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# 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 antinide 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 ewalized 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 5*f*-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]

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

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. $f_k(l^N, \alpha\alpha' LS)$, $f_k(ll', LS)$ and $g_k(ll', LS)$ 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

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

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

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