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STUDIES OF $6s$ IONIZATION ENERGY OF LANTHANIDES

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This work is aimed at the multiconfiguration Hartree–Fock calculations of the $6s$ ionization energies of lanthanides with configurations [Xe]$4f^N6s^2$. Authors use the ATSP MCHF version in which there are new codes for calculation of spin-angular parts of matrix elements of the operators of intraatomic interactions written on the basis of the methodology developed by Gaigalas, Rudzikas, and Froese Fischer, based on the second quantization in coupled tensorial form, the angular momentum theory in three spaces (orbital, spin, and quasispin), graphical technique of spin-angular integrations and reduced coefficients (subcoefficients) of fractional parentage. This methodology allows us to study the configurations with open f-shells without any restrictions, thus providing the possibility to investigate heavy atoms and ions as well as to obtain reasonably accurate values of spectroscopic data for such complex many-electron systems.

Keywords: complex many-electron systems, ionization energies, lanthanides, multiconfiguration Hartree–Fock method

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1. Introduction

There is considerable interest in understanding the physics and chemistry of heavy atoms and ions. The main problem in the investigation of such systems is their complexity, caused by a large number of electrons and the importance of both the correlation and relativistic effects. Therefore, accurate description of heavy atoms and ions requires generaly the correct treatment of the correlation as well as the relativistic effects. There are a number of approaches developed for this purpose: *configuration interaction* (CI) [1] and *multiconfiguration* methods such as multiconfiguration Hartree–Fock (MCHF) [2], Dirac–Fock (MCDF) methods, *many-body perturbation theory* (MBPT) [3], etc. However, the domains of their applicability are very different. Some of these methods so far may be applied only for atoms and ions having closed electronic shells or one electron above closed shells.

Relativistic nature of motion implies the use of relativistic wave functions and relativistic Hamiltonian [1]. However, complete and rigorous treatment of the correlation effects together with the relativistic nature of the motion for heavy atoms and ions is, unfortunately, practically outside of today's computation possibilities.

Fortunately, there exists a fairly large variety of atoms and their ionization degrees, for which the relativistic effects are small compared to the nonspherical part of Coulomb interactions and, therefore, may be accurately taken into account as corrections of the order α^2 (α is the fine structure constant) in the Pauli approximation, considered in detail in [1]. This is particulary true for the spectroscopic properties and processes connected with the outer electronic shells of an atom or ion. Also, there are some spectroscopic quantities which are described as the difference of two large numbers. The ionization energies belong to such category of quantities. Relativistic effects are most important for the electrons in inner shells. The latter practically do not "feel" the loss of the outer electron in the process of the ionization, therefore, the main relativistic effects cancel out while calculating ionization energies. This supports the use of the approach described in this paper. Moreover, analysis of the energy spectra of atoms considered clearly shows that the fine structure of the terms is really "fine", there are even no traces of splitting of a shell f^N into relativistic subshells $f_-^{N_1}f_+^{N_2}$, typical of the relativistic approach. All this gives us the confidence that the main attention while studying the ionization energies must be paid to efficient accounting for correlation effects.

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Thus, this paper is supposed to show that some properties (such as ionization energies of valence electrons) of heavy atoms can be quite accurately determined using the nonrelativistic wave functions, accounting for correlation effects by the MCHF method and for relativistic effects as corrections of the order of α^2. In addition, in the paper we describe a method of selection of the basis for accurate accounting for the correlation effects important for the property under consideration, namely, the determination of $6s$ ionization energies (IE) of lanthanides.

The authors were able to find only one consistent and rigorous study of ionization energies of lanthanides [5] including the correlation effects, performed using *ab initio* methods. In the study [5] the CI method with Gaussian-type functions was applied. This approach is typically used in molecular physics. The authors suppose that it is relevant to study the ionization energies of lanthanides using the accurate methods common in atomic physics.

The problem in both CI and MCHF methods is to find the bases of atomic functions satisfying two conditions: one is to yield accurate data and the other is to be manageable by today's computation possibilities. The right choice of the basis would allow us not only to reproduce the ionization energies and other atomic data by *ab initio* methods, but it would also lead us to better understanding of the importance and structure of the correlation and relativistic effects.

For this purpose we perform MCHF calculations using the multiconfiguration Hartree–Fock code from the atomic structure package (ATSP MCHF) [2, 6] in which there are new codes for calculation of spin-angular parts of matrix elements of the operators of intraatomic interactions written on the basis of the methodology by Gaigalas, Rudzikas, and Froese Fischer [7, 8], based on the second quantization in coupled tensorial form, the angular momentum theory in three spaces (orbital, spin, and quasispin), graphical technique of spin-angular integrations and reduced coefficients (subcoefficients) of fractional parentage. The tables of such coefficients are presented in [8]. They allow us to study configurations with open f-shells without any restrictions. The basic concepts of our approach are presented in Section 2.

We assume that in the case of lanthanides with configurations $[\mathrm{Xe}]4f^N6s^2$ the relativistic and correlation effects between the electrons of "inner shells" (core–core correlations) are the same for the neutral atom and ion and then these effects (corresponding energies) cancel out in calculation of *ionization energy* (E_I). The mean distance to the nucleus of "outer" electrons (calculated, for example, by *single-configuration Hartree–Fock* (HF) method [9, 10]) is much larger than that of "inner" electrons. Therefore, we expect that the correlations between "inner" and "outer" electrons (core–valence correlations) will be negligible. For the same reason we expect relativistic effects for "outer shells" to be not so much important as for "inner shells" (the mean value of electron velocity is inversely proportional to the mean distance to the nucleus) and they can be treated rather accurately by adding relativistic corrections to the nonrelativistic Hamiltonian. Then it may be possible to get quite accurate values of the ionization energies by MCHF approach while accounting for relativistic effects as corrections.

Section 3 is aimed at checking this assumption. In Section 4 we present our final results. The results are compared with the previous theoretical investigations [5] and with the values of IE compiled from experimental data [11–14]. The details of the experimental investigation of the ionization energies of lanthanides can be found in [15–17]. Section 5 presents for conclusions.

2. Approach

We define the ionization energy as $E_\mathrm{I} = E_\mathrm{ion} - E_\mathrm{g}$, where E_g and E_ion are the ground state energies of neutral and singly ionized atoms correspondingly. The ground state of a neutral lanthanide atom is

$$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^64f^N6s^2 \equiv [\mathrm{Xe}]4f^N6s^2, \tag{1}$$

and that of a singly ionized one is

$$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^64f^N6s^1 \equiv [\mathrm{Xe}]4f^N6s^1. \tag{2}$$

Here N corresponds to $3, \ldots, 7$ for Pr, …, Eu, and to $9, \ldots, 14$ for Tb, …, Yb.

In our calculations we account for the relativistic effects by the following relativistic shift operator (notations for $\mathcal{H}_i$ are taken from [1]):

$$\mathcal{H}_\mathrm{RelCor} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 + \mathcal{H}'_5 + \mathcal{H}_\mathrm{mp}. \tag{3}$$

Here the *mass correction* term $\mathcal{H}_1$ and *orbit–orbit* term $\mathcal{H}_2$ are given by

$$\mathcal{H}_1 = -\frac{\alpha^2}{8}\sum_{i=1}^{N}\mathbf{p}_i^4, \tag{4}$$

$$\mathcal{H}_2 = -\frac{\alpha^2}{2}\sum_{i<j}^{N}\left[\frac{(\mathbf{p}_i\cdot\mathbf{p}_j)}{r_{ij}} + \frac{(\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\mathbf{p}_i)\mathbf{p}_j)}{r_{ij}^3}\right]. \tag{5}$$

The $\mathcal{H}_3$ stands for the one-particle ($\mathcal{H}_3'$) and two-particle ($\mathcal{H}_3''$) *Darwin terms.* They are given by

$$\begin{aligned}\mathcal{H}_3 &= \mathcal{H}_3' + \mathcal{H}_3''\\ &= \frac{Z\alpha^2\pi}{2}\sum_{i=1}^{N}\delta(\mathbf{r}_i) - \pi\alpha^2\sum_{i<j}^{N}\delta(\mathbf{r}_{ij}),\end{aligned} \tag{6}$$

and *spin–spin contact* term $\mathcal{H}_5'$ is

$$\mathcal{H}_5' = -\frac{8\pi\alpha^2}{3}\sum_{i<j}^{N}(\mathbf{s}_i\cdot\mathbf{s}_j)\delta(\mathbf{r}_{ij}). \tag{7}$$

The operators (4)–(7) are of the order of α^2.

The *mass-polarization* correction term $\mathcal{H}_{\mathrm{mp}}$ is given by

$$\mathcal{H}_{\mathrm{mp}} = -\frac{1}{M}\sum_{i<j}(\mathbf{p}_i\cdot\mathbf{p}_j). \tag{8}$$

The expressions (4–8) are presented in atomic units.

We expect the operator (3) to enable us to take into account the main relativistic corrections to ionization energy.

For the calculation of ionization energy we used the MCHF method. In this approach, the atomic state function $\Psi(\gamma LS)$ is expressed as a linear combination of *configuration state functions* (CSFs) $\Phi(\gamma_i LS)$, i. e.

$$\Psi(\gamma LS) = \sum_i c_i\Phi(\gamma_i LS). \tag{9}$$

A set of orbitals, or *an active set* (AS), determines the set of all possible CSFs or the *complete active space* (CAS) for MCHF calculation. The size of the latter grows rapidly with the number of electrons and also with the size of the orbital AS. Most MCHF expansions are therefore limited to a *restricted active space* (RAS) [2]. The RAS is spanned by all CSFs that can be generated from a given active set of orbitals, with some constrains. The constrains are derived from the notions of different types of correlations discussed below. No "relaxation" effects were included.

For complex atoms and ions, considerable part of the effort must be devoted to integrations over spin-angular variables, occurring in the matrix elements of the operators under consideration. In the papers [1, 7, 18] an efficient approach for finding matrix elements of any one- and two-particle operator between complex configurations is suggested. It is based on the extensive exploitation of the symmetry properties of the quantities of the theory of complex atomic spectra, presented in the secondly quantized form, in orbital, spin, and quasispin spaces. It is free of shortcomings of previous approaches. This approach allows one to generate fairly accurate databases of atomic parameters [19, 20], and will be used in our paper.

According to the approach of [7, 18], a general expression of the submatrix element for any scalar two-particle operator between functions with u open shells, valid for both nonrelativistic and relativistic wave functions, can be written down as follows:

$$\begin{aligned}&(\psi_u(LS)\|\widehat{G}^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}\|\psi_u(L'S'))\\ &= \sum_{n_il_i,n_jl_j,n_i'l_i',n_j'l_j'}(\psi_u(LS)\|\widehat{G}(n_il_i,n_jl_j,n_i'l_i',n_j'l_j')\\ &\qquad\times\|\psi_u(L'S'))\\ &= \sum_{n_il_i,n_jl_j,n_i'l_i',n_j'l_j'}\ \sum_{\kappa_{12},\sigma_{12},\kappa_{12}',\sigma_{12}'}\ \sum_{K_l,K_s}(-1)^{\Delta}\\ &\quad\times\Theta'(n_i\lambda_i,n_j\lambda_j,n_i'\lambda_i',n_j'\lambda_j',\Xi)\\ &\quad\times T(n_i\lambda_i,n_j\lambda_j,n_i'\lambda_i',n_j'\lambda_j',\Lambda^{\mathrm{bra}},\Lambda^{\mathrm{ket}},\Xi,\Gamma)\\ &\quad\times R(\lambda_i,\lambda_j,\lambda_i',\lambda_j',\Lambda^{\mathrm{bra}},\Lambda^{\mathrm{ket}},\Gamma),\end{aligned} \tag{10}$$

where Γ refers to the array of coupling parameters connecting the recoupling matrix $R(\lambda_i,\lambda_j,\lambda_i',\lambda_j',\Lambda^{\mathrm{bra}},\Lambda^{\mathrm{ket}},\Gamma)$ to the submatrix element $T(n_i\lambda_i,n_j\lambda_j,n_i'\lambda_i',n_j'\lambda_j',\Lambda^{\mathrm{bra}},\Lambda^{\mathrm{ket}},\Xi,\Gamma)$, $\lambda_i\equiv l_is_i$, parameter Ξ implies the array of coupling parameters that connect Θ to the tensorial part, $\Lambda^{\mathrm{bra}}\equiv(L_iS_i,L_jS_j,L_i'S_i',L_j'S_j')^{\mathrm{bra}}$ is the array for the bra function shells' terms, and similarly for Λ^{ket}. The expression (10) has summations over intermediate ranks κ_{12}, σ_{12}, κ_{12}', σ_{12}', K_l, K_s in $T(n_i\lambda_i,n_j\lambda_j,n_i'\lambda_i',n_j'\lambda_j',\Lambda^{\mathrm{bra}},\Lambda^{\mathrm{ket}},\Xi,\Gamma)$.

In calculating the spin-angular parts of the submatrix element using Eq. (10), one has to compute the following quantities (for more details, see [7]):

1. Recoupling matrix $R(\lambda_i,\lambda_j,\lambda_i',\lambda_j',\Lambda^{\mathrm{bra}},\Lambda^{\mathrm{ket}},\Gamma)$. This recoupling matrix accounts for the change in going from the matrix element $(\psi_u(LS)\|\times\widehat{G}(n_il_i,n_jl_j,n_i'l_i',n_j'l_j')\|\psi_u(L'S'))$, which has u

open shells in the bra and ket functions, to the submatrix element $T(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{\mathrm{bra}}, \Lambda^{\mathrm{ket}}, \Xi, \Gamma)$, which has only the shells being acted upon by the two-particle operator in its bra and ket functions.

2. Submatrix element $T(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{\mathrm{bra}}, \Lambda^{\mathrm{ket}}, \Xi, \Gamma)$ for tensorial products of creation/annihilation operators that act upon a particular electronic shell. So, all the advantages of tensorial algebra and quasispin formalism may be efficiently exploited in the process of their calculation.
3. Phase factor Δ.
4. $\Theta'(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Xi)$, which is proportional to the radial part and corresponds to one of $\Theta(n\lambda, \Xi), \ldots, \Theta(n_\alpha\lambda_\alpha, n_\beta\lambda_\beta, n_\gamma\lambda_\gamma, n_\delta\lambda_\delta, \Xi)$. It consists of a submatrix element $(n_i\lambda_i n_j\lambda_j \| \times g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_i'\lambda_i' n_j'\lambda_j')$, and in some cases of simple factors and $3nj$-coefficients.

The above-mentioned method of the definition of spin-angular parts becomes especially important in the investigation of the complex systems in both relativistic and nonrelativistic approaches.

The usage of MCHF as well as MCDF methods gives accurate results only when the RAS is formed properly. Therefore, the next section is devoted to the analysis of this problem.

3. RAS construction

Large scale systematic MCHF calculations (except for Er [10] and Gd [9]) of E_{I} of lanthanides have not been done yet. Therefore, following the methodology of [2], it is important to investigate the structure of ground configurations, to impose the *core* and *valence* shells and to evaluate *valence–valence* (VV), *core–valence* (CV), and *core–core* (CC) correlations.

It is always a question when we can assume that a shell is part of the core, and when it should be treated as a valence shell. The answer is not trivial even for boron-like ions, and in our case it is even more complicated because of the complexity of configurations under consideration. Our purpose is to take care of the correlation effects that do not cancel each other between the ion and atom.

In this section we will discuss some practical possibilities of RAS construction using Er as an example [10].

Table 1. Results of single-configuration HF calculations for Er. Ground state energies and mean values of various operators in a.u. (values for Er$^+$ presented in parentheses).

nl	$\langle 1/r\rangle$	$\langle r\rangle$	$\langle r^2\rangle$
$1s$	67.45598	0.02229	0.00066
$2s$	15.76448	0.09452	0.01048
$2p$	15.76098	0.08018	0.00780
$3s$	6.01686	0.24164	0.06657
$3p$	5.94849	0.23182	0.06215
$3d$	5.84288	0.20492	0.04918
$4s$	2.55502	0.54479	0.33457
$4p$	2.45573	0.55702	0.35245
$4d$	2.24072	0.58791	0.40085
$4f$	1.72460	0.75423	0.73896
$5s$	0.94798	1.37069	2.17737
	(0.93256)	(1.38534)	(2.16005)
$5p$	0.81825	1.56941	2.80348
	(0.81981)	(1.56529)	(2.78491)
$6s$	0.25106	4.63012	24.27349
	(0.29939)	(4.09340)	(18.75251)
Energy:			
Er		−12498.1528	
Er$^+$		−12497.9809	

3.1. Single-configuration HF calculations

We can get the first insight into the structure of Er and Er$^+$ ground states from the single-configuration HF calculations. The resultant ground state energies and mean values of various operators of nl radial functions are presented in Table 1. Resultant energies are practically the same as those presented in [21, 22].

The fact that the mean values $\langle r\rangle$, $\langle r^2\rangle$ of the corresponding operators are much higher, and at the same time the value of $\langle 1/r\rangle$ is much smaller for the $6s$-function than those for $5s$-, $5p$-, and $4f$-functions, shows that the $6s$-function is much more remote from the nucleus than the others.

Similar analysis shows that the open $4f$-shell is closer to the nucleus than $5s$ or $5p$.

The same situation remains for the Er$^+$ ion (the corresponding values are presented in parentheses). Therefore, we have a difficulty in treatment of "outer" electrons: usually the open shells are considered as outer (valence) ones, but sometimes the closed shells ($6s^2$ in our case) are included, too [2]. For the light atoms these shells are spatially "outer".

The same qualitative picture is valid for other lanthanides considered.

It is interesting to notice that $2p$- and $3p$-, $3d$-electrons are spatially closer to the nucleus than respectively $2s$ or $3s$. This fact may be explained by the increasing role of relativistic effects for inner electrons in

Table 2. Results of MCHF calculations. Numbers of CSFs (NCSF) and values of E_{I} (in eV).

Basis	$\mathrm{NCSF}_{\mathrm{Er}}$	$\mathrm{NCSF}_{\mathrm{Er}^+}$	E_{Er} (a.u.)	E_{Er^+} (a.u.)	$E_{\mathrm{I\ Er}}$	$E_{\mathrm{I\ Ho}}$
I_a	2838	2769	−12498.58517	−12498.38073	5.563	–
I_b	12811	12054	−12498.66977	−12498.46502	5.572	–
II_a	236	8	−12498.17664	−12497.96000	5.895	6.041
II_c	2600	23	−12498.17741	−12497.96451	5.793	5.932
II_d	5565	32	−12498.17743	−12497.96456	5.793	5.927
II_e	10347	43	−12498.17744	−12497.96457	5.792	–
III_a	70	4	−12498.17657	−12497.95988	5.896	19.189
III_b	272	7	−12498.17729	−12497.96428	5.796	5.929
III_c	733	11	−12498.17733	−12497.96446	5.792	–
III_d	1569	15	−12498.17735	−12497.96451	5.792	5.923
III_e	2938	20	−12498.17735	−12497.96452	5.792	5.922
CI [5]			−12498.6887	–	5.077	5.040
Nonrelativistic HF [5]					4.677	4.621
Experiment [14]					6.108	6.022

heavy atoms, which may already need proper account for the so-called indirect relativistic effects.

3.2. Core I

In this case we use core I, [Xe] ^1S, and we treat $4f$ and $6s$ as valence shells. We treat $4f$-shell as a valence shell because it is open, and $6s$ because the corresponding radial function is much more remote from the nucleus than others. This approach is close to the advices given in [2].

The basis for the MCHF expansion was formed using the CSFs of the configurations made of single and double (S, D) excitations from the valence shells to some *destination set*. There were two types of destination sets used:

$$a = \{5d, 5f, 5g, 6p, 6d\}, \tag{11}$$

$$b = a + \{6f, 6g, 6h, 7s, 7p, 7d\}. \tag{12}$$

Further on we denote the basis as a core having a subscript of the destination set. For example, I_a denotes the basis consisting of CSFs of the configurations made by S, D excitations from $4f^{12}6s^2$ for Er and $4f^{12}6s^1$ for Er^+ to the destination set a and cores [Xe]. The numbers of CSFs in the bases (NCSF) are presented in Table 2.

The weight for the main CSF was found to be 0.977 for I_a (and similar for I_b). This value is close to that (0.949) found by the CI method [5]. The mean distances of radial functions from the nucleus are found to be up to 2% smaller than those for single-configuration HF calculations. For example, $\langle r\rangle_{4f} = 0.752$ a.u. for I_a (0.748 a.u. for I_b), and $\langle r\rangle_{6s} = 4.550$ a.u. for I_a (4.534 a.u. for I_b).

3.3. Cores II and III

In this case, only $6s$ is treated as a valence shell, because of its spatial location. We expect this strategy to be more efficient for the calculations of $6s$ ionization energy because, as we can see from single-configuration HF calculations, the mean distance of $4f$ radial functions is not much different for Er and Er^+. As the cores we use core II, [Xe]$4f^{12}$, with term not fixed, and core III, [Xe]$4f^{12}$, with a fixed term ^3H.

There were five types of destination sets used with these cores, namely, (11) and (12) as for core I and three more

$$c = b + \{7f, 7g, 7h, 7i, 8s, 8p, 8d\}, \tag{13}$$

$$d = c + \{8f, 8g, 8h, 8i, 8k, 9s, 9p, 9d\}, \tag{14}$$

$$e = d + \{9f, 9g, 9h, 9i, 9k, 9l, 10s, 10p, 10d\}. \tag{15}$$

The results of MCHF calculations (Er and Er^+ ground state energies and ionization energies) are also presented in Table 2. The weights of the main CSFs in MCHF expansions are in the range of 0.960–0.980 for all bases with cores II and III. The mean distance from the nucleus for the $6s$ radial function is greater than obtained from single-configuration HF calculations, but smaller than obtained using the bases with core I. For example, $\langle r\rangle_{6s} = 4.560$ a.u. for III_a and 4.564 a.u. for $\mathrm{III}_{b,d,e}$.

Here we would like to point out the fact that in order to accurately account for the correlation effects of some type (e. g., CC or CV) the destination set should be large enough. In the calculation of the ionization energy it is especially important to properly account for the correlation effects of the same nature for an atom and ion. For example, the destination sets a for the cores II and III are too small and, therefore, lead to the far from true values in the ionization energy because the number of CFSs in the ions MCHF expansion is too small. It becomes particularly obvious in the case of III$_a$ for Ho, where the obtained ionization energy $E_\mathrm{I} = 19.189$ (see Table 2) is far from the real one. But the increase of the destination set up to the b already gives balanced inclusion of the correlation effects for an atom and ion and reasonable values of IE. Further increase of the destination set gives the convergence of IE to the value determined by the choice of the core and of the approach (Hamiltonian).

3.4. Strategy of RAS formation

As we can see from Table 2, the basis formed with the same destination sets is the largest for core I, medium for core II, and the smallest for core III. Correspondingly, the energies are the lowest for core I, medium for core II, and the highest for core II. This means that the bases of core I account for more correlation effects than the ones of cores II and III. Nevertheless, the ionization energies obtained using cores II and III are practically the same, and the ones obtained using core I are much worse. This is due to the fact that the basis formed using the destination set b for core I is not sufficient to account for the correlation effects of $4f$-electrons, which, when represented in full, cancel between Er and Er$^+$.

So, the most efficient strategy is to use MCHF expansions with a frozen core of the type [Xe]$4f^{N\ 2S+1}L$ and S, D excitations from $6s$. This strategy was used when forming the bases for E_I calculations of other lanthanides. The corresponding sizes of the bases are similar to those for Er. For example, the bases of the type similar to III$_e$ consisted of 3018 CSFs for Pr, Nd, Dy, Ho, of 2938 CSFs for Pm, Tb, and of 2240 CSFs for Sm, Tm.

4. $6s$ ionization energy

4.1. Nonrelativistic

The nonrelativistic $6s$ ionization energies of the atoms considered are presented in Table 3. There E_I stands for the ionization energy value calculated by the MCHF method, Exp. denotes the experimental results [14, 17]. For comparison we also present single-configuration HF and CI [5] results. We were unable to obtain the relevant result for europium due to the problems with the convergence of MCHF equations.

Table 3. $6s$ ionization energies of lanthanides (in eV).

Z	Atom	HF	CI [5]	E_I	Exp. [14, 17]
59	Pr	4.254	4.942	4.961	5.464
60	Nd	4.288	4.949	5.086	5.525
61	Pm	4.321	4.941	5.065	5.554
62	Sm	4.352	4.932	5.117	5.644
65	Tb	4.505	4.985	5.355	5.864
66	Dy	4.564	5.000	5.384	5.939
67	Ho	4.621	5.040	5.757	6.022
68	Er	4.677	5.077	5.792	6.108
69	Tm	4.731	5.119	6.101	6.184
σ		0.501	0.314	0.163	

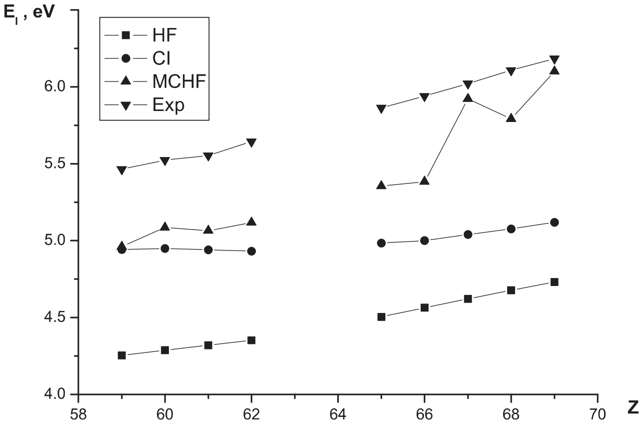

Fig. 1. $6s$ ionization energies in various approximations.

Figure 1 shows Z-dependence of ionization energies calculated by single-configuration HF, CI, MCHF methods, and the experimental one.

The differences between the MCHF energies of the ground states and the ones obtained by the single-configuration HF method (ΔE) for all Z vary from 0.626 eV to 0.707 eV. Their absolute value is smaller than that predicted in [5]. So, in general we encounter less correlation effects for the ground states. For example, for Er in [5] there is $\Delta E = -15.339$ eV, and our value is $\Delta E = -0.669$ eV.

Nevertheless, our computed values of ionization energies are closer to the experimental ones than CI [5] (see the root-mean-square deviations σ of the calculated results from the experimental measurements in Table 3). For example, for Er in [5] there is 5.077 eV, and our value is 5.792 eV, whereas the experimental value is 6.108 eV [14, 17]. So, though we account for less correlation effects in general, we still get a better value of ionization energy because we account for more

Table 4. Results of MCHF calculations of E_{I} with various relativistic corrections (in eV).

Z	Atom	RHF [5]	$\mathrm{CI}_{\mathrm{Est}}$ [5]	E_{I}^{1}	E_{I}^{2}	E_{I}^{3}	Exp. [14, 17]
59	Pr	4.45	5.24	5.180	5.180	5.178	5.464
60	Nd	4.50	5.28	5.191	5.191	5.190	5.525
61	Pm	4.54	5.31	5.242	5.242	5.240	5.554
62	Sm	4.59	5.33	5.485	5.485	5.482	5.644
65	Tb	4.79	5.45	5.530	5.528	5.528	5.864
66	Dy	4.86	5.47	5.577	5.577	5.575	5.939
67	Ho	4.93	5.52	6.686	6.686	6.680	6.022
68	Er	5.00	5.58	5.878	5.878	5.877	6.108
69	Tm	5.08	5.64	7.566	7.567	7.556	6.184
σ		0.398	0.152	0.215	0.215	0.214	

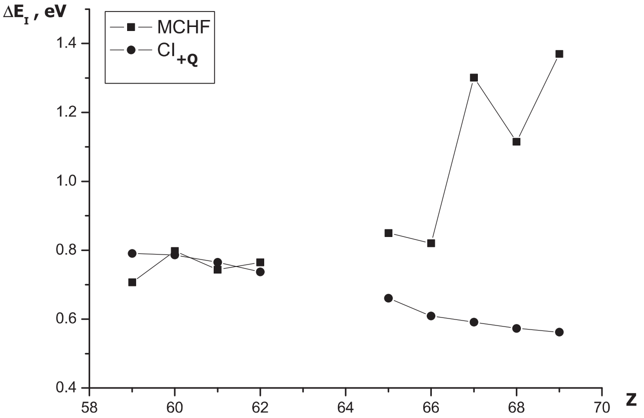

Fig. 2. Influence of correlation effects ΔE_{I} on E_{I}.

correlation effects that do not cancel between the atom and the ion.

For smaller Z the results of CI and MCHF calculations are quite close. For example, for Pr ($Z = 59$) the difference between CI and MCHF values is only 0.019 eV (i. e. less than 1%). Meanwhile, the MCHF results grow faster with increasing Z, and for large Z they are much closer to the experimental ones. For example, for Tm ($Z = 69$) the difference between CI and MCHF values of E_{I} grows up to 0.982 eV (i. e. 16%).

Figure 2 shows the Z-dependence of the influence of correlation effects ΔE on E_{I} calculated by the CI method with Davidson Q correction (CI_{+Q}) [5] and by the MCHF method. The Davidson Q correction is supposed to aproximately account for the higher-order correlation effects. We define the influence as $\Delta E_{\mathrm{I}} = E_{\mathrm{I}} - E_{\mathrm{I\ HF}}$, where $E_{\mathrm{I\ HF}}$ stands for the ionization energy value calculated by the single-configuration HF method.

As we see in Fig. 2, the values of ΔE_{I} calculated by MCHF and CI_{+Q} methods show different Z-behaviour. While CI_{+Q} results tend to decrease with Z, the MCHF ones increase. We expect the increase of influence of correlation effects with Z to be real because of two reasons: the MCHF results are closer to the experimental ones and it is more realistic to expect that with increasing number of electrons the influence of their correlation effects grows, too.

4.2. With relativistic corrections

The $6s$ ionization energies calculated with various relativistic corrections are presented in Table 4. There E_{I}^{i} stands for the ionization energy value calculated by the MCHF method using nonrelativistic Hamiltonian with relativistic corrections $\mathcal{H}^{i}$. Here $i = 1, 2, 3$, and $\mathcal{H}^{1} = \mathcal{H}_{1} + \mathcal{H}_{3} + \mathcal{H}_{5}'$, $\mathcal{H}^{2} = \mathcal{H}^{1} + \mathcal{H}_{\mathrm{mp}}$, $\mathcal{H}^{3} = \mathcal{H}^{2} + \mathcal{H}_{2}$.

For comparison we also present ionization energies calculated using the relativistic Hartree–Fock method (RHF), the ones of CI with the Davidson Q correction and estimated relativistic corrections ($\mathrm{CI}_{\mathrm{Est}}$) [5] (these values practically cannot be considered as *ab initio*), as well as the experimental results [14, 17] (Exp.).

Two-electron relativistic corrections $\mathcal{H}_{2}$, $\mathcal{H}_{3}''$, and $\mathcal{H}_{5}'$ are generally of the same order of magnitude, but their contribution may have different signs, therefore, they all must be taken into account simultaneously. Consequently, the results E_{I}^{3} in Table 4 must be considered as the most correct, in spite of the fact that the data of the columns E_{I}^{1}, E_{I}^{2} seem to be slightly closer to the experimental values. The point is that one-electron operators $\mathcal{H}_{1}$ and $\mathcal{H}_{3}'$ have large contributions of opposite signs, and hence, they are very sensitive to the accuracy of the wave functions used.

The results of Table 4 also suggest that accounting for relativistic effects as relativistic corrections of the order of α^{2} usually improves the ionization energies of rare earths (compare with the E_{I} column of Table 3), but there may occur cases (for example, Ho, Tm) where such an improvement worsens the final result. Therefore, taking into consideration the relativistic effects for heavy atoms having open f-shells requires further studies.

The results presented in this section show that our values of ionization energies are the closest to the experimental ones with respect to other ones obtained by pure *ab initio* methods, and in most cases they are even better than the ones obtained by using semiempirical corrections, in spite of the fact that the RAS is formed in such a way that the corresponding bases are relatively small. The results obtained allow us to evaluate more precisely the influence of correlation effects to the ionization energies of the $6s$-electrons.

The results of Section 4.2 show that the relativistic effects accounted in the form of Eq. (3) in the MCHF approach are not appropriate for the elements Ho, Tm. The values of their ionization energies with the corresponding corrections are larger than the experimental ones.

The strategy of RAS formation presented in Section 3.4 gives a hint for the formation of the corresponding bases in the relativistic approach, too. The bases III_a–III_e presented in Section 3.4 contain the minimum number of CSFs, but the correlation effects are adequately accounted for an atom and ion. So, such bases (but with the relativistic splitting of subshells) should be used for the corresponding study by the relativistic MCHF method as well.

5. Conclusion

The results obtained show that if the correlation effects of inner shells cancel each other between atom and ion, then it is possible to get quite accurate data on ionization energies by the MCHF method while accounting for the correlation effects of the outer electrons only. This assumption is valid in the case of ionization energy of lanthanides with configurations $[\mathrm{Xe}]4f^N6s^2$.

Our results on $6s$ ionization energy of lanthanides with configurations $[\mathrm{Xe}]4f^N6s^2$ are more accurate than the data found using the CI method [5].

The influence of the correlation efects on the ionization energy of lanthanides with configurations $[\mathrm{Xe}]4f^N6s^2$ is higher than it has been found before [5], and this influence grows with Z (or with N). However, the convergence of the value studied to the true one is often not smooth with increase of the basis. This statement is very well illustrated by the intermediate value of E_I for Ho, 19.189 eV (basis III_a in Table 2).

The results presented demonstrate the ability of the approach by Gaigalas et al. [1, 7, 8] based on the second quantization in coupled tensorial form, the graphical technique of spin-angular integration, quasispin formalism, and reduced coefficients (subcoefficients) of fractional parentage to obtain reasonably accurate data on the ionization energies of heavy atoms and ions having open f-shells.

Accounting for the relativistic effects as the corrections of the order of α^2 improves in general the ionization energies. However, some inhomogeneities in their behaviour with respect to Z or N indicate that it is necessary to refine the value of $6s$-functions at the nucleus: to accurately account for the finite size of the nucleus, or simply to use the relativistic wave functions.

In conclusion, the accurate studies of the structure and spectral properties of rare earth elements require further improvement of the accounting for both the correlation and relativistic effects, but some properties determined by valence electrons may be successfully studied by the nonrelativistic approach (MCHF method) accounting for relativistic effects as corrections of the order of α^2, even for heavy atoms (such as lanthanides).

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LANTANIDŲ $6s$ JONIZACIJOS ENERGIJOS TYRIMAI

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Santrauka

Sunkiųjų atomų bei jonų tyrimai yra viena iš labiausiai plėtojamų atomo fizikos sričių. Problemas, su kuriomis susiduriama tokiuose tyrimuose, daugiausia nulemia nagrinėjamų sistemų sudėtingumas (didelis elektronų skaičius) bei reliatyvistinių efektų svarba.

Teoriškai tirtos lantanidų jonizacijos energijos vertės daugiakonfigūraciniu Hartree ir Fock'o metodu. Tirta [Xe]$4f^N6s^2$ ($N = 3{-}7, 9{-}14$) konfigūracijų lantanidų $6s$ elektronų jonizacijos energija. Tyrimui panaudotas ATSP MCHF programų paketas, kuriame įdiegti matricinių elementų kampinių dalių skaičiavimo metodai, paremti antriniu kvantavimu surištu tenzoriniu pavidalu, judėjimo kiekio momentu trijose (orbitinėje, sukinio ir kvazisukinio) erdvėse, grafine integravimo technika bei subkilminių koeficientų naudojimu. Tokie kampinių dalių skaičiavimo metodai leidžia tirti atomines sistemas su atvirais f sluoksniais, apimant ir itin sunkius atomus bei jonus. Nagrinėjant jonizacijos energijos vertes, apskaičiuotas naudojant įvairias banginių funkcijų bazes, pasiūlyti bazių, skirtų išorinių elektronų nulemtoms savybėms tirti, sudarymo principai. Be to, tyrimo metu nustatyta didesnė negu manyta iki šiol koreliacinių efektų svarba. Remiantis darbo rezultatais, galima geriau suvokti sudėtingų atomų (šiuo atveju lantanidų) vidinę sandarą, koreliacinių ir reliatyvistinių efektų svarbą bei įtaką jonizacijos energijai.