Studies of Lanthanides 6s Ionization Energy

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Abstract

This work is aimed at the multi-configuration Hartree-Fock calculations of the 6s ionization energies of lanthanides with configurations \([Xe]4f^N6s^2\). Authors have used 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 Gaigalas, Rudzikas and Froese Fischer, based on the second quantization in coupled tensorial form, the angular momentum theory in 3 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.
1 Introduction

There is a 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 an accurate description of heavy atoms and ions requires generally 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) and multi-configuration methods such as multi-configuration Hartree–Fock (MCHF), Dirac–Fock (MCDF) methods, many body perturbation theory (MBPT), 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. However a 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 ionisation degrees, for which the relativistic effects are small compared to the non-spherical part of Coulomb interactions and, therefore, may be accurately taken into account as corrections of the order \( \alpha^2 \) (\( \alpha \) is the fine structure constant) in the Pauli approximation, considered in details in [1]. This is particular 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. Latters practically do not ”feel” the loss of the outer electron in the process of the ionization, therefore the main relativistic effects cancel each other 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 \( f_{N1}^N f_{N2}^N \), typical for 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.

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 \( \alpha^2 \). In addition in the paper we describe the method of selection of the basis for the accurate accounting of the correlation effects important for the property under consideration, namely, the determination of the 6s ionization energies (IE) of the lanthanides.

The authors were able to find only one consistent and rigorous study of lanthanides ionization energies, including the correlation effects, performed using ab initio methods. In the study the CI method with Gaussian-type functions was used. 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 obtain 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 \emph{ab initio} methods, but it would also lead us to a better understanding of the importance and structure of the correlation and relativistic effects.

For this purpose we perform MCHF calculations using the multi–configuration Hartree–Fock code from the atomic–structure package (ATSP MCHF) \cite{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 Gaigalas, Rudzikas and Froese Fischer \cite{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 \cite{8}. They allow us the study of configurations with open $f$-shells without any restrictions. The basic concepts of our approach are presented in Section 2.

We assume that in case of lanthanides with configurations $[Xe]4f^N6s^2$ 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 each other in calculation of ionization energy ($E_I$). Mean distance to the nucleus of ”outer” electrons (calculated for example by \emph{single-configuration Hartree-Fock} (HF) method \cite{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” (mean value of electron velocity is proportional to the $-1$ power of mean distance to the nucleus) and they can be treated rather accurately by adding relativistic corrections to the non-relativistic Hamiltonian. Then it may be possible to get quite accurate values of the ionization energies by MCHF approach and 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 \cite{5} and with values of IE compiled from experimental data \cite{11, 12, 13, 14}. The details of the experimental investigation of the ionization energies of lanthanides can be found in \cite{15, 16, 17}. Section 5 serves for conclusions.

\section{Approach}

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

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

and that of singly ionized one

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

Here $N$ corresponds to 3, ..., 7 for $Pr, ..., Eu$ and to 9, ..., 14 for $Tb, ..., Yb$.\pagebreak
In our calculations we account for the relativistic effects by the following relativistic shift operator (notations for $H_i$ are taken from [1]):

$$H_{\text{RelCor}} = H_1 + H_2 + H_3 + H'_3 + H_{mp}. \tag{3}$$

Here the mass correction term $H_1$ and orbit–orbit term $H_2$ are given by

$$H_1 = -\frac{\alpha^2}{8} \sum_{i=1}^{N} p_i^4, \quad H_2 = -\frac{\alpha^2}{2} \sum_{i<j}^{N} \left[ \frac{(p_i \cdot p_j)}{r_{ij}} + \frac{(r_{ij} \cdot (r_{ij} \cdot p_i) p_j)}{r_{ij}^3} \right]. \tag{4}$$

The $H_3$ stands for the one-particle ($H'_3$) and two-particle ($H''_3$) Darwin terms. They are given by

$$H_3 = H'_3 + H''_3 = \frac{Z\alpha^2\pi}{2} \sum_{i=1}^{N} \delta(r_i) - \pi\alpha^2 \sum_{i<j}^{N} \delta(r_{ij}), \tag{5}$$

and spin–spin contact term $H'_5$ is

$$H'_5 = -\frac{8\pi\alpha^2}{3} \sum_{i<j}^{N} (s_i \cdot s_j) \delta(r_{ij}). \tag{6}$$

The operators (4-6) are of the order $\alpha^2$.

The mass–polarization correction term $H_{mp}$ is given by

$$H_{mp} = -\frac{1}{M} \sum_{i<j} (p_i \cdot p_j). \tag{7}$$

The expressions (4-7) 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 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.

$$\Psi(\gamma LS) = \sum_i c_i \Phi(\gamma_i LS). \tag{8}$$

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 a 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, a 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 second 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 by \([7, 18]\), a general expression of submatrix element for any scalar two–particle operator between functions with \(u\) open shells, valid for both non–relativistic and relativistic wave functions, can be written down as follows:

\[
(\psi_u (LS) \left\| \hat{G}(\kappa_1 \kappa_2, \sigma_1 \sigma_2) \right\| \psi_u (L'S')) = \sum_{n_i l_i, n_j l_j, n_i' l_i', n_j' l_j'} (\psi_u (LS) \left\| \hat{G}(n_i l_i, n_j l_j, n_i' l_i', n_j' l_j') \right\| \psi_u (L'S')) = \sum_{n_i l_i, n_j l_j, n_i' l_i', n_j' l_j'} \sum_{\kappa_i, \kappa_j, \sigma_i, \sigma_j} (-1)^\Delta \Theta' (n_i \lambda_i, n_j \lambda_j, n_i' \lambda_i', n_j' \lambda_j', \Xi) \times T \left( n_i \lambda_i, n_j \lambda_j, n_i' \lambda_i', n_j' \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma \right) R \left( \lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Gamma \right),
\]

(9)

where \(\Gamma\) refers to the array of coupling parameters connecting the recoupling matrix \(R \left( \lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Gamma \right)\) to the submatrix element \(T \left( n_i \lambda_i, n_j \lambda_j, n_i' \lambda_i', n_j' \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma \right)\), parameter \(\Xi\) implies the array of coupling parameters that connect \(\Theta\) to the tensorial part, \(\Lambda^{bra} \equiv \left( L_i S_i, L_j S_j, L_i' S_i', L_j' S_j' \right)^{bra}\) is the array for the bra function shells’ terms, and similarly for \(\Lambda^{ket}\). The expression (9) has summations over intermediate ranks \(\kappa, \sigma_i, \sigma_j, \kappa_i, \kappa_j, \) in \(T \left( n_i \lambda_i, n_j \lambda_j, n_i' \lambda_i', n_j' \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma \right)\).

In calculating the spin–angular parts of a submatrix element using (9), one has to compute the following quantities (for more details see \([7]\):

1. The recoupling matrix \(R \left( \lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Gamma \right)\). This recoupling matrix accounts for the change in going from matrix element

\[
(\psi_u (LS) \left\| \hat{G}(n_i l_i, n_j l_j, n_i' l_i', n_j' l_j') \right\| \psi_u (L'S'))
\]

which has \(u\) open shells in the bra and ket functions, to the submatrix element

\(T \left( n_i \lambda_i, n_j \lambda_j, n_i' \lambda_i', n_j' \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma \right)\), which has only the shells being acted upon by the two–particle operator in its bra and ket functions.

2. The submatrix element \(T \left( n_i \lambda_i, n_j \lambda_j, n_i' \lambda_i', n_j' \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma \right)\) 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 \(\Delta\).

4. \(\Theta' \left( n_i \lambda_i, n_j \lambda_j, n_i' \lambda_i', n_j' \lambda_j', \Xi \right)\), which is proportional to the radial part and corresponds to one of \(\Theta \left( \lambda_l, \Xi \right)\), etc, \(\left( n_{\alpha l} \lambda_{\alpha l}, n_{\beta l} \lambda_{\beta l}, n_{\gamma l} \lambda_{\gamma l}, n_{\delta l} \lambda_{\delta l}, \Xi \right)\). It consists of a submatrix element \(\left( n_i \lambda_i n_j \lambda_j \right) g^{(\kappa_1 \kappa_2, \sigma_1 \sigma_2) \left( n_i' \lambda_i' n_j' \lambda_j' \right) \Xi}\), and in some cases of simple factors and \(3n_j–\)coefficients.
The abovementioned method of the definition of spin–angular parts becomes especially impor-
tant 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 chapter is dedicated to the analysis of this problem.

3 RAS construction

Large scale systematic MCHF calculations (except for Er \cite{10} and Gd \cite{9}) of \( E_I \) of lanthanides
have not been done yet. Therefore, following the methodology of \cite{2}, it is important to in-
vestigate 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 a 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
ion and atom.

In this chapter we will discuss some practical possibilities of RAS construction using an example
of Er \cite{10}.

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 I. Resultant energies are practically the
same as those presented in \cite{21, 22}.

The fact that the mean values of \(< r >\), \(< r^2 >\) operators are much higher and at the same
time the mean value of \(< 1/r >\) is much smaller for 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 and 5p.

The same situation remains for the Er\(^+\) ion (corresponding values presented in brackets).
Therefore, we have a difficulty in treatment of ”outer” electrons: usually as outer (valence)
shells the open ones are considered, but sometimes the closed shells (6s\(^2\) in our case) are
included too \cite{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 nucleous
than respectively 2s and 3s. This fact may be explained by the increasing role of relativistic
effects for inner electrons in heavy atoms, which may need already proper account for so called
indirect relativistic effects.

3.2 Core I

In this case we use the core
and we treat $4f$, $6s$ 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 advice 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:

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

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

Further on we denote the basis as a core with subscript of 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 II.

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 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, $<r>_{4f} = 0.752$ a.u. for $I_a$ (0.748 a.u. for $I_b$) and $<r>_{6s} = 4.550$ a.u. for $I_a$ (4.534 a.u. for $I_b$).

3.3 Cores $II$, $III$

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 $II$. [Xe]$4f^{12}$ with not fixed term and $III$. [Xe]$4f^{12}$ with fixed term $3H$.

There were five types of destination sets used with these cores, namely, (10) and (11) as for core $I$ and three more

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

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

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

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

Here we would like to draw an attention to the fact that in order to accurately account for the correlation effects of some type (e.g. core-core or core-valence) the destination set should be big 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 CSFs in the ions MCHF expansion is too small. It becomes particularly obvious in the case of $III_a$ for Ho for which the value of ionization energy $E_I = 19.189$ (see Table II) 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. The further increase of destination set gives the convergence of the IE to the value defined by the choice of the core, and the approach (Hamiltonian).

### 3.4 Strategy of RAS formation

As we can see from Table II, the basis formed with the same destination sets is the biggest for core $I$, the medium for core $II$ and the smallest for core $III$. Correspondingly the energies are the lowest for core $I$, the 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 enough to account for the correlation effects of 4f electrons, which, represented in full, cancel between Er and Er$^+$. 

So, the most efficient strategy is to use the MCHF expansions with a frozen core of the type $[Xe]4f^N 2S+1L$ and single, double excitations from 6s. This strategy was used when forming the bases for $E_I$ calculations of other lanthanides. Corresponding sizes of the bases are similar to the ones 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 atoms considered are presented in Table III. There $E_I$ stands for a value of ionization energy calculated by MCHF method, Exp - experimental results [14, 17]. For comparison we also present single-configuration HF and CI [5] results. We were not able to obtain the relevant result for Europium due to the problems with the convergence of MCHF equations.

Fig. 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 single-configuration HF method ($\Delta E$) 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 $\sigma$ of calculated results from experimental measurements in Table III). 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, however we get better value of ionization energy because we account for more correlation effects that do not cancel between the atom and the ion.

For the 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 the increasing Z and for large Z they are much more 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%).

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

As we see in Fig. 2, the values of $\Delta E_I$ calculated by MCHF and by $CI+Q$ 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 a real one 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 IV. There $E_I^i$ stands for a value of ionization energy calculated by MCHF method using nonrelativistic Hamiltonian with relativistic corrections $\mathcal{H}_i$. Here $i = 1, 2, 3$ and $\mathcal{H}_1 = \mathcal{H}_1 + \mathcal{H}_3 + \mathcal{H}_5$, $\mathcal{H}_2 = \mathcal{H}_1 + \mathcal{H}_{mp}$, $\mathcal{H}_3 = \mathcal{H}_2 + \mathcal{H}_2$.

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

Two–electron relativistic corrections $\mathcal{H}_2$, $\mathcal{H}_2'$ 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. Therefore the results $E_I^3$ in Table IV 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 ones. The point is that one–electron operators $\mathcal{H}_1$ and $\mathcal{H}_3'$ have large contributions but of opposite signs therefore are very sensitive to the accuracy of the wave functions used.

The results of Table IV also suggest that accounting for relativistic effects as relativistic corrections of the order $\alpha^2$ usually improves the ionization energies of rare earths (compare with
$E_I$ column of Table III), 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 the subsections 4.1 and 4.2 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 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 to evaluate more precisely the influence of correlation effects to the ionization energies of the 6$s$ electrons.

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

The strategy of RAS formation presented in subsection 3.4 gives a hint for the formation of corresponding bases in relativistic approach too. The bases ($III_a$ – $III_e$) presented in the subsection 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 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 MCHF method accounting for the correlation effects of the outer electrons only. This assumption takes place in the case of ionization energy of lanthanides with configurations $[Xe]4f^N6s^2$.

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

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

The results presented demonstrate the ability of the approach by Gaigalas et al. [11] [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 order $\alpha^2$ 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 6$s$ functions at 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 defined by valence electrons may be successfully studied by non-relativistic approach (MCHF method) accounting for relativistic effects as corrections of order $\alpha^2$, even for heavy atoms (such as lanthanides).

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Figures

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

*Fig. 2.* Influence of correlation effects $\Delta E_I$ on $E_I$. 
Tables
Table I. 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 brackets).

| $nl$ | $<1/r>$  | $<r>$  | $<r^2>$ |
|------|----------|--------|---------|
| 1s   | 67.45598 | .02229 | .00066  |
| 2s   | 15.76448 | .09452 | .01048  |
| 2p   | 15.76098 | .08018 | .00780  |
| 3s   | 6.01686  | .24164 | .06657  |
| 3p   | 5.94849  | .23182 | .06215  |
| 3d   | 5.84288  | .20492 | .04918  |
| 4s   | 2.55502  | .54479 | .33457  |
| 4p   | 2.45573  | .55702 | .35245  |
| 4d   | 2.24072  | .58791 | .40085  |
| 4f   | 1.72460  | .75423 | .73896  |
| 5s   | .94798   | 1.37069| 2.17737 |
|      | (.93256) | (1.38534)| (2.16005)|
| 5p   | .81825   | 1.56941| 2.80348 |
|      | (.81981) | (1.56529)| (2.78491)|
| 6s   | .25106   | 4.63012| 24.27349|
|      | (.29939) | (4.09340)| (18.75251)|

Energy:
Er       -12498.1528
Er$^+$    -12497.9809

Table II. Results of MCHF calculations. Numbers of CSFs (NCSF) and
values of $E_I$ (in eV).

| Basis | NCSF$_{Er}$ | NCSF$_{Er^+}$ | $E_{Er}$ (a.u.) | $E_{Er^+}$ (a.u.) | $E_I$  | $E_I$  |
|-------|-------------|---------------|-----------------|-------------------|-------|-------|
| $I_a$ | 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 -
Nonrelativistic HF [5] 4.677 4.621
Experiment [14] 6.108 6.022
Table III. 6s ionization energies of lanthanides (in eV).

| Z | Atom | HF   | CI   | 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

Table IV. Results of MCHF calculations of E_I with various relativistic corrections (in eV).

| Z | Atom | RHF [5] | CI_{Est} [5] | E_I | E_I \_E | E_I \_E | 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