

Energy level structure of the ground configuration in the Er^{3+} free ion

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Abstract. Energy levels of the ground configuration $[\text{Xe}]4f^{11}$ in the Er^{3+} ion are reported from relativistic configuration interaction calculations. Calculations are performed using the relativistic atomic structure package GRASP2K, which implements the multiconfiguration Dirac-Hartree-Fock method. The Breit transverse interaction and leading QED effects are included as perturbations. The final energies of 41 levels are compared with results from experiment and semi-empirical methods.

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1. Introduction

Er_2O_3 is a good candidate for blanket system in fusion reactors, because of its chemical and physical properties [1]. **However, even for free ions of Er^{3+} , spectroscopic data are available only for 12 lowest levels of ground state configuration.** Energy levels of free Er^{3+} were obtained by Carter from emission spectra of a high-current spark [2], however, most authors [3, 4, 5, 6] used semi-empirical methods. The idea of this work is to calculate all 41 levels of the $[Xe]4f^{11}$ ground configuration in Er^{3+} using an *ab initio* approach. In our previous work [7] the 12 lowest levels of the ground configuration were calculated. The good accuracy of these data (**the discrepancy with experiment is less than 6.9%**) encouraged us to compute higher levels using the previously described method for accounting for electron correlations effects. **Our results were obtained with the multiconfiguration Dirac-Hartree-Fock (MCDHF) and relativistic configuration interaction (RCI) [8] methods, using the GRASP2K (A General-Purpose Relativistic Atomic Structure Program) code [9].**

2. Computational procedure

The MCDHF method for computing energy levels has been reviewed by Grant [10], and here we just give a brief outline.

2.1. Multiconfiguration Dirac-Hartree-Fock

In this method wave functions of fine-structure states are approximated by atomic state functions. The atomic state functions (ASFs) are expanded in symmetry adapted configuration state functions (CSFs)

$$\Psi(K\gamma JM_J) = \sum_{K'\gamma'}^{N_{CSFs}} c_{K'\gamma'} \Phi(K'\gamma' JM_J). \quad (1)$$

In the expression above, J and M_J are the angular quantum numbers and γ' denotes a state of configuration K' . The K and γ are labels of the reference configuration and the reference state. The CSFs are anti-symmetrized and coupled products of one-electron Dirac orbitals. In the relativistic self-consistent field (RSCF) procedure both the radial parts of the Dirac orbitals and the expansion coefficients of the CSFs are optimized to self-consistency with respect to an energy functional built on the Dirac-Coulomb Hamiltonian

$$H_{DC} = \sum_{i=1}^N (c\alpha_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V_i^N) + \sum_{i>j}^N \frac{1}{r_{ij}}, \quad (2)$$

where V^N is the monopole part of the electron-nucleus Coulomb interaction. The transverse Breit interaction

$$\begin{aligned}
H_{\text{Breit}} &= - \sum_{i < j}^N \left[\alpha_i \cdot \alpha_j \frac{\cos(\omega_{ij} r_{ij}/c)}{r_{ij}} \right. \\
&\quad \left. + (\alpha_i \cdot \nabla_i) (\alpha_j \cdot \nabla_j) \frac{\cos(\omega_{ij} r_{ij}/c) - 1}{\omega_{ij}^2 r_{ij}/c^2} \right] \quad (3)
\end{aligned}$$

as well as leading QED corrections, vacuum polarization and self-energy, can be included
in subsequent RCI calculations [11], where now only the expansion coefficients are
optimized. Calculations can be done for single states, but also for portions of a spectrum
in the extended optimal level (EOL) scheme, where optimization is on a weighted sum
of energies. Using the latter scheme a balanced description of a number of fine-structure
states belonging to one or more configurations can be obtained in a single calculation.
All calculations were performed with GRASP2K [9] in which for calculations of spin-
angular parts of matrix elements the second quantization method in coupled tensorial
form and the quasispin technique [12] were adopted.

In relativistic calculations the ASFs are given in jj -coupling. To adhere to the
labeling conventions used by the experimentalists, the ASFs are transformed from jj -
coupling to LS -coupling using the methods developed in [13, 14].

2.2. Configuration interaction strength

The selection of the configurations and the corresponding CSFs that enter the
calculations is a crucial step in multiconfiguration methods. The method of analyzing
configuration interaction strength (CIS) [15, 16] has been employed to find the most
important admixed configurations for the considered ground configuration of Er^{3+} . The
same approach has been successfully applied for the investigation of Auger cascades
[17, 18, 19], electric dipole [20] and magnetic dipole [21, 22] transitions.

The CIS:

$$T(K, K') = \frac{\sum_{\gamma\gamma'} \langle \Phi(K\gamma) | H | \Phi(K'\gamma') \rangle^2}{\bar{E}(K, K')^2}, \quad (4)$$

divided by the statistical weight $g(K)$ of the studied configuration K ($[Xe]4f^{11}$) has the
meaning of the average weight of the admixed configuration K' in the expansion of the
wave functions for K . The larger the $T(K, K')/g(K)$ value, the larger the influence of the
admixed configuration K' to the energy levels of the considered $[Xe]4f^{11}$ configuration.
The summation in (4) is performed over all states γ and γ' of the configurations
 K and K' , respectively. The list of the admixed configurations is built by taking
into account single and double excitations from the $[Xe]4f^{11}$ configuration. A single-
configuration pseudorelativistic method [23] is then applied to obtain radial orbitals
for the corresponding configurations and $\langle \Phi(K\gamma) | H | \Phi(K'\gamma') \rangle$ is the interconfiguration

63 matrix element of the pseudorelativistic Hartree-Fock Hamiltonian H [23]. $\bar{E}(K, K')$ is
 64 the average energy distance between the configurations:

$$\begin{aligned} \bar{E}(K, K') &= \frac{1}{\sum_{\gamma\gamma'} \langle \Phi(K\gamma) | H | \Phi(K'\gamma') \rangle^2} \\ &\times \sum_{\gamma\gamma'} [\langle \Phi(K\gamma) | H | \Phi(K\gamma) \rangle - \langle \Phi(K'\gamma') | H | \Phi(K'\gamma') \rangle] \\ &\times \langle \Phi(K\gamma) | H | \Phi(K'\gamma') \rangle^2. \end{aligned} \tag{5}$$

65 3. Calculations

66 In this work calculations were done by configuration, i.e. wave functions for all states
 67 belonging to the ground configuration were determined simultaneously in an EOL
 68 calculation. The energy functional, on which the orbitals were optimized, was the
 69 weighted energy average of the two lowest states of $[Xe]4f^{11}$ with $J=1/2$, the six lowest
 70 states with $J=3/2$, the seven lowest states with, respectively, $J=5/2$, $7/2$, $9/2$, the
 71 five lowest states with $J=11/2$, the three lowest states with $J=13/2$, three lowest with
 72 $J=15/2$, and finally the lowest state with $J=17/2$.

73 Two sets of calculations were performed using different strategies for selecting the
 74 CSFs. In the first strategy, called the **SD C+V+CV** strategy, the CSFs were generated
 75 by single (S) excitations from the core (C) shells with $n = 3..5$ and from the valence
 76 (V) shell $4f$ of the reference configuration to orbitals in active sets up to principal
 77 quantum numbers $n = 6$ and angular symmetries $s..h$. Double (D) excitations were
 78 restricted in such a way, that one excitation would be from the core and another from
 79 the valence shell (CV) **more details can be found in [7, 27]**. The radial orbitals
 80 were calculated using smaller active sets generated with only S excitation. In the second
 81 strategy, based on the analysis of CIS, 3461 configurations were generated by including
 82 all SD excitations from the core shells with $n = 3..5$ and from the valence shell $4f$
 83 of the ground configuration to virtual orbitals with principal quantum numbers up to
 84 $n = 7$ and with angular symmetries $l = s..g$. The configuration list included all type
 85 of correlations: valence, core, valence-valence, core-core, core-valence. In the second
 86 step a ranking of the configurations was done based on the CIS parameter. Guided by
 87 previous work [7] only configuration with $T(K, K')/g(K)$ larger than 4.293×10^{-6} were
 88 retained, leading to 183 configurations. These configurations were then used for the
 89 final calculations.

90 4. Results and evaluation of data

91 Table 1 compares computed energy levels with results from other theories and
 92 experiment. Levels are notated in the form $(^{2S+1})L_J^{Nr}$ where, instead of the group labels

Table 1. Comparison of calculated (Th.^a and Th.^b) energy levels with values from semi-empirical methods and experiment (Exp). Contributions of the Dirac-Coulomb (DC), BREIT, and QED interactions to the energy (in cm^{-1}) are presented. All energies are relative to the ground state.

LSJ	Th. ^a	Th. ^b			Semi-empirical				Exp. NIST		
	Total	DC	BREIT	QED	Total	[3]	[4]	[6]	[5]	[2]	[28]
$4I_{15/2}^1$ *	0	0	0	0	0	0	0	0	0	0	0
$4I_{13/2}^1$ *	6311	6646	-281	4	6369	6540	6502	6405	6511	6485	6480
$4I_{11/2}^1$ *	10165	10317	-254	5	10067	10123	10125	10022	10043	10123	10110
$4I_{9/2}^1$ *	12841	12612	-83	4	12534	12328	12340	12241	12003	12345	12350
$4F_{9/2}^1$ *	16425	16137	70	1	16209	15266	15181	15076	14913	15182	15180
$4S_{3/2}^1$ *	20089	19121	301	0	19423	18433	18427	18320	18018	18299	18290
$2H_{11/2}^2$ *	20748	20140	-68	2	20075	19166	19284	19175	18851	19010	
$4F_{7/2}^1$ *	21835	21841	-41	3	21803	20524	20327	20123	20034	20494	20400
$4F_{5/2}^1$ *	23647	23579	9	3	23591	22065	21990	21870	21713	22181	22070
$4F_{3/2}^1$ *	24074	23692	85	3	23780	22477	22344	22227	21978	22453	22410
$2G_{9/2}^1$ *	25987	25490	-321	6	25174	24539	24537	24322	23874	24475	
$4G_{11/2}^1$ *	28291	28487	-238	3	28252	26615	26447	26327	25929	26376	
$4G_{9/2}^1$	29369	29527	-37	3	29493	27663	27431	27305			
$2K_{15/2}^1$	29713	29657	-160	4	29501	27041	27293	27176			
$2G_{7/2}^1$	30255	30404	-321	2	30085		27994	27877			
$2P_{3/2}^1$	33797	32952	-121	5	32836		31605	31477			
$2K_{13/2}^1$	34993	34557	51	3	34611		32521	32392			
$4G_{5/2}^1$	35584	35878	-517	5	35366		33315	33178			
$2P_{1/2}^1$	35829	36018	-229	7	35796			33336			
$4G_{7/2}^1$	35959	36218	-374	5	35849	28110	33918	33783			
$2D_{5/2}^1$	37550	36920	-150	5	36775		34794	34641			
$2H_{9/2}^2$	37974	37970	-875	10	37105		36408	36268			
$4D_{5/2}^1$	42247	41741	256	0	41997		38649	38526			
$4D_{7/2}^1$	43125	43375	175	1	43551		39205	39067			
$2I_{11/2}^1$	44363	44323	-532	9	43799		40309	40164			
$2L_{17/2}^1$	44686	45413	-107	1	45307		40664	40508			
$2D_{3/2}^1$	44985	46618	-1	3	46619		42199	42802			
$4D_{3/2}^1$	46361	47489	-531	2	46961		42946	42044			
$2I_{13/2}^1$	46509	47931	-531	4	47404		42947	42797			
$4D_{1/2}^1$	50552	51541	-343	6	51204			46808			
$2L_{15/2}^1$	50695	52999	-222	3	52780		46836	46667			
$2H_{9/2}^1$	51680	53002	-199	5	52807			46989			
$2D_{5/2}^2$	52987	53685	-798	6	52892			48873			
$2H_{11/2}^1$	54438	56141	-626	6	55521			50061			
$2D_{3/2}^2$	58851	58335	-86	3	58252			54910			
$2F_{7/2}^2$	60100	59478	-633	9	58854			55055			
$2F_{5/2}^2$	68234	67812	-602	9	67218			62909			
$2G_{7/2}^2$	72071	73630	48	0	73679			64688			
$2G_{9/2}^2$	75942	77955	-392	3	77566			68765			
$2F_{5/2}^1$	103064	101651	139	0	101789			93134			
$2F_{7/2}^1$	107321	107053	-237	3	106819			96726			

^a SD C+V+CV strategy

^b CIS strategy

93 νWU , single character "numbers" Nr are used [26]. Previous work [7] showed that LS -
 94 coupling is more preferable for labeling than jj -coupling for the ground configuration.
 95 Labels for ASFs usually are assigned as the label of the CSF making the largest
 96 contribution to the composition but such labels may not be unique. An algorithm
 97 that has been proposed for assigning unique labels [29] starts with a set of, say m ASFs
 98 of the same J and the m CSFs with large expansion coefficients. Of the CFSs in the set
 99 the one with the largest expansion coefficient of all m ASFs defines label of the ASF in
 100 which it occurs. The labeled ASF and the associated CSF are eliminated from further
 101 consideration. Each assignment gives the CSFs with the largest expansion coefficient
 102 to an ASF as the label. In this scheme, the last remaining label may be based on a
 103 contribution that is not the largest.

104 The levels we identify with ${}^2G_{9/2}^1$ (composition: 18% + 23% ${}^2H^2$ + 21% ${}^4F^1$ +
 105 15% ${}^2G^2$ + 11% ${}^4I^1$) and ${}^4G_{9/2}^1$ (80 + 12% ${}^2H^2$) were originally identified in [3, 4, 5] with
 106 ${}^2H_{9/2}$ and ${}^2G_{9/2}$ respectively. In a similar way the level we identify as ${}^2H_{9/2}^2$ (composition:
 107 31% + 24% ${}^2G^1$ + 16% ${}^2G^2$ + 14% ${}^4G^1$) was originally identified with ${}^4G_{9/2}$ in paper [4].
 108 Our identifications agree with semi-empirical results of Weber [6].

109 The SD C+V+CV strategy calculations (see column 'Th.^a') give the positions of
 110 the first three levels in agreement with experiment. For the higher levels the agreement
 111 is less satisfactory. For calculations performed using the CIS strategy (see column 'Th.^b')
 112 contributions to the excitation energy arising from different parts of the Hamiltonian
 113 are presented separately. **Theoretical energy values for 12 lowest levels (from**
 114 **to ${}^4I_{15/2}^1$ to ${}^4G_{11/2}^1$) marked by "*" are given by [7].** Using the CIS strategy
 115 improves the agreement of energy levels with up to 2.6%. As expected, the Dirac-
 116 Coulomb contribution is the largest, with the transverse photon (Breit) interaction
 117 giving a significant correction. The vacuum polarization and self-energy corrections
 118 (QED) are less important.

119 Experimental data for centers of gravity of Stark manifolds were obtained by
 120 measuring Stark levels of the Er^{3+} absorption spectrum in LaF_3 [3]. In the paper
 121 [4] the authors have extended the measured absorption spectrum in the same crystal
 122 into the ultraviolet region up to 2000 Å. With the help of small variations of parameters
 123 (F_2 , F_4 , F_6 and ζ), originally described by Wybourne [30], the free ion spectrum [3, 4]
 124 was determined from the experimental centers of gravity data. The eigenstates and
 125 the corresponding energy levels [6] were found (in LSJ coupling) by diagonalizing
 126 the interaction matrix defined by the spin-orbit and electrostatic energies. The spin-
 127 orbit parameter ζ and the Racah parameters E^1 , E^2 , E^3 were determined in a fitting
 128 procedure in which centers of gravity were taken from [3] and [4]. Semi-empirical data for
 129 the spectrum in [5] were evaluated by measuring the Er^{3+} center of gravity in $ZnGa_2O_4$.
 130 Experimental data of free ion Er^{3+} were obtained by Carter [2] from emission spectra
 131 of a high-current spark. Energy levels recommended by NIST (National Institute of
 132 Standards and Technology) [28] were derived from the spectrum of Er^{3+} in LaF_3 crystal.
 133 In the last column of the tables the energies from NIST [28] are given. Comparing with
 134 NIST our energy levels agrees to within 9.8% for the **SD C+V+CV** strategy and

135 better than 6.9% for the CIS strategy. It should be noted that order of levels agree with
136 the one given in the NIST database.

137 5. Conclusions

138 The MCDHF and RCI methods were used to compute the energy spectrum of the
139 $[Xe]4f^{11}$ configuration in Er^{3+} . Comparing with NIST recommended values we see that
140 our *ab initio* calculations for the energy spectrum agrees to within 9.8 % for the free
141 ion in the **SD C+V+CV** strategy and better than 6.9% in the CIS calculations. Our
142 identification of the levels fully agree with the one in the NIST [28] database and as well
143 as with the one from semi-empirical data [6].

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