

Electronic structure of free and doped actinides: N and Z dependences of energy levels and electronic structure parameters

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Abstract

Theoretical study of electronic structure of actinide ions and its dependence on N and Z are presented in this paper. The main $5f^N$ and excited $5f^N n' l'^{N'}$ configurations of actinides have been studied using Hartree–Fock–Pauli approximation. Results of calculations of radial integrals and the energy of X-ray lines for all $5f$ ions with electronic state AC^{+1} – AC^{+4} show approximate dependence on N and Z . A square of N and cubic of Z are equalized for the primary electronic parameters of the actinides. Theoretical values of radial integrals for free actinides and for ions in a cluster $AC^{+n}:[L]_k$ are compared, too.

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0. Introduction

In recent years, interests in theoretical studies of super-heavy atoms and ions increase together with synthesis of new elements. Electronic structure of many-electron ions of the actinium, the AC group with unfilled $5f$ -electronic shell has been studied but not as thoroughly as needed in applications. Separate electronic and chemical properties of the actinides are similar to the properties of the rare earths, RE which are the ions with unfilled $4f$ -shell [1–4]. On the other hand, separate optical properties of AC ions in solids are similar to the spectra of the ions of the iron or palladium group elements, i.e. ions with unfilled nd -shell.

Nuclei of the most actinides are unstable and serious problems may appear in investigation of optical and X-ray spectra of AC ions. Not so many papers that included results of the electronic structure and spectra of AC ions in the free-ion state and solids have been

published in the recent years [5–17]. In papers of Blaise and co-workers [5–12], particularly in a communication [13], the energy level schemes and optical spectra of actinides with the main and separate excited configurations of atoms, once and twice-ionized free ions: Th I–III, Pa I, U I, Pu I, Bk I–II, Cm I–II, Np I, etc. were presented. Papers of Carnal and co-workers are devoted to the optical spectra of actinides in halide and other crystals [14,15]. Particularly, in a brilliant work in analysis of the actinide spectra [14] W.T. Carnal included the full and systematic analysis of the spectra of actinides in solids. Theory of the optical transitions of actinides was developed in several books [1–3] and yet there is a division of the fundamental theory of the energy level schemes for many-shell configurations.

It is well known that data for energy, line-shape and other characteristics of X-ray spectra contain important information of the structure of AC ions and interaction of electrons and ions in solids. Similar data may be very useful as supplement to results of the optical, ESR, etc., investigations. Moreover, data of X-ray spectroscopy have been analyzed by a more simpler way and included

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detailed information of surroundings of AC ions in crystals and solids. The complete experimental data of X-ray spectra of actinides in free-ion state and solids were not presented for reference. Separate data of the energy of characteristic X-ray bands of actinides were published in papers [17–20].

Ab initio calculation of the electronic structure of super-heavy ions in free-ion state and in solids is quite a complex problem. Separate preliminary results of the ab initio calculation of the energy of optical transitions and data for energy of K , L , etc., X-ray lines of RE and AC ions in the free-ion state and clusters or solids were published in Refs. [4,18–20]. Accuracy of the theoretical results is quite high; relative error, for example, for the energy of $L\alpha_1$ lines is near 0.5%. In several papers [18–20] qualitative analysis of the dependence of the energy of X-ray lines of actinides as a function of $5f$ -electrons number was made, too. Dependence of the energy and parameters of electronic structure on the number of nf -electrons and nucleus charge may be useful for analysing electron–electron interactions which determine the spectra and properties of super-heavy ions.

The theoretical procedure of studying actinides optical spectra is based on semi-empirical calculations, in general. There is a powerful approach to qualitative and quantitative description of the spectroscopic properties of nf -ions. Deviation of the calculated data of the semi-empirical free ion and cluster approximation includes the main information of the peculiarities of the electronic density and interaction of the electrons and ions in the crystals. Thus, results of semi-empirical theory were compared in Ref. [12] to the experiments of $5f^N$ and $5f^N7s$ configurations.

One of the peculiarities of the electronic structure of AC ions relates to the possibility and conditions of collapse of the nf -shell which were considered in [21,22]. Collapse of nf shell leads to the change of the type of the main configuration and the energy levels schemes, optical and X-ray spectra of the ions, too. The conditions of the change of the main configuration of rare earths and actinides on growth of nucleus charge, Z of high ionized nf -ions result in the change of the main configuration $nf^2(n+1)p^6$ to $nf^{2+x}(n+1)p^{6-x}$ one were discovered, earlier [25]. It is naturally that consideration of the collapse conditions of nf shell must be based on the data of ab initio electronic structure calculations.

In this paper we attempt to study electronic structure, energy level schemes and X-ray lines of AC ions in the free-ion state and in clusters in the framework of ab initio self-consistent field approach and discuss separate numerical results of our work. Separate results of the study of the electronic structure of AC ions in clusters are considered in this paper, too. The next task of our investigation of actinides is simplification of theoretical data tables.

1. Free ions: parameters of energy levels and N-dependence

We study the electronic spectra of two-shell configurations and X-ray spectra of the ions with unfilled nf -shell and use the central field approximation [4,17–22]. Separate modifications of the method are well known [1–4]. For configuration containing two unoccupied shells the expression for energy of LS term of an ion has been written as [4]

$$E(nl^N n'l^{N'}, \alpha\alpha' LS) = E_0(nl^N n'l^{N'}) + \sum_{k,nl} f_k(l^N, \alpha\alpha' LS) F_k(nl, nl) + \sum_{k,n'l'} f_k(l'^{N'}, \alpha\alpha' LS) F_k(n'l', n'l') + \sum_{k,nl,n'l'} f_k(l'l', LS) F_k(nl, n'l') + \sum_{k,nl,n'l'} g_k(l'l', LS) G_k(nl, n'l'), \quad (1)$$

where $E_0(nl^N n'l^{N'})$ is energy of “center of gravity” of ion configuration. The second and third terms in Eq. (1) determine the energy of Coulomb interaction for electrons of nl and $n'l'$ shells. The last terms are the energies of Coulomb and exchange interactions between nl and $n'l'$ electrons of different shells. $f_k(l^N, \alpha\alpha' LS)$, $f_k(l'l', LS)$ and $g_k(l'l', LS)$ are the angular coefficients. $F_k(nl, nl)$, $F_k(nl, n'l')$, and $G_k(nl, n'l')$ are the radial integrals [2]. In Eq. (1) $\alpha\alpha'$ are additional quantum numbers which mark the multiple LS terms. The more detailed expressions for all terms of $E(nl^N n'l^{N'}, \alpha\alpha' LS)$ were published in books [1–4,23]. For l^N configuration the expression for the angular coefficients $f_k(l^N, \alpha\alpha' LS)$ in Eq. (1), according to [23] can be written as

$$f_k(l^N, \alpha\alpha' LS) = \frac{1}{2} (l || C^k || l)^2 \{ [(2L+1)(2S+1)]^{-1} \times \sum_{\alpha'' L''} (l^N, \alpha LS || U^k || l^N, \alpha'' L'' S) \times (l^N, \alpha' LS || U^k || l^N, \alpha'' L'' S) - \delta(\alpha, \alpha') N(nl) (2l+1)^{-1} \} \delta(LS, L'S'), \quad (2)$$

where $k > 0$, and $(l || C^k || l)$ and $(f^+, \alpha LS || U^k || f^N, \alpha' L'' S)$ are the sub-matrix elements of the spherical operator C^k and unit Racah's operator U^k [23,24]. $N(nl)$ is the number of nl electrons.

It should be noted that expression for $E_0(nl^N n'l^{N'})$ in Eq. (1) can be overwritten following [4,23] as

$$E_0(nl^N n'l^{N'}) = \sum_{n_i l_i} N(n_i l_i) I(n_i l_i)$$

$$\begin{aligned}
& + \frac{1}{2} \sum_{n_i l_i} N(n_i l_i) [N(n_i l_i) - 1] \\
& \times \left\{ F_o(n_i l_i, n_i l_i) - \frac{1}{4l_i + 1} (l_i \| C^2 \| l_i)^2 F_2(n_i l_i, n_i l_i) \right. \\
& + \left. \frac{1}{4l_i + 1} (l_i \| C^4 \| l_i)^2 F_4(n_i l_i, n_i l_i) \right\} \\
& + \sum_{n_i l_i \neq n' l'} N(n_i l_i) N(n' l') \\
& \times \left\{ F_o(n_i l_i, n' l') - \frac{1}{(4l_i + 1)^{1/2} (4l' + 1)^{1/2}} \right. \\
& \times \left. \sum_k (l_i \| C^2 \| l')^2 G_k(n_i l_i, n' l') \right\}. \quad (3)
\end{aligned}$$

It is easy to see that the dependence of the angular coefficients in $E_0(nl^N n' l'^N)$ is a square function of occupation numbers. The angular coefficients $f_k(l^N, \alpha\alpha' LS)$ in Eqs. (1)–(2) according to papers of Racah [24] may be transformed to the linear combinations of $e_i(f^N, \alpha\alpha' LS)$ coefficients. The last ones may be presented as matrix elements of the irreducible unit tensors for group R_{2l+1} . A simple mathematical procedure may be used to get the square function of the angular coefficients of $N(nl)$ or/and $N(n'l')$ [4,23,24].

Radial integrals in Eqs. (1) and (3) are determined as

$$\begin{aligned}
F_k(nl, nl) &= D_k \int P^2(nl|r) \frac{r^k}{r^{k+1}} P^2(nl|r') dr dr', \\
F^k(nl, n'l') &= \int P^2(nl|r) \frac{r^k}{r^{k+1}} P^2(n'l'|r') dr dr', \\
G^k(nl, n'l') &= \int P(nl|r) P(n'l'|r) \frac{r^k}{r^{k+1}} \\
&\quad \times P(n'l'|r') P(n'l'|r') dr dr', \quad (4)
\end{aligned}$$

where $P(nl|r)$ is radial part of the one-electron wave function (radial orbital) and D_k are the numerical coefficients. The N dependence of the radial integrals was discovered using the approximation of the numerical data for different $N(nl)$. Theoretical N dependence for the electrostatic, $F_k(nl, nl)$, spin–orbit, $\eta(nl)$ radial integrals for the energy levels of the main configurations of the separate RE or AC ions were studied in papers [17–19,25,26]. Linear N dependence of $F_k(nf, nf)$ is only valid for the nf ions as a first approximation, only. Significant deviation of N dependence from the linear function for the radial integrals can be seen for example, for the transition from AC^{+n} to AC^{+n+1} ions [15]. Well-known lanthanide (actinide) contraction [1,22] confirms this conclusion.

In the final form, N dependence of the level energy, $E(nl^N n' l'^N | \alpha\alpha' LSJ)$, is a function of the fourth degree of $N(nl)$ [17,27]. Following the paper of Slater and co-workers [28] we may consider $N(nl)$ as a variable parameter and develop the effective occupation number

approach. By this way, the expression for $E(nl^N n' l'^N | \alpha\alpha' LSJ)$ can be overwritten as

$$\begin{aligned}
& E(nl^N n' l'^N | \alpha\alpha' LSJ) \\
& = A(\alpha\alpha' LSJ) + \sum_{i,i'=1}^4 B_{i i'}(\alpha\alpha' LSJ) N^i(nl) N^{i'}(n'l'), \quad (5)
\end{aligned}$$

where $A(\alpha\alpha' LSJ)$ and $B_{i i'}(\alpha\alpha' LSJ)$ are the numerical coefficients depending on $\alpha\alpha' LSJ$ state of nl -ion.

Other standard ways permit the consideration of $N(n_i l_i)$ as a classical occupation number and to calculate the coefficients in Eq. (5) more precisely than earlier work.

It should be noted that Eqs. (1)–(5) are written for non-relativistic approximation. For heavy atoms with unfilled nf shell we cannot neglect the relativistic effects [1,2,22,29]. We have studied the electronic structure of actinides using the Hartree–Fock–Pauli approximation which takes into account the main parts of Breit’s operator: dependence of electron mass on velocity, spin–spin and spin–contact interactions [2,23,29]. A similar approach was used to calculate separate parameters of the electronic structure of RE and AC ions in free-ion state and for the ions in crystals [19].

Eqs. (1)–(5) determine the energy levels of two shells configuration and are right for $5f^N 7s$, and for $nl^{4l+1} 5f^N$ ones. The last configurations determine the energy of X-ray lines as transition between LSJ levels of “initial” $nl^{4l+1} 5f^N$ —and “final”— $n'l^{4l'+1} 5f^N$ configurations.

Analytical dependence of the angular coefficients, $f_k(l^N, \alpha\alpha' LS)$, $f_k(l^N l'^N, \alpha_1 \alpha'_1 L_1 S_1)$ and $g_k(l^N l'^N, \alpha_1 \alpha'_1 L_1 S_1)$ on occupation numbers of nl and $n'l'$ shells was studied in papers [17,19], using the sub-matrix elements of Racah’s operators U^k with $N(nl)$ and $N(n'l')$. Dependence of the angular coefficients is quadratic with $N(nl)$ for single nl shell matrix elements and includes terms depending on the product of $N(nl)N(n'l')$ for two-shell open configurations.

Dependence of the radial integrals in Eqs. (4) and (5) can be discovered by statistical approximation of the numerical data of Hartree–Fock–Pauli calculations [18]. Similar calculations were made for all AC atoms and separate actinides for the following electronic states: AC^{+1} – AC^{+2} – AC^{+3} . Software programs were described in the book [4].

For $5f^N$ configuration more simple dependence of the energy of LS levels on $N(nl)$ may be discovered when we use Racah’s integrals, $E_i(nf, nf)$ not Slater’s ones, $F_k(nf, nf)$. Following to Racah [24] for the angular coefficients $e_1(f^N, \alpha\alpha' LS)$ we can write

$$e_1(f^N, vLS) = 9(N - v)/2 + v(v + 2)/4 - S(S + 1), \quad (6)$$

where v is the “seniority number” of LS term. Moreover, the analytical N dependence of $e_i(f^N, \alpha\alpha' LS)$ for $i = 2$ and 3 is quadratic, exactly [2,19,25–27].

The results of the theoretical calculation of N dependence of the radial integrals $E_k(5f, 5f)$ [22]:

$$E_1(5f, 5f)$$

$$:= \frac{7}{9}\{10F_2(5f, 5f) + 33F_4(5f, 5f) + 286F_6(5f, 5f)\},$$

$$E_2(5f, 5f) = \frac{1}{9}\{F_2(5f, 5f) - 3F_4(5f, 5f) + 7F_6(5f, 5f)\},$$

$$E_3(5f, 5f) = \frac{1}{3}\{5F_2(5f, 5f) + 6F_4(5f, 5f) - 91F_6(5f, 5f)\}. \quad (7)$$

are given in Table 1.

In Eq. (6): $F_k(5f, 5f) = F^k(5f, 5f)/D_k$, and $D_2 = 225$, $D_4 = 1089$, $D_6 = 7361.62$.

Hence, N dependence of $E_k(5f, 5f)$ or $F_k(5f, 5f)$ for the ions with $5f^N$ -configuration as a first approximation may be presented by the quadratic function

$$E_i(5f, 5f) = a + b \cdot N + c \cdot N^2, \quad (8)$$

where the values of coefficients a , b and c are presented in Table 1.

It should be noted that relative deviation of data of Table 1 and results of Hartree–Fock–Pauli calculations are near 2% for the first AC ions and less than 1% for last ones.

N dependence of $E_k(5f, 5f)$ of the first members of actinides is unusual; the sign of the coefficient b in Eq. (8) changes along the $U \rightarrow Np$ transition and relative influence of linear and quadratic terms is different. In particular, the ratio b/c is smaller than 1 for the first members of actinides and is bigger than 1 for the ions of the second part of AC elements. Moreover, the influence of the last term in Eq. (8) is strong for actinides, as opposed to the rare earths. On the other hand, the ratio a/b for AC is less than for RE.

Similar results of the N dependence of spin–orbit constant, $\eta(5f)$, “average” radius of $5f$ -shell, $\langle 5f|r|5f \rangle$ or $\langle r \rangle_{5f}$ and radial integral, $I(5f)$ were published in paper [18]. The sign of b for spin–orbit coupling constant is negative for all actinides. The sign of the constant c

changes along the $Cm \rightarrow Bk$ transition. The ratio b/c is smaller for the first members of actinides and decreases with growth of an element number.

When we study N dependence of $\langle r \rangle_{5f}$ we discover the negative sign of b and positive one of c constants for all actinides. Relative influence of the quadratic term in Eq. (8) decrease, and value of relation a/b grows. This is an unusual result which requires for future investigation.

When we used the square function of the radial integrals of N , the final dependence of energy levels of $5f^N$ configuration is the function of the fourth degree of N :

$$E(5f^N, \alpha\alpha'LS) = a' + b' \cdot N + c' \cdot N^2 + d' \cdot N^3 + e' \cdot N^4, \quad (9)$$

where constants $a' > b' > c' > d' > e'$ depend on $\alpha\alpha'LS$ state. It should be noted that the relative influence of d' and e' coefficients decreases when nucleus charge increases.

Eq. (9) was discovered for a one-configuration approach and influence of correlation effects was not considered. According to results which were published in [4,21,22] we can note that influence of the correlation effects for nf ions leads to the appearance of the terms $N^5(nl)$ and $N^6(nl)$ in Eq. (9).

When we study X-ray lines we may conclude that N' dependence of the one-electron radial integrals, such as $I(n'l)$, $\langle r \rangle_{n'l}$ and $\eta(n'l)$ for the inner electrons is immaterial with $N(nl)$ to the three or four decimal places. And values of $I(n'l)$, $\langle r \rangle_{n'l}$ and $\eta(n'l)$ radial integrals can be used as “card” of actinides. It should be noted, that value of the radial integral, $I(n'l)$ may be used for estimations of the energy of X-ray lines of the ions. But in this way we lose the effect of change of the energy of X-ray lines with alteration of ions valency (change of ion oxidation state). There is the so-called, valency shift of X-ray lines [4].

N dependence of the energy of K and L X-ray lines as the function of the second degree of N is presented in

Table 1
 N dependence of Racah's integrals $E_k(5f, 5f)$ for AC ions (in cm^{-1})

Ion I, Z	$E_1(nf, nf)$			$E_2(nf, nf)$			$E_3(nf, nf)$		
	a	b	c	a	b	c	a	b	c
Pa, 91	5927	−86	−93	31.22	−0.32	−0.43	78.9	−6.65	−9.25
U, 92	6378	−48	−68	37.95	−2.22	−0.12	712.9	−34.81	−3.20
Np, 93	6081	10	−56	34.70	0.17	−0.29	672.0	2.03	−5.50
Pu, 94	6940	42	−47	35.64	0.57	−0.27	688.1	9.60	−5.00
Am, 95	7312	36	−38	37.85	0.34	−0.20	735.5	4.85	−3.75
Cm, 96	7593	52	−33	39.93	0.29	−0.17	762.4	6.35	−3.25
Bk, 97	7940	46	−28	40.70	0.40	−0.15	793.3	6.40	−2.80
Cf, 98	8219	55	−25	43.37	0.20	−0.12	829.4	5.19	−2.40
Es, 99	8528	63	−23	44.43	0.29	−0.11	833.7	6.92	−2.20
Fm, 100	8808	58	−20	45.90	0.31	−0.10	874.8	7.60	−2.00

Table 2

Values of the coefficients a and b for the N dependence of the energy of $K\alpha_1$ and $L\alpha_1$ X-ray lines of actinides (in eV)

Ion, Z	AC $K\alpha_1$ -line			AC $L\alpha_1$ -line		
	E_0	a	$-b$	E_0	a	$-b$
Ac, 89	88 951.080	0.431	0.070	12 671.789	0.424	0.052
Th, 90	91 233.519	0.467	0.034	12 989.542	0.326	0.032
Pa, 91	93 553.072	0.540	0.034	13 311.565	0.479	0.030
U, 92	95 910.145	0.605	0.033	13 637.868	0.539	0.029
Np, 93	98 305.122	0.659	0.032	13 968.481	0.580	0.028
Pu, 94	100 738.542	0.691	0.031	14 303.356	0.640	0.027
Am, 95	103 210.648	0.724	0.030	14 641.226	0.682	0.026
Cm, 96	105 721.613	0.767	0.028	14 986.249	0.711	0.025
Bk, 97	108 272.134	0.826	0.026	15 334.323	0.728	0.023
Cf, 98	110 862.572	0.882	0.025	15 686.806	0.740	0.021
Es, 99	113 493.397	0.920	0.024	16 043.560	0.784	0.021
Fm, 100	116 165.234	0.935	0.023	16 405.048	0.790	0.020
Md, 101	118 877.847	0.977	0.022	16 770.396	0.851	0.020
No, 102	124 428.762	1.035	0.021	17 140.694	0.875	0.019

Table 2. Radial integrals $F_k(5f, nl)$ and $G_k(5f, nl)$ depend on $N(5f)$, as a first approximation, similar to a linear function. In Table 3 separate results of calculation are presented additionally to our data which were published in paper [20].

2. Free ions: parameters of energy levels: Z dependence

Analytical Z dependence of the energy levels of ions can be obtained easily using analytical expressions for the radial wave functions. The angular coefficients in Eq. (1) do not depend on nucleus charge. Z dependence of energy levels is determined by the radial integrals. The most popular form of the analytical radial wave functions is the well-known Slater-type functions [28]. Similar radial wave functions and corresponding radial integrals are very simple and effective for s and p ions. For many-electrons nf ions the analytical functions of Lowdin–Roothaan (for more detail information see [4]) are more effective. But this way we cannot obtain the analytical Z dependence of the radial integrals.

For the radial integrals we used ab initio calculated data approximated by the quadratic, cubic functions and sometimes the fourth degree Z dependence (for different radial integrals, only). Data of Hartree–Fock–Pauli calculations of the radial integrals: $I(nl)$, $\eta(nl)$, $\langle r \rangle_{nl}$, and $R_k(5f, nl)$ were published in papers [17,18]. These data were used to study the Z dependence of the radial integrals, energy levels and X-ray lines of separate actinides. Results of the numerical calculations of Racah's integrals, spin–orbit coupling constant and energy of K and L X-ray lines for AC II–AC IV ions were used, too.

First of all, the minimum of the standard deviation under statistical reduction of the values of the radial

integrals $I(n'l')$ for $1s$, $2p$, $3d$ shell was calculated for function of the third degree of Z :

$$Q(n'l'|Z) = a_0 + a_1 \cdot Z + a_2 \cdot Z^2 + a_3 \cdot Z^3. \quad (10)$$

Results of calculation of the coefficients a_i for $E_f(5f, 5f)$ radial integrals and energy of separate X-ray lines are presented in Tables 3 and 4.

Deviation of the statistical reduction of the Z dependence in Eq. (10) for $I(n'l')$, $\eta(nl)$ and $\langle r \rangle_{nl}$ is less than 0.1%. Data of the calculation of a_i coefficients for Racah's integrals, for example, are presented in Table 3. Similar results were obtained for statistical calculation of Z dependence of the spin–orbit coupling constant for $2p$ and $3d$ electrons [18]. It should be noted that deviation for quadratic and cubic Z dependences of “average radius” of $1s$ shell are similar but for $\langle r \rangle_{1s}$, only. We can obtain an error that was more than three times larger if we use the quadratic dependence for other radial integrals and electronic shells.

We discover that the diminishing of $\langle r \rangle_{1s}$ with Z and for No ion the value of $\langle r \rangle_{1s}$ is equal 7.8×10^{-3} a.u. Influence of linear and quadratic terms in Eq. (10) is stronger for $\langle r \rangle_{2p}$ than for $\langle r \rangle_{1s}$ or $\langle r \rangle_{6p}$. Ions “size”, $\langle r \rangle_{nl}$ for actinides ($6p$ inner shell) decreases with Z at 28% from 1.138 Å for Ac to 0.816 Å, for No. Value of “radius” of $5f$ shell, $\langle r \rangle_{5f}$ changes largely from 0.999 to 0.459 Å, accordingly. Moreover, relative change (diminish) of the active $5f$ shell “size” is more than 50%.

The radial integrals with weak N dependence, such as $F_k(5f, nl)$ and $G_k(5f, nl)$ can be described by Eq. (10), too. It was found that the ratio of $x = F_k(5f, nl)/F_2(5f, nl)$ depends on nucleus charge and number of $5f$ electrons. For example, value of $x = F_4(5f, 2p)/F_2(5f, 2p)$ decreases from 48.56 for Ac I to 42.61 for Ac III. Value of x decreases up to 33.1 for Es I and 30.7 for Es IV. Note, that values of mixed exchange

Table 3
Z dependence of Racah's integrals $E_i(5f, 5f)$ for AC II–AC IV (in cm^{-1})

Valency	Integral	a_0	a_1	a_2	a_3
AC II	$E_1(nf, nf)$	−122100.60261	37414.84339	−382.36852	1.30941
AC III	$E_1(nf, nf)$	−344149.98852	10141.74910	−99.45206	0.33094
AC IV	$E_1(nf, nf)$	−269938.67372	7938.85191	−77.50055	0.25774
AC II	$E_2(nf, nf)$	−6303.64391	193.39947	−1.97868	0.00678
AC III	$E_2(nf, nf)$	−1724.24411	50.80092	−0.49779	0.00165
AC IV	$E_2(nf, nf)$	−2290.95647	68.86751	−0.68837	0.00232
AC II	$E_3(nf, nf)$	−122238.63101	3749.34853	−38.34952	0.13143
AC III	$E_3(nf, nf)$	−33793.24188	996.29288	−9.76979	0.03252
AC IV	$E_3(nf, nf)$	−38030.67385	1137.24773	−11.30297	0.03801

Table 4
Z dependence of energy of K and L X-ray lines (in eV)

Line	A_0	a_1	a_2	A_3
AC $K\alpha_1$	−13643.3308	565.7362	0.7005	0.0662
AC $K\alpha_2$	−21410.8092	774.5912	−0.7089	0.0633
AC $K\beta_1$	−24535.1740	888.6820	−1.2659	0.0800
AC $K\beta_3$	−12226.1898	490.4316	3.1271	0.0627
AC $L\alpha_1$	351.2985	−24.4352	1.6653	0.0019
AC $L\alpha_2$	1042.9522	−48.8459	1.9839	0.0002
AC $L\beta_1$	−2540.6690	102.2080	−0.4045	0.0164
AC $L\beta_3$	−2111.3787	92.2695	−0.3238	0.0165

integrals $G_k(5f, nl)$ is three orders less than Coulomb ones.

For actinides we could not neglect the exchange effects, naturally. The ratio of $R_k(5f, nl)$ integrals: $y = F_1(5f, 2p)/G_2(5f, 2p)$ decreases with the number of $5f$ electrons and growth of Z , too. Moreover, relative influence of exchange terms increases with Z more than 2 times. Direction of change of ratios $x_1 = F_k(5f, 3d)/F_1(5f, 3d)$ and $y_1 = F_1(5f, 3d)/G_1(5f, 3d)$ is similar for x and y .

In Table 5, we present the coefficients a_i for Z dependence of energy of K and L X-ray lines. We used the “mean” values of energy of K and L X-ray lines under calculation of a_i values. Deviation of results of Table 5 from abinitio theoretical or experimental data is very small—less than 0.1% and high accuracy of approximation permits to reveal the separate technical errors in paper [18]. After repeated calculation of energies of separate X-ray lines we obtained the results with a very small deviation. Standard deviation for $K\alpha_1$ and for $K\beta$ lines is near 0.1 eV and for other K lines, is less than 1 eV. For L lines the error due to the used approximation is near 0.01–0.1 eV that is quite good accuracy. It is very important that, we discovered the change of sign of the coefficient a_1 for $K\alpha_2$ line and $K\beta_1$ lines. Similar results were calculated for L lines.

A sign of a_0 in Eq. (10) for $L\alpha_{1,2}$ X-ray lines is negative and for other coefficients is positive. For other L lines we observed the change of sign for the following

a_i coefficients: a_0 , a_1 , and a_2 . Similar change of the coefficients for Z dependence of separate X-ray lines is the result of interaction processes in different electronic shells.

3. Electronic structure of AC ions in clusters

We now consider the change of separate radial integrals under free-ion-to-cluster transition. As the first step, we consider the electronic structure of $AC^{+n}:[L]_k$ cluster where AC ion locates to the environment of k ligands L on distance R . Symmetry of the cluster corresponds to real crystallographic structure of a crystal.

Using the one-electron approximation for the wave functions of the central field approximation, the energy of the cluster may be written as [4,21]:

$$E(AC^{+n} : [L]_k) = E_0 + kE_1 + k'(E_Z + E_c + E_{ex}), \quad (11)$$

where E_0 (E_1) is the energy of the central ion (ligand), in the free state.

The terms E_z , E_c and E_{ex} in Eq. (11) correspond to the energy of the interaction of electrons with other nucleus of the cluster, the Coulomb interaction and the exchange one for all electrons. k' , is a numerical coefficient depending on the symmetry of the cluster. Expressions for the terms E_z , E_c and E_{ex} in Eq. (11) were written in [4,30–33]. These terms include two-electrons

Table 5

Z dependence of parameters E_0 , a and b for N dependence of energy of X-ray lines of actinides (in eV)

Li ne	E_0				a				B			
	a_0	a_1	a_2	a_3	a_0	a_1	a_2	a_3	a_0	a_1	a_2	a_3
$K\alpha_1$	86 705.507	2227.352	18.186	0.065	0.307	0.124	−0.012	0.0006	−0.058	0.007	−0.0006	0.00001
$K\alpha_1$	84 160.798	2386.681	−42.390	3.284	0.225	0.134	−0.017	0.0009	−0.051	0.006	−0.0003	−0.000017
$K\beta_3$	98 389.789	2522.052	20.143	0.066	0.640	0.219	−0.019	0.0008	−0.111	0.013	−0.0009	0.00003
$K\beta_3$	97 881.926	2496.974	19.590	0.066	0.691	0.166	−0.006	0.0000	−0.114	0.015	−0.0014	0.00006
$L\alpha_1$	12 358.395	311.267	2.141	0.002	0.309	0.089	−0.009	0.0004	−0.048	0.005	−0.0002	0.00001
$L\beta_3$	14 484.803	411.649	3.796	0.022	0.434	0.028	0.008	−0.0006	−0.057	0.008	−0.0009	0.00001
$L\beta_4$	14 738.904	418.193	3.989	0.017	0.310	0.094	−0.009	0.0004	−0.048	0.006	−0.0004	0.00001
$L\beta_5$	14 230.828	393.168	3.432	0.018	0.496	0.016	0.004	−0.0003	−0.072	0.011	−0.0008	0.00002

two-center penetrating integrals of the wave functions of nl ion and $n'l'$ ligand, the one-electron two-center matrix elements of operator describing the interaction of electrons with the other nucleus, and two-electron two-center matrix element of the Coulomb or exchange interaction.

The system of equations for the radial functions of the nl ion, $P(nl|r)$ and the ligand, $P(n'l'|r)$ was taken as a result of minimization of Eq. (11) with respect to the radial wave functions of the nl ion and ligands (see in detail in [4,22]).

The following system of equations may be written for each ion in the cluster [4,30]:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} Y'(nl|r) - \varepsilon_{nl} - \frac{l(l+1)}{r^2} \right] P(nl|r) = X'(nl|r) + \sum_{n' \neq n} \varepsilon_{n'l'} P(n'l'|r), \quad (12)$$

where ε_{nl} is the one-electron energy. Coulomb and exchange potentials $Y'(nl|r)$ and $X'(nl|r)$ differ from the original Hartree–Fock potentials [1–3] by the following additional terms:

$$\Delta Y(nl|r) = r/2 \sum_{k, k_1, n'l'} [a_{ll'}^{kk_1} Y_{kk_1}(n'l', n'l'|r) + b_{ll'}^{kk_1} Y_{kk_1}(nl, n'l'|r)],$$

$$\Delta X(nl|r) = - \sum_{k, k_1, n'l'} [\alpha_{ll'}^{kk_1} Y_{kk_1}(nl, n'l'|r) + \beta_{ll'}^k r^{k_1}] P(n'l'|r). \quad (13)$$

System of equations (12) describe the self-consistent field of the cluster depending on all electrons of the system. In Eq. (13) the tensor function, $Y_{kk_1}(nl, n'l'|r)$ and the coefficients $a_{ll'}^{kk_1}$, $b_{ll'}^{kk_1}$, $\alpha_{ll'}^{kk_1}$, β^k are given by the following expressions:

$$Y_{kk_1}(nl, n'l'|r) = \delta(k, k_1 + k_2) \frac{r^{k_1}}{R^{k+1}} \int P(nl|r') P(n'l'|r') r'^{k_2} dr',$$

$$a_{ll'}^{kk_1} = v \sum_m O_{m_1 m_1} O_{m_2 m_2} (m_1 m_2 | r_{12}^{-1} | m'_1 m'_2)_\varphi + A(SS') v' \sum_m O_{m_2 m_2}^{\bar{m}_1 \bar{m}'_1} O_{m_2 m_2}^{\bar{m}_2 \bar{m}'_2} (m_1 | m'_2)^* \times (m_2 | m'_1) (\bar{m}_1 \bar{m}_2 | r_{12}^{-1} | \bar{m}'_1 \bar{m}'_2)_\varphi,$$

$$b_{ll'}^{kk_1} = v' A(SS') \sum_m O_{m_1 m'_1}^{\bar{m}_1 \bar{m}'_1} O_{m_2 m'_2} \times (m_1 | m'_2) (\bar{m}_1 \bar{m}'_2 | r_{12}^{-1} | \bar{m}'_1 m')_\varphi, \quad (14)$$

$$\alpha_{ll'}^{kk_1} = v' A(SS') \sum_m O_{m_1 m'_1} O_{m_2 m_2} (m_1 m_2 | r_{12}^{-1} | m'_2 m'_1)_\varphi,$$

$$\beta_{ll'}^k = \frac{Z_2 v'}{R^{k+1}} \sum_m O_{m_2 m_2} (m'_1 | m_2) \times [O_{m_1 m'_1} + O_{m_1 m'_1}^{\bar{m}_1 \bar{m}'_1} (m_1 | m_2) (m_1 | r_{Z_2}^{-1} | m'_2)_\varphi].$$

Eqs. (14) contain the angular part of the matrix elements of different operators, only. v and v' are numerical coefficients. It is easy to see that solutions of Eqs. (12) for the cluster depend on the wave functions of all ions in the cluster.

The energy of Stark-levels of LSJ state in crystalline field for nl ion may be written as

$$E(nl^N | \alpha \alpha' LSJ \Gamma) = E_0 + \sum_i e_k(l^N, \alpha \alpha' LS) E_i(nl, nl) + \chi(LSL'S', J) \eta(nl) + \sum_{k, q, i} B_{kq} C_q^k(\Theta_i \Phi_i), \quad (15)$$

where E_0 , is the center of gravity of nl^N configuration, and B_{kq} , the crystal field parameters.

Data of calculation of the separate parameters of electronic structure for separate actinides in clusters are presented in Table 6. We consider the change of following radial parameters: One-electron energy, ε_{nl} , spin–orbit coupling constant, η_{5f} , $\langle r \rangle_{nl}$ and Racah's integrals $E_i(5f, 5f)$ etc., under transition of separate actinides from the free state to cluster with environment of F^- , Cl^- and O^{2-} ions. It should be noticed that we observed the qualitatively right picture under transition

Table 6
Theoretical values of the radial integrals for actinides in free state and in the $AC^{+n}:[L]_k$ cluster

Integral <i>R</i>	U III	U ⁺² : $[F^-]_9$ 2.2 Å	U ⁺² : $[O^{-2}]_{12}$ 2.37 Å	U ⁺² : $[Cl^-]_9$ 2.4 Å	Units
ε_{5f}	0.8935	0.9104	0.9218	0.9342	a.u.
ε_{6p}	1.3552	1.3662	1.3796	1.3815	a.u.
$E_1(5f, 5f)$	4832.90	4240.35	3894.0	3805.47	cm ⁻¹
$E_2(5f, 5f)$	25.94	22.784	20.890	20.429	cm ⁻¹
$E_3(5f, 5f)$	556.8	438.46	402.09	393.07	cm ⁻¹
η_{5f}	2161.1	2086.7	2040.0	2011.8	cm ⁻¹
$\langle r \rangle_{5f}$	1.3249	1.4611	1.4784	1.4814	a.u.
$\langle r \rangle_{6p}$	1.9452	2.0977	2.1831	2.2212	a.u.
	Fm IV	Fm ⁺³ : $[F^-]_9$	Fm ⁺³ : $[O^{-2}]_{12}$	Fm ⁺³ : $[Cl^-]_9$	
ε_{5f}	1.9516	1.9741	1.9940	1.9985	a.u.
ε_{6p}	2.3189	2.3267	2.3377	2.3406	a.u.
$E_1(5f, 5f)$	6648.88	6469.99	6411.29	6332.37	cm ⁻¹
$E_2(5f, 5f)$	35.31	35.35	34.10	33.768	cm ⁻¹
$E_3(5f, 5f)$	686.87	668.68	663.39	653.97	cm ⁻¹
η_{5f}	5294.7	5158.8	5105.4	5007.0	cm ⁻¹
$\langle r \rangle_{5f}$	0.9746	1.0376	1.0490	1.0572	a.u.
$\langle r \rangle_{6p}$	1.7297	1.7421	1.7568	1.7589	a.u.

(a.u.) atomic units.

of the free ion to the clustered the values of the Racah's integrals and spin-orbit constant decrease, values of average radius increase. Calculated data for radial integrals are more than experimental ones and change of the integrals is less than experimental data. There is a well-known problem of Hartree-Fock approximation and task of choice of the initial wave functions. We hope the next version of the program decides this problem.

As it has been shown in papers [30,31] solutions of the system of equations (12) depend on boundary conditions. We can use the conditions for unit cluster (free ion conditions) or Wigner-Zeits ones for crystals. The variation of the radial integral values in this case is near 3–8%. We discovered a stronger dependence of the radial integrals on boundary conditions for actinides than for rare earth ions.

The results of calculation of the energy of X-ray lines for AC ions in the clusters correspond satisfactorily to the experimental data. During transition of the free AC ion to a cluster one-electron radial functions transform and the radial integrals change. First of all, the value of the center of gravity of the excited configuration changes at 5–8%. Change of the parameters a_i in Eqs. (7)–(9) is very important to study electronic states of ions in crystals.

The change of the energy of X-ray lines for AC ions in solids is closely related to the experimental data for valency shift of X-ray lines. Mixed valency of the actinides in separate solids and change of oxidation state of some part of the ions upon irradiation or thermal treatment of compounds can be studied successfully in the framework of our approach. The change of X-ray

lines energy during free ion-to-cluster transition is near 0.3 eV and it is similar to the energy change under the change of ion oxidation state. And by this way we can determine the concentration of the ions changed the oxidation state during crystals growth or influence of radiation [4]. Data for shift of X-ray lines of the heavy ions and separate data of calculations of the values of a_i as functions N and Z were published in paper [34] as a confirmation of the conclusion.

4. Conclusion

In summary, we found that the cubic dependence of all radial integrals and energy of X-ray lines on nucleus charge is a surprise. The strong Z dependence of the parameters of electronic structure of actinides testifies the appearance of the more complex picture of super-heavy ion electronic structure. We discovered the N and Z dependence of the interaction parameters, and predicted the separate properties of the actinides. Moreover, we can predict the properties of ions or atoms with charge or electron number up to 137.

Ab initio calculations of the crystal field potentials using self-consistent field theory permits one to calculate electronic structure of AC ions in clusters and solids. The calculated results qualitatively correspond to the experimental data for the energy of Stark-levels and quantitatively correspond to the energy of X-ray lines. Errors of the theoretical values for the valency shift of X-ray AC ions in clusters are less than 0.2 eV which is

quite good for study of the oxidation state change of the ions in solids or plasma.

The influence of crystal field potential on the radial distribution of the wave functions of the actinides is more intensive than that for the rare earths and less than that for the ions of the iron group elements or other *nd* ions. For the *nd*-ions this way leads to good results [21,22]. For free *nf* ions the radial distribution of the *nf* and $(n+1)p$ -shells is violated due to strong exchange interaction. The effect of screening of the *nf*-shell is stronger than for the *nd*-ions. There is a cause of relatively weak influence of the crystal environment to the *nf*-ions. The second way for development of the approach is to introduce theory for the correlation effects. On the base of the approach, we can solve the problem of collapse of *nf*-shell, too.

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