Studies of Er ionization energy

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Abstract

This work is aimed at the multiconfigurational Hartree-Fock calculations of the Er ionization energy. Authors have used the ATSP MCHF version in which there are new codes for calculation of spin-angular parts written on the basis of the methodology Gaigalas, Rudzikas and Froese Fischer [4, 5], based on the second quantization in coupled tensorial form, the angular momentum theory in 3 spaces (orbital, spin and quasispin) and graphical technique of spin-angular integrations. They allow the study of configurations with open $f$-shells without any restrictions and lead to fairly accurate values of spectroscopic data.
1 INTRODUCTION

There is considerable interest in understanding the physics and chemistry of heavy atoms and ions. The main problem in investigation of such systems is their complexity, caused by the large number of electrons and the importance of relativistic effects. Therefore the detailed description of heavy atoms and ions requires the correct treatment of correlation effects as well as relativistic description of the system. The correlation effects in the theory of many-electron atoms are treated mainly by the two methods: configuration superposition (CI) and multiconfigurational Hartree-Fock (MCHF). Relativistic effects are usually included adding the relativistic corrections to the non-relativistic Hamiltonian (for example, the Breit-Pauli approximation), or using relativistic two component wave functions and relativistic Hamiltonian (for example, the Breit approximation) [1]. The complete and rigorous treatment of both relativistic and correlation effects for heavy atoms and ions is, unfortunately, practically outside of today’s computational possibilities.

Nevertheless, we expect that in case of Er relativistic effects as well as correlation effects between the electrons of ‘inner shells’ (core-core correlations) are the same for the neutral atom and ion. We assume that these effects (corresponding energies) cancel each other in calculation of ionization energy (IE). Only correlation between ‘outer’ (valence) electrons gives significant contribution to IE. And then it may be possible to get quite accurate values of ionization energies taking into account of them by MCHF approach.

This work is aimed at checking this assumption. For this purpose we perform MCHF calculations using the ATSP MCHF [2, 3] version in which there are new codes for calculation of spin-angular parts written on the basis of the methodology Gaigalas, Rudzikas and Froese Fischer [4, 5], based on the second quantization in coupled tensorial form, the angular momentum theory in 3 spaces (orbital, spin and quasispin) and graphical technique of spin-angular integrations. They allow the study of configurations with open f-shells without any restrictions.

2 APPROACH

Ionization energy we define as $IE = E_{ion} - E_g$, where $E_g$ and $E_{ion}$ are the ground state energies of neutral and singly ionized atom correspondingly. The ground state of neutral Er is

$$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^64f^{12}6s^2 \ 3H \equiv [Xe]4f^{12}6s^2 \ 3H \ (1)$$

and that of singly ionized Er

$$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^64f^{12}6s^1 \ 4H \equiv [Xe]4f^{12}6s^1 \ 4H. \ (2)$$

2.1 Hamiltonian

We calculate the ground state energies making use of the Hamiltonian
\[ \mathcal{H} = \mathcal{H}_{\text{NonRel}} + \mathcal{H}_{\text{RelCor}}, \]

where \( \mathcal{H}_{\text{NonRel}} \) is the usual non-relativistic Hamiltonian and \( \mathcal{H}_{\text{RelCor}} \) stands for relativistic corrections. In our calculations we separate relativistic corrections into following three parts:

\[ \mathcal{H}_{\text{RelCor}} = \mathcal{H}_{\text{Sh}} + \mathcal{H}_{\text{mp}} + \mathcal{H}_{\text{OO}} \]

with mass-polarization correction given by the Hamiltonian

\[ \mathcal{H}_{\text{mp}} = -\frac{1}{M} \sum_{i<j=1}^{N} \left( \mathbf{p}_i \cdot \mathbf{p}_j \right), \]

orbit–orbit term given by

\[ \mathcal{H}_{\text{OO}} = -\frac{\alpha^2}{2} \sum_{i<j=1}^{N} \left[ \frac{(\mathbf{p}_i \cdot \mathbf{p}_j)}{r_{ij}} + \frac{(r_{ij} (\mathbf{r}_{ij} \cdot \mathbf{p}_i) \mathbf{p}_j)}{r_{ij}^3} \right], \]

and the remaining part of relativistic corrections

\[ \mathcal{H}_{\text{Sh}} = \mathcal{H}_{\text{MC}} + \mathcal{H}_{\text{D1}} + \mathcal{H}_{\text{D2}} + \mathcal{H}_{\text{SSC}}, \]

consisting of the mass correction term

\[ \mathcal{H}_{\text{MC}} = -\frac{\alpha^2}{8} \sum_{i=1}^{N} \mathbf{p}_i^4, \]

as well as the contact interactions, described by the one– and two–body Darwin terms \( \mathcal{H}_{\text{D1}} \) and \( \mathcal{H}_{\text{D2}} \). They are

\[ \mathcal{H}_{\text{D1}} = \frac{Z \alpha^2 \pi}{2} \sum_{i=1}^{N} \delta (\mathbf{r}_i) \quad \text{and} \quad \mathcal{H}_{\text{D2}} = -\pi \alpha^2 \sum_{i<j=1}^{N} \delta (\mathbf{r}_{ij}). \]

The last addant in Eq. \( \text{[7]} \) stands for the spin–spin contact term

\[ \mathcal{H}_{\text{SSC}} = -\frac{8 \pi \alpha^2}{3} \sum_{i<j=1}^{N} (\mathbf{s}_i \cdot \mathbf{s}_j) \delta (\mathbf{r}_{ij}). \]

The corrections presented in Eq.\( \text{[8]} \) are (except mass polarization\( \text{[5]} \)) of the order of square of fine structure constant. They enable us to make a study of contribution of the main relativistic corrections to the calculations of ionization energy. Let us also mention that the Hamiltonian is presented in atomic units.
2.2 MCHF

For calculation of ionization energy we used MCHF method. In this approach, the wave function is expressed as a linear combination of configuration state functions (CSFs) which are antisymmetrized products of one-electron spin-orbitals. A set of orbitals, or 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]. No ‘relaxation’ effects were included.

3 RAS construction

Large scale systematic MCHF calculations of IE of lanthanides has not been done yet. Therefore, following the methodology of [2], it is important to investigate the structure of Er and Er\textsuperscript{+} 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 subshell 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 complexity of configurations of Er and Er\textsuperscript{+}, and our attempt is to take care of the correlation effects that do not cancel each other between ion and atom. Because we treat IE in non-relativistic approach, and in the neighbourhood of the ground level there are no levels with the same L, S, J values, methodics based on the consideration of energy spectra described in [2] could not be straightforward adapted to impose core and valence shells in our case.

Therefore in this chapter we will study some possibilities of RAS construction.

3.1 HF calculations

First insight into the structure of Er and Er\textsuperscript{+} ground states we can get from the Hartree-Fock (HF) calculations. The resultant ground state energies and mean distances of \( nl \) radial functions are presented in TABLE I.

Resultant energies are in agreement with those presented in [6]. The important note is that 6s function is much more remote from the nucleus than the ones of 5s, 5p and 4f. And the open 4f shell is closer to the nucleus than the 5s and 5p. 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 are included too [2]. For light atoms these shells are spatially ‘outer’.

3.2 CORE I

In this case we use the core
TABLE I. Results of HF calculations. Values of mean distance from the nucleus $<r>$ and energies of ground states (in a. u.)

| Function | $<r>_E$ | $<r>_E^+$ |
|----------|---------|-----------|
| 1s       | 0.022   | 0.022     |
| 2s       | 0.094   | 0.094     |
| 2p       | 0.080   | 0.080     |
| 3s       | 0.242   | 0.242     |
| 3p       | 0.232   | 0.232     |
| 3d       | 0.205   | 0.205     |
| 4s       | 0.545   | 0.545     |
| 4p       | 0.557   | 0.557     |
| 4d       | 0.588   | 0.588     |
| 5s       | 1.371   | 1.385     |
| 5p       | 1.563   | 1.565     |
| 4f       | 0.754   | 0.754     |
| 6s       | 4.630   | 4.093     |

Energy: -12498.1528 -12497.9809

$I = [Xe]^{1}S$

and the 4f, 6s we treat as valence shells. The 4f shell we treat as valence shell because it is open and 6s because the corresponding radial function in 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 CSF’s of 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:

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

(11)

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

(12)

Further on we denote the basis as core with subscript of destination set. For example, $I_a$ denotes the basis, consisting of CSF’s of 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 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 [7]. The mean distances of radial functions from the nucleus are found to be smaller than for 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, we treat as valence shell only 6s, 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 HF calculations mean distance of 4f radial functions is not much different for Er and Er+. As a 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:

(11) and (12) as for core I and three more

\[ c = b + \{7f, 7g, 7h, 7i, 8s, 8p, 8d\} , \] (13)

\[ d = c + \{8f, 8g, 8h, 8i, 8k, 9s, 9p, 9d\} , \] (14)

\[ e = d + \{9f, 9g, 9h, 9i, 9k, 9l, 10s, 10p, 10d\} . \] (15)

As we can see from TABLE II, the basis formed with the same destination sets is the biggest for the core I, the medium for core II and the smallest for core III.

The weights of main CSFs in MCHF expansions are about 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 HF calculations but smaller than obtained using bases with core I. For example, \(<r>_{6s} = 4.560 \text{ a.u. for } III_a, 4.564 \text{ a.u. for } III_{b,d,e}.

4 6s IONIZATION ENERGY

The results of MCHF calculations are presented in TABLE II.

For the bases obtained using II, III cores in non-relativistic approach, we get that increasing destination set the value of IE decreases until certain value (in our case 5.792 eV). This value should be considered as the result of ‘frozen core’ method. The result that for certain core using smaller (for example ’a’) destination set and correspondingly smaller basis we obtain the IE value closer to experimental one is treated by us as casual, because in smaller destination set (basis) we account for smaller part of valence correlations or (and) take into account it with different precision for Er and Er+. Adding the relativistic corrections raise the value of IE up to 5.877 eV. This value is fairly close to the experimental one 6.108 eV (the error is less than 4%).
TABLE II. Results of MCHF calculations. Numbers of CSFs (NCSF) and values of IE (in eV.)

| Basis | NCSF (Er) | NCSF (Er$^+$) | $IE_{NonRel}$ | $IE_{Rel}$ |
|-------|-----------|---------------|---------------|------------|
| I$_a$  | 2838      | 2769          | 5.563         | 5.739      |
| I$_b$  | 12811     | 12054         | 5.572         | 5.807      |
| II$_a$ | 236       | 8             | 5.895         | 6.640      |
| II$_c$ | 2600      | 23            | 5.793         | 5.877      |
| II$_d$ | 5565      | 32            | 5.793         | 5.874      |
| II$_e$ | 10347     | 43            | 5.792         | 5.877      |
| III$_a$ | 70        | 4             | 5.896         | 6.073      |
| III$_b$ | 272       | 7             | 5.796         | 5.856      |
| III$_c$ | 733       | 11            | 5.792         | 5.876      |
| III$_d$ | 1569      | 15            | 5.792         | 5.873      |
| III$_e$ | 2938      | 20            | 5.792         | 5.877      |

Non relativistic HF: 4.677 [7]
CI: 5.077 [7]
CI$_Q$ with Davidson Q correction: 5.250 [8]
Estimated: 5.58 [7]
Experiment: 6.108 [9]
Using core I the corresponding basis is 10 times larger than the one of II (or about 40 times larger than formed using core III). Nevertheless, the results obtained using these bases are much worse. For example, in non-relativistic approach IE value for the $I_b$ basis is 5.572 eV, whereas the corresponding value for the $I_b$ is 5.796 eV. It is due to the fact that basis formed using destination set 'b' for the core I is not enough to account for the correlation effects of 4$f$–electrons, which, represented in full, cancels between Er and Er$^+$. Relativistic corrections improve the value of IE, but it is still worse than those obtained using cores II, III. Of course, the results obtained using core I could be improved using larger bases (and should overtake the ones obtained using II, III cores), but at present it is unreachable because of our computational resources.

So, we recommend to use core III for the calculations of IE. In this case it is possible to get quite good value of IE taking into account VV (6$s$–6$s$) correlations only. The inclusion of CV$_4$f and CC$_4$f correlations requires much more computational resources and with the present ones doesn’t lead to the better result.

And finally, let us compare our results with the previous calculations of IE, where correlation effects were treated using CI method [7].

The authors used well-tempered Gaussian type functions (GTF’s) and augmented diffuse $p$-, $d$– and $f$–functions to describe the 6$s$–6$s$, 6$s$–4$f$ and 6$s$–5$d$ electron correlations as well as 8$g$ and 7$h$ to describe the angular correlation effects. The total number of GTF’s was (29$s$, 25$p$, 22$d$, 17$f$, 8$g$, 7$h$). Since authors could not perform full single- and single-double excitation configuration interaction (SDCI), important CSF’s were selected by performing the second order perturbation calculations, reducing number of CSF’s. They performed so-called natural orbital iterations to obtain compact CI expansions for the ground state as well as for the ionized state. The error of the correlation energies due to unselected CSF’s was estimated to be 0.001 a.u. and the error in the IE was estimated to be less than 0.05 eV. As one can see from the TABLE II, the result of CI calculation was 5.077 eV, and the one with Davidson correction [8] CI$_Q$ 5.250 eV. The result with estimated relativistic effects is 5.58 eV.

Comparing the results [7] with ours, (5.792 eV for non-relativistic value of IE), we can see that it is possible to obtain much better value of IE only accounting for the valence (6$s$–6$s$) correlation, whereas incomplete inclusion of correlation effects of inner shells just disimproves results.

5 CONCLUSION

For the calculations of Er ionization energy the most efficient strategy is to use the MCHF expansions with frozen core [Xe]$4f^{12}3H$ and single, double excitations from (6$s$). CV$_4$f and CC$_4$f correlations are not important in this case.

Our results on erbium are more accurate than data found using the Davidson $CI_{+Q}$ method [8] and adding the relativistic corrections [7].
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 by MCHF method accounting for correlation effects of outer electrons only. And this assumption takes place in the case of Er ionization energy.

The results demonstrate the ability of the approach by Gaigalas et al.\cite{4,5} to obtain fairly accurate data for heavy atoms and ions, having open $f$-shells.

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