excitation from the $6s$ state is not very important. On the other hand, having the $6s$ state in the core creates a problem on the stage of calculating the one-electron correlation operator Σ_1 . It turns out that the many-body perturbation theory for Σ_1 does not work due to the presence of terms with small energy denominators. This manifests itself in the absence of convergence in solving the SD equations for s or d valence states. Let us consider an example of Σ_1 operator for d states of Es. The diagram representing dominating term in Σ_1 is presented in Fig. 1. Corresponding energy denominator is $\epsilon_v + \epsilon_c - \epsilon_n - \epsilon_m$, where v is the valence state, c is the core state, and m, n are virtual excited states. If we take $\epsilon_v = \epsilon_{5d_{5/2}} = -11.092$ a.u., $\epsilon_c = \epsilon_{6s} = -15.490$ a.u., and $\epsilon_n = \epsilon_m = \epsilon_{6p_{3/2}} = -13.097$ a.u., then $\epsilon_v + \epsilon_c - \epsilon_n - \epsilon_m = 0.388$ a.u., which is small and leads to problems. One way around this is to take $\epsilon_v = \epsilon_{6p}$ or $\epsilon_v = \epsilon_{5f}$. This is justified because our states of interest have only $6p$ or $5f$ electrons. A more radical way around the problem is to move the $6s$ electrons into valence space. One more reason for doing this is that the problem may manifest itself in calculating the Σ_2 operator. Note that the problem of small energy denominators is common for many atoms or ions with

an ns^2 subshell on the border between core and valence states. It may not manifest itself. For example, neutral Tl, with the $6s^26p$ configurations of external electrons, can be successfully treated as an atom with one valence electron (see, e.g., [22]). However, it is important to be aware of the problem.

To calculate the sensitivity of atomic transitions to the variation of α we present the frequencies of the transition in the form

$$\omega(x) = \omega_0 + q \left[\left(\frac{\alpha}{\alpha_0} \right)^2 - 1 \right] \equiv \omega_0 + qx, \quad (6)$$

where the index 0 indicate present-day value and q is the sensitivity coefficient found from calculations by varying the value of α in compute codes:

$$q = \frac{\omega(+\delta) - \omega(-\delta)}{2\delta}. \quad (7)$$

We use small values of δ ($10^{-3} \leq \delta \leq 10^{-2}$) to avoid nonlinear effects. It is also convenient to have the so-called *enhancement factors* K ($K = 2q/\omega$), which connect the variation of the transition frequencies to the variation of α :

$$\frac{\delta(\omega_1/\omega_2)}{(\omega_1/\omega_2)} = (K_1 - K_2) \frac{\delta\alpha}{\alpha}. \quad (8)$$

To have high sensitivity to α variation one should measure variation of the ratio of two transition frequencies with a large difference in the enhancement factors $K_1 - K_2$.

Accuracy of the calculations depends on the number of external electrons. The most important factor is adequate treatment of interelectron correlations. In our approach core-core and core-valence correlations are treated very well within the SD method. Note that the closed-shell core and corresponding SD equations are the same for all ions of a specific element. This means that the SD equations are to be solved only once for an element, and the Σ_1 and Σ_2 operators are the same for all ions of the element. In contrast, the valence-valence correlations are treated within the CI approach, and the accuracy varies significantly with the number of valence electrons. The uncertainty is on the level of 1% for the simplest systems with just three valence electrons (including the $6s$ electrons). It increases to about 6% for systems with five electrons (see a more detailed discussion below on the Es^{16+} ion). Ions with eight external electrons (six if $6s$ electrons are attributed to the core) and open $6p$ and $5f$ subshells have a dense spectrum, and the uncertainty is larger than the distance between states on the energy scale. However, even for such systems calculations produce much useful information (see a more detailed discussion below on the case of Am^{9+} ion).

III. RESULTS AND DISCUSSION

The search for optical transitions in HCI of heavy actinides is reflected in Table I. We study the ions from U^{11+} to Es^{13+} . For each element we consider ions with three to eight external electrons which form configurations from $6s^26p$ or $6s^25f$ to $6s^26p^n5f^m$ ($m + n = 6$). Thus, we are looking for transitions which in the single-electron approximation correspond to the $6p - 5f$ transition. Table I indicates ground states of each

ion and first state of a different configuration. The energies of the states are presented in the form E_J , where E is the energy in cm^{-1} with respect to the ground state and J is total angular momentum of the state. Dominating configurations are presented in first column. Note that the $6s^2$ subshell is omitted in the configurations for shorter records. However, the $6s$ electrons are always included in the valence space. Note also that the first state of a different configuration is not necessarily the first excited state. There may be several states below it which belong to the same configuration as the ground state. The energies of excited states, which are in the optical region, are shown in bold. The aim of the table is to identify all ions which have optical transitions between states of different configurations. These ions are further studied in following subsections.

The table indicates that most of the studied transitions are between states of the configurations with more than two $6p$ electrons and fewer than six $5f$ electrons. This means that the $6p_{1/2}$ subshell is fully occupied, and we are dealing with the open $6p_{3/2}$ and $5f_{5/2}$ subshells. Corresponding transitions in single-electron approximations are the $6p_{3/2} - 5f_{5/2}$ ($\Delta j = 1$) transitions, i.e., they are not most sensitive to the variation of α [see formula (1)]. The most sensitive transitions can be found in first two lines of the table. The correspond to the $6p_{1/2} - 5f_{5/2}$ or $6p_{1/2} - 5f_{7/2}$ in which ($\Delta j = 2, 3$). The sensitivity coefficient q in these transitions is large, $q \sim 4 \times 10^5 \text{ cm}^{-1}$. Most of these transitions have been studied [12–14]. The transitions in Bk^{15+} ion have been studied in the present work.

The ions in first two lines of Table I have a relatively simple electron structure and only a couple of transitions in optical region. This might be a disadvantage from experimental point of view. In contrast, the ions with more than two $6p$ electrons have more complicated spectra with a number of optical transitions. Some of them have more than one optical transitions and are good candidates for clock transitions and have different sensitivities to the variation of the fine-structure constant.

A. Uranium and neptunium

We start our study from uranium ions. Uranium is attractive in terms of its availability and relatively low radioactivity. Therefore, it is important to check whether its ions have suitable transitions. Unfortunately, we have not found any. We studied the ions from U^{11+} to U^{6+} , which have from three to eight external electrons (including $6s$). The minimal $6p - 5f$ distance on the energy scale is $\sim 6 \times 10^4 \text{ cm}^{-1}$ for the $6p^3 J = 3/2$ to $6p^25f J = 5/2$ transition in U^{9+} . This is outside of the optical region. For other ions the interval is even larger.

The lightest actinides ions which have optical $6p - 5f$ transitions are Np^{10+} and Np^{9+} ; see Table II. These ions have a relatively simple electron structure and only two excited states, which are within the optical region with respect to the ground state. Both excited states of Np^{10+} ion are not very long lived. The first is connected to the ground state by a M1 transition. It is suppressed due to domination of different configurations in upper and lower states. It goes due to configuration mixing, and the lifetime of the upper state is

TABLE I. Transition energies E_J (in cm^{-1}) between states of different configurations in HCl of heavy actinides. All transitions correspond to the $6p - 5f$ single-electron transition. All energies are given with respect to the ground state. Subscript J indicates the value of the total angular momentum J . Zero energy means ground state. Nonzero energy corresponds to the first state of a different configuration. Numbers in bold indicate optical transitions between ground and excited state. The dash “—” indicates highly excited states ($E_J > 10^5 \text{ cm}^{-1}$). N_v is the number of valence electrons above $6s^2$; ionization degree Z_i is given by $Z_i = Z - N_v - 80$. All numbers represent results of present work unless indicated otherwise. Comparison with earlier calculations (where available) are shown in footnotes.

N_v	Conf.	${}_{92}\text{U}$	${}_{93}\text{Np}$	${}_{94}\text{Pu}$	${}_{95}\text{Am}$	${}_{96}\text{Cm}$	${}_{97}\text{Bk}$	${}_{98}\text{Cf}$	${}_{99}\text{Es}$
1	6p	$0_{1/2}$	$0_{1/2}$	$0_{1/2}$	$0_{1/2}$	$0_{1/2}$	$0_{1/2}$	23 398 $_{1/2}$ ^b	$57643_{1/2}$
	5f	—	—	$91\,293_{5/2}$	$63\,190_{5/2}$	38 375 $_{5/2}$ ^a	8880 $_{5/2}$ ^a	$0_{5/2}$	$0_{5/2}$
2	$6p^2$	0_0	0_0	0_0	0_0	0_0	0_0	7284 $_0$ ^c	70850_0
	$6p5f$	—	—	—	$83\,759_2$	$48\,543_3$	20 715 $_3$	0_3	7403 $_2$ ^f
	$5f^2$	—	—	—	—	—	$65\,482_4$	13 681 $_4$ ^d	0_4
3	$6p^3$	$0_{3/2}$	$0_{3/2}$	6853 $_{3/2}$	$46\,157_{3/2}$	$87\,135_{3/2}$	$94\,521_{3/2}$	—	—
	$6p^25f$	$59\,418_{5/2}$	26 707 $_{5/2}$	$0_{5/2}$	$0_{5/2}$	$0_{5/2}$	$0_{5/2}$	$0_{5/2}$	24 712 $_{9/2}$
	$6p5f^2$	—	—	—	—	$86\,584_{9/2}$	$81\,932_{9/2}$	11 383 $_{9/2}$ ^e	$0_{9/2}$
	$5f^3$	—	—	—	—	—	—	$48\,970_{9/2}$	10 975 $_{9/2}$ ^g
4	$6p^4$	0_2	0_2	0_2	$69\,455_2$	—	—	—	—
	$6p^35f$	$69\,206_3$	39 652 $_3$	5027 $_3$	16 664 $_3$	$50\,646_3$	—	—	13 837 $_5$
	$6p^25f^2$	—	—	—	0_4	0_4	0_4	0_4	0_4
	$6p5f^3$	—	—	—	—	—	$61\,631_5$	34 722 $_5$	—
5	$6p^5$	$0_{3/2}$	$0_{3/2}$	$0_{3/2}$	32 200 $_{3/2}$	—	—	—	—
	$6p^45f$	$66\,355_{5/2}$	$52\,593_{5/2}$	8534 $_{5/2}$	$0_{5/2}$	$0_{5/2}$	19 671 $_{5/2}$	—	—
	$6p^35f^2$	—	—	—	$75\,530_{7/2}$	37 541 $_{7/2}$	$0_{7/2}$	—	—
	$6p^25f^3$	—	—	—	—	—	—	$0_{9/2}$	$0_{9/2}$
	$6p5f^4$	—	—	—	—	—	—	—	$51\,290_{9/2}$
6	$6p^6$	0_0	0_0	0_0	6812 $_0$	3746 $_0$	—	—	—
	$6p^55f$	$92\,144_1$	$65\,544_1$	15 296 $_1$	0_1	14 656 $_2$	—	—	—
	$6p^45f^2$	—	—	—	14 595 $_0$	0_2	28 336 $_4$	—	—
	$6p^35f^3$	—	—	—	$53\,650_0$	—	0_4	0_4	—
	$6p^25f^4$	—	—	—	—	—	—	—	0_4

^aRef. [14]

^b $E = 18\,686 \text{ cm}^{-1}$ in Ref. [12].

^c $E = 5267 \text{ cm}^{-1}$ in Ref. [12].

^d $E = 9711 \text{ cm}^{-1}$ in Ref. [12].

^e $E = 12\,314 \text{ cm}^{-1}$ in Ref. [13].

^f $E = 7445 \text{ cm}^{-1}$ in Ref. [13].

^g $E = 10\,591 \text{ cm}^{-1}$ in Ref. [13].

$\lesssim 1$ s. The second excited state is connected to the ground state by the E2 transition, but it can also decay to a lower state via the M1 transition. Its lifetime is ~ 0.1 s.

TABLE II. Excitation energies (cm^{-1}) of low-lying states of Np ions and their sensitivities to the variation of the fine-structure constant.

Ion	Leading configuration	J	This work		
			E	q	K
Np^{10+}	$6p^3$	$3/2$	0	0	0
	$6p^25f$	$5/2$	26 700	66 000	4.9
	$6p^25f$	$7/2$	41 400	76 000	3.7
Np^{9+}	$6p^4$	2	0	0	0
	$6p^4$	0	18 535	1400	0.15
	$6p^35f$	3	39 652	55 400	2.9

The Np^{9+} ion is more interesting. Its first excited state is connected to the ground state by the E2 transition and the lifetime is ~ 4 s. The second excited state is connected to the ground state by suppressed M1 transition, and its lifetime is likely to be < 1 s. The two transitions have different sensitivity to the variation of the fine-structure constant. The comparing of two frequencies can be used for the search of this variation.

B. Plutonium

Plutonium ions have many optical transitions between states of different configurations. The results of calculations for ions from Pu^{11+} to Pu^{8+} are presented in Table III. Note that we also included the percentage of leading configurations to illustrate the level of configuration mixing. Many transitions are quite sensitive to the variation of the fine-structure constant. However, we do not see good candidates for clock transitions. Practically all states can decay to lower states via M1 transitions. Many of these transitions are suppressed due

TABLE III. Excitation energies (cm^{-1}) of low-lying states of Pu ions and their sensitivities to the variation of the fine-structure constant.

Ion	Leading configuration		J	This work		
				E	q	K
Pu ¹¹⁺	95%	$6p^25f$	5/2	0	0	0
	94%	$6p^3$	3/2	6845	-72 700	-15
	95%	$6p^25f$	7/2	16 060	11 900	1.5
Pu ¹⁰⁺	82%	$6p^4$	2	0	0	0
	92%	$6p^35f$	3	5027	63 700	25
	82%	$6p^35f$	2	11 545	62 800	11
	91%	$6p^35f$	4	12 231	67 700	11
	91%	$6p^35f$	1	15 388	67 600	8.8
	88%	$6p^4$	0	19 878	-1800	-0.18
Pu ⁹⁺	82%	$6p^5$	3/2	0	0	0
	92%	$6p^45f$	5/2	8534	80 400	19
	91%	$6p^45f$	7/2	11 468	78 600	14
	89%	$6p^45f$	3/2	11 600	79 700	14
	90%	$6p^45f$	1/2	14 214	73 200	10
Pu ⁸⁺	88%	$6p^6$	0	0	0	0
	88%	$6p^55f$	1	15 296	89 700	11
	86%	$6p^55f$	2	21 794	87 700	7.6
	76%	$6p^55f$	4	23 113	79 600	6.6
	84%	$6p^55f$	3	27 178	81 400	5.6

to the difference in leading configurations, but not strongly suppressed because of the noticeable admixture of different configuration, which is clear from the presented percentages.

The values of the sensitivity coefficients q for most of transitions are positive and close in value. This is because the transitions correspond to the transition from the lower state $6p$ to upper state $5f$. The values of enhancement factors K are different mostly due to the difference in the frequency of the transitions ($K = 2q/\omega$).

Calculations for Pu¹¹⁺ and Pu¹⁰⁺ are done with the $6s$ electrons in the valence space. Calculations for Pu⁹⁺ and Pu⁸⁺ are simplified in several ways. First, the $6s$ electrons are moved to the core; only the second-order core-valence correlation operators Σ_1 and Σ_2 were used. Finally, a relatively small effective CI matrix, corresponding to few configurations, was used. All other configurations are included perturbatively [see Eq. (4)]. Consecutively, the accuracy for the Pu⁹⁺ and Pu⁸⁺ ions is lower than for the Pu¹¹⁺ and Pu¹⁰⁺ ions. The uncertainty is comparable to the distance between energy levels. However, the ground states are established with a high level of confidence.

C. Americium

The Am¹¹⁺, Am¹⁰⁺, and Am⁹⁺ ions do have optical transitions between states of different configurations (see Table I). However, corresponding excited states are not metastable. They can decay to lower states via partly suppressed M1 transitions. Since there are many decay channels, the lifetime of these states is not likely to be very long. The energy interval between states of different configurations goes down with an increasing number of valence electrons and thus decreasing

TABLE IV. Excitation energies (cm^{-1}) of low-lying states of Am⁹⁺ ion and their sensitivities to the variation of the fine-structure constant.

Leading configuration	J	This work			
		E	q	K	
93%	$6p^55f$	1	0	0	
55%	$6p^55f$	2	2885	26 900	19
91%	$6p^55f$	4	7079	1900	0.5
58%	$6p^55f$	3	7729	23 900	6.2
93%	$6p^45f^2$	0	10 263	61 100	12
99%	$6p^45f^2$	4	11 039	71 900	13
59%	$6p^45f^2$	2	11 082	46 500	8.4
77%	$6p^45f^2$	3	12 608	59 000	9.4
95%	$6p^45f^2$	1	15 578	71 700	9.2

ionization degree. This leads to strong configuration mixing for the Am⁹⁺ ion, which has six electrons in open $6p$ and $5f$ subshells. The spectrum of this ion is dense, and calculations for it are difficult. Table IV presents the results of sample calculations for the ion. Note, however, that the uncertainty of the calculations are larger than the energy interval between states. This means that we cannot guarantee the order of the states nor can we find real sensitivity to the variation of the fine-structure constant. However, there is still much useful information which comes from the calculations:

(i) The ground state of the ion is most probably one of the two lowest states of the configurations presented in Table IV. The transition between these states is likely to be narrow and sensitive to the variation of the fine-structure constant. This comes from the very different mixing of the configurations in the states (see the percentage of leading configurations presented in the table), which leads to suppression of the M1 transition and enhancement of the sensitivity to the variation of α .

(ii) It is very likely that there is another metastable state with different sensitivity to the variation of α . In present calculations this is state with $E = 7079 \text{ cm}^{-1}$ and $J = 4$. In reality, it can be some other state.

Note that the values of enhancement factor K are not reliable since they strongly depend on the energy of the transition ($K = 2q/\omega$). The values of q are more stable. Note, however, that swapping of the states leads to sign change in both q and K . In the end we conclude that the Am⁹⁺ ion is an interesting system which probably deserves further study with more advanced techniques.

D. Curium and berkelium

The Cm¹⁵⁺ and Bk¹⁶⁺ ions were studied before [14]. The Cm¹⁵⁺ ion has only one optical transition, which is the transition between the $6s^26p_{1/2}$ ground and the $6s^25f_{5/2}$ excited states. The transition is actually the $6p_{1/2} - 5f_{5/2}$ transition, and it is sensitive to the variation of α . The study of other ions did not reveal any promising systems. The Cm¹¹⁺ and Cm¹⁰⁺ ions do have optical transitions between states of different configurations. However, they are relatively high in the spectra and have many channels of decay into lower states via

TABLE V. Excitation energies (cm^{-1}) of low-lying states of Bk^{15+} ion and their sensitivities to the variation of the fine-structure constant.

Leading configuration		J	This work		
			E	q	K
96%	$6p^2$	0	0	0	0
98%	$6p5f$	3	20 715	150 000	14
94%	$6p5f$	2	29 400	196 000	13
97%	$6p5f$	3	43 471	205 000	9.4

M1 or E2 transitions. Therefore, corresponding states are not metastable and cannot serve as clock states. Berkelium ions are more promising. The Bk^{16+} ion has two optical transitions with very high and different sensitivity to the variation of α [14]. The next ion, Bk^{15+} , also has several optical transitions sensitive to the variation of α (see Table V). It has at least one very narrow clock transition, which is the transition between ground and first excited states ($\Delta J = 3$). The leading contribution to the transition probability is mediated by the hyperfine interaction. For example, the magnetic dipole hyperfine interaction mixes states with $J = 3$ and $J = 2$. This opens the electric quadrupole (E2) transition to the ground state. The next excited state is not metastable since it can decay to the lower state via the M1 transition.

E. Californium and einsteinium

Some ions of californium and einsteinium were studied previously. The Cf^{17+} and Cf^{16+} ions were studied in Ref. [12]; the Cf^{15+} , Es^{16+} , and Es^{17+} ions were studied in Ref. [13]. Here we present a more detailed study of these and other ions of californium and einsteinium. First, it is instructive to compare the results of present and earlier calculations in a nontrivial case of many valence electrons (four or five electrons). The calculations were performed in sufficiently different ways so that the comparison of the results reveals important information about the accuracy of both approaches. Both works used the combined SD+CI method [15,23] but in different implementations. Our earlier work followed Ref. [23], while the present work followed Ref. [15]. Different approximations were used in Refs. [15] and [23] to relate single-electron energies to the many-electron energies of CI states. Another difference comes from the fact that the $6s$ states were attributed to the core in [13], while they are in valence space in present work. However, the most important difference is the use of the CIPT technique in the present work to improve the efficiency of the calculations [see Eqs. (4) and (5)]. Neglecting off-diagonal matrix elements between high-energy states allows one to reduce the size of the effective CI matrix and improve the efficiency by many orders of magnitude. This comes with the price of some loss in accuracy. It is important to know the value of this loss. Comparing two works is a good way to get some idea about this, since the earlier work [13] used the full-scale CI calculations.

Table VI compares energy levels and g factors of the Cf^{15+} ion calculated in the present work and in Ref. [13]. There is

TABLE VI. Excitation energies (cm^{-1}) and g factors of low-lying states of Cf^{15+} ion. Comparison with earlier calculations.

Leading configuration		J	This work		Ref. [13]	
			E	g	E	g
87%	$6p^25f$	5/2	0	0.848	0	0.843
95%	$6p5f^2$	9/2	11 386	0.813	12 314	0.813
72%	$6p^25f$	7/2	22 285	1.116	21 947	1.083
89%	$6p5f^2$	5/2	27 395	0.701	26 665	0.715
89%	$6p5f^2$	7/2	29 723	0.838	27 750	0.868
91%	$6p5f^2$	3/2	30 064	0.735	28 875	0.765

very good agreement between two calculations. The difference in energies is between 1% and 8%. Good agreement in the g factors indicates very similar composition of the states. If we attribute all the difference in the results to the neglecting of the off-diagonal matrix elements in the CI matrix between high-energy states, then a few percent uncertainty in the results is not a big price to pay for many orders of magnitude improvement in the efficiency of the calculations.

Further study of the californium ions with more than two electrons on the $6p$ and $5f$ subshells reveals no more interesting systems. The Cf^{14+} ion does have an optical transition between states of different configurations. This is a transition between ground state $6s^26p^25f^2$ $J = 4$ and excited state $6s^26p5f^3$ $J = 5$ at $E = 34 722 \text{ cm}^{-1}$ (see Table I). However, the excited state is relatively high in the spectrum and is not metastable. It has many channels of decay into lower states via the M1 transitions.

Table VII shows energy levels and sensitivity coefficients [q and K ; see Eqs. (6) and (8)] calculated in the present and earlier [13] works. In the case of Cf^{15+} the agreement with previous calculations is very good. This illustrates once more the usefulness of the CIPT technique. It brings a huge gain in efficiency while the loss of accuracy is insignificant.

All three Es ions have many transitions with different sensitivity to the variation of the fine-structure constant. The first excited state of each ion is relatively long-living state connected to the ground state by a suppressed M1 transition.

IV. SUMMARY

We conducted a comprehensive study of HCI of heavy actinides from U to Es with the $6s^26p^m5f^n$ ($1 \leq m+n \leq 6$) configurations of external electrons. The study was aimed at finding optical transitions which correspond to the $6p-5f$ transitions in a single-electron approximation and therefore are sensitive to the variation of the fine-structure constant α . We also checked which of the transitions have features of atomic clock transitions to ensure high accuracy of the measurement. We identified a number of promising systems in addition to what was considered before. These include the Np^{10+} , Np^{9+} , Pu^{11+} , Pu^{10+} , Pu^{9+} , Pu^{8+} , Bk^{15+} , Cm^{12+} , and Es^{15+} ions. Some ions studied previously (Cf^{15+} , Es^{17+} , Es^{16+}) were studied in more detail. The majority of the considered ions have at least two narrow transitions with different

TABLE VII. Excitation energies (cm^{-1}) of low-lying states of Es ions and their sensitivities to the variation of the fine-structure constant.

Ion	Leading configuration		J	This work			Ref. [13]
				E	q	K	E
Es ¹⁷⁺	97%	$5f^2$	4	0	0		0
	90%	$5f^2$	2	7403	-26 000	-6.5	7445 ^a
	98%	$5f^2$	5	23 652	17 000	1.3	
	87%	$6p5f$	3	23 736	-159 000	-11	
	90%	$5f^2$	4	27 654	-14 000	-0.9	
	84%	$5f^2$	3	29 338	-310 000	-17	
Es ¹⁶⁺	86%	$6p5f^2$	9/2	0	0	0	0
	56%	$6p5f^2$	5/2	6879	-165 000	-48	6994 ^b
	82%	$5f^3$	9/2	10 404	254 000	49	10 591
	56%	$6p5f^2$	3/2	10 986	120 000	22	11 056
	94%	$6p5f^2$	7/2	16 368	88 000	11	15 441
	43%	$6p5f^2$	5/2	23 351	-154 000	-13	24 301
Es ¹⁵⁺	96%	$6p^25f^2$	4	0	0	0	
	82%	$6p^25f^2$	2	4791	51 700	22	
	96%	$6p5f^3$	5	13 837	398 400	57	
	89%	$6p^25f^2$	5	22 554	57 500	5.1	
	54%	$6p^25f^2$	4	24 278	156 400	13	
	62%	$6p5f^3$	4	33 090	316 400	19	

^aRef. [13] gives $q = -46\,600\text{ cm}^{-1}$, $K = -13$, leading configuration is $6p5f$.

^bRef. [13] gives $q = -184\,000\text{ cm}^{-1}$, $K = -53$, leading configuration is the same.

sensitivity to the variation of α . The transitions are either E2 or suppressed (due to difference in composition of the states) M1 transitions between the ground and lowest excited states.

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