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Parametric study of hyperfine structure of Zr II even-parity levels

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Abstract:

Up to now experimental hyperfine structure (hfs) data of twelve even-parity Zr II levels were given in literature. Recently new hyperfine splitting measurements of eleven other Zr II levels, of the same parity are achieved, applying fast-ion-beam laser-fluorescence spectroscopy. The hfs of these 23 gathered levels has been analysed by simultaneous parametrisation of the one-and two-body interactions, first in model space $(4d + 5s)^3$ and secondly in extended one. For the three lowest configurations, radial parameters of the magnetic dipole A and quadrupole electric B factors are deduced in their entirety for $^{91}\text{ZrII}$, compared and discussed with calculated values, available in literature and also with ours, computed by means of ab-initio method. For instance we give the main experimental values of the extracted single-electron hfs parameters of $4d^25s$: $a_{5s}^{10} = -2701$ MHz, $a_{4d}^{01} = -122.4$ MHz and $b_{4d}^{02} = -113.5$ MHz.

Keywords : Fine Structure, Hyperfine Structure, Landé-factors, Zr II spectrum and Ab-initio calculations.

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1.Introduction.

The ZrII hyperfine splitting has been measured by Young et al. [1] and analysed theoretically by Beck and Datta[2] and by us[3]. We have to add furthermore that with help of on-line laser spectroscopy at the IGISOL facility in Jyväskylä the ionic ground state was studied by Thayer et al. [4]. Young et al., using the laser-rf double-resonance technics measured hyperfine splitting of ZrII levels arising exclusively from the metastable $4d^3$ and $4d^25s$ configurations. For the first time hfs constants of the two only existing states of $4d5s^2$ and also those of other new two lowest configuration levels are measured [5]. The complete details of the experiments are given for instance in [6].

We plan to extend in near future these experimental data to other ions of transition elements with an open d- and p-shells, like Moll for instance and to analyse their systems using a semi-empirical parameterisation method. Some hfs parameters of transition elements for d- and p-shells are poorly evaluated up to now and it is interesting first to repertory their general trends. The big problem concerns mainly s-electron behaviour seeing its contribution to hfs A factor. What is exactly contact-electron impact and what is its real interaction with nucleus? by what is it influenced when penetrating into the nucleus?

2. Hfs considerations.

Table 1 presents gathered experimental hfs data and for comparison we inserted computed hfs A and B factor values, done for angular momentum $J=1/2$ and $J=3/2$ by Beck and Datta [2] and also ours. We have two possibilities for semi-empirical analysis of the twenty three experimental data of table1, all concerning the three lowest configuration levels. The latter are close each others in energy and quite well isolated from the other configuration ones. For this reason it is better to study at first the model space $(4d + 5s)^3$ and in the second step the extended model. Furthermore the model space generally

permits to extract more accurate many-body parameter values.

For our hfs analysis we follow the many-body parameterisation method [7] which allows taking advantage of similarities between configuration interaction effects observed independently in spin-orbit and hyperfine splitting. The radial parameters $a_{nl}^{\kappa\kappa}$, $b_{nl}^{\kappa\kappa}$, α_i and β_i have been evaluated by fitting them to experimentally determined hfs constants A and B using the theoretical expressions (equations 4 and 5 of [8]).

The values of single-electron parameters, extracted by least square fitting procedure, quoted with their uncertainties, are presented in Table 2.

Usually these parameters are discussed for each configuration separately while in Table 2 some parameters are common to all configurations. The corresponding parameters for each configuration (Table 3) can be deduced from the model space parameters using:

$$a_{nl}^{\kappa\kappa} (I^{N+M} s^{2-M}) = a_{nl}^{\kappa\kappa} + [2/(I+1)][1-(N+M)]\alpha_1 - [2/(I+1)]^{1/2}(2-M)\alpha_4 + [2/(I+1)]\alpha_5\delta(M,0)$$

for $\kappa\kappa = 01, 12$. In the case of $\kappa\kappa = 10$ one reads:

$$a_{nl}^{10} (I^N s^2) = a_{nl}^{10}$$

$$a_{nl}^{10} (I^{N+1} s) = a_{nl}^{10} - [2/(I+1)]\alpha_9$$

$$a_{nl}^{10} (I^{N+2}) = a_{nl}^{10} + [2/(I+1)][\alpha_{10} - \alpha_9]$$

Here $N=1$ and $M=0, 1, 2$. The values of α_i are given in Table 2.

For our hfs analysis we had recourse also to extended model, composed from $4d5s^2$, $4d^25s$, $4d^3$, $4d^26s$ and $4d^25d$. The fs study was feasible except for experimental $4d^25d$ levels, given in literature, since some of them are really questionable.

For hfs analysis, model space and extended model display very close single-electron parameter values, but more accurate by means of model space, as expected. For this reason in Table 1 are reported only computed hfs constants obtained by this way. We give those obtained with the second path only in supplementary Table (Table S1) in order to insert hfs A and B of some $4d^26s$ levels.

As in the case of odd-parity ZrII levels for configuration with open s-shell, i.e. $4d5s5p$, one parameter value is huge comparatively to other ones: a_{5s}^{10} ($4d^25s$). So our first reflex is to check its validity. One can note a fact that calculated ratio a_{5s}^{10}/g_i is in good interval in Table 4.

Let us try now to evaluate monoelectronic parameters for s- and d-electrons involved in this study:

$$\text{for } 5s\text{-electron } a_{5s}^{10} = 63.6145 g_i \langle r^{-3} \rangle_{5s}^{10} \quad (1)$$

$$= 63.6145 g_i 4\pi |\psi(0)|^2. \quad (1 \text{ twice})$$

$$\text{with } g_i = \mu_i / I = 1.30362 / 2.5 = 0.521448.$$

and for 4d-electrons we have:

$$a_{nl}^{\kappa\kappa} = 2\mu_0\mu_B\mu_i (\zeta_{\text{exp}}/\zeta_{\text{ab-initio}}) \langle r^{-3} \rangle_{nl}^{\kappa\kappa} / 4\pi I = 95.4128 g_i (\zeta_{\text{exp}}/\zeta_{\text{ab-initio}}) \langle r^{-3} \rangle_{nl}^{\kappa\kappa} \quad (2)$$

with $\kappa\kappa = 01, 12, 10$

$$b_{nl}^{\kappa\kappa} = \frac{e^2}{h} Q (\zeta_{\text{exp}}/\zeta_{\text{ab-initio}}) \langle r^{-3} \rangle_{nl}^{\kappa\kappa} = 234.9624 Q (\zeta_{\text{exp}}/\zeta_{\text{ab-initio}}) \langle r^{-3} \rangle_{nl}^{\kappa\kappa} \quad (3)$$

with $\kappa\kappa = 02, 13, 11$ and $Q = -0.206$ barn

ζ_{exp} and $\zeta_{\text{ab-initio}}$ represent respectively spin-orbit constant values obtained experimentally and computed through ab-initio method [9]. We introduced the ratio $\zeta_{\text{exp}}/\zeta_{\text{ab-initio}}$ in order to weight expectation values found in many-body parameter relations. These corrections are very useful to get good agreements when p-electrons are particularly involved since $\zeta_{\text{exp}}/\zeta_{\text{ab-initio}} =$ around 1.4 generally. For d-electrons the impact of its introduction in (2) and (3) is less determinant since this ratio is around 0.92 (average value). In present study we will omit to use this ratio because we want to compare our data with those given in literature where this weight is not taken into account: multireference relativistic configuration-interaction [2] and relativistic self-consistent-field calculations of the radial hyperfine integrals. The latter were done by Jonas R. Persson[10], using relativistic wavefunction of Hartree-Fock type and wavefunctions obtained by the so-called Optimised Hartree-Fock-Slater method [11].

We summarised in Table 5 expectation values obtained By Persson and those we obtained using pseudo-relativistic Hartree-Fock method [9]. Unfortunately we cannot use directly relation (1 twice) and $4\pi|\psi(0)|^2$ value given in Table 5 of [3] because we need to scale the latter by a factor determined through experimental data of isotope shift [12].

We compare our extracted single-electron parameter values of Table 6 with those computed with aid of equations (1-3), through different ways. On the whole we have observed a good agreement between our extracted single-electron parameter values and those deduced from relativistic Hartree-Fock[10] or from our pseudo relativistic Hartree-Fock expectation values. Those computed from optimised Hartree-Fock seem overestimated.

Moreover we have noted previously that our extracted parameter a_{4d}^{12} values for Nb II, Mo II and Ta II are smaller than a_{4d}^{01} . This trend is confirmed in present work, in total opposition with ab-initio calculations of Persson for a set of singly ionized atoms and those of Olsson and Rosen for a set of neutral atoms where systematically a_{4d}^{12} values are bigger than a_{4d}^{01} values. Dembczynski et al have confirmed our data trends when studying La II [13]. Let us indicate also that comparatively to experimental values contact- electron-d parameter a_{4d}^{10} values are really under evaluated for the three configurations with ab-initio method even if a_{4d}^{10} stands, in Table 5, only for relativistic effects, neglecting core polarisation contributions. In this latter Table a_{5s}^{10} represent too only relativistic participation. So we have to add core polarisation contribution. For Zr I we have evaluated this contribution to 8.6%. [14]. Once again, as for d-electrons, the method which gives good agreement between experimental and calculated a_{5s}^{10} (when multiplying values given in Table 5 by a 1.086 factor) is Hartree-Fock one. The value obtained, using OHFS method seems on the other hand overestimated.

If we compare experimental A and B hfs constants given in Table 1 with those we computed, the agreement is excellent: we have only to point out that for level $^2F_{7/2}$ of $4d^25s$, whose energy is: 6467.61 cm^{-1} hfs constants A should be positive while B should be negative. On the other hand this comparison of experimental hfs data with those computed by Beck et al. [2], recurring to relativistic configuration-interaction approach is rather mitigated as in the cases of Ti II and Hf II. The methodology proposed by Beck consists in generating wave functions from Dirac-Coulomb Hamiltonian to which it is possible to insert Breit contribution, considered as a perturbation. Furthermore multiconfigurational Dirac-Fock solutions, extracted with help of Desclaux code [16] are used as zeroth-order functions.

3.Conclusion.

In this work we have taken advantage of new hfs measurements, very accurate, concerning for the first time $4d5s^2$ configuration levels. All these experimental values are confirmed perfectly by our parametric calculations which are different from those given by Beck and Datta using three methods: Configuration Interaction (CI), Dirac-Fock (DF) i.e. Relativistic Hartree-Fock and multiconfiguration

relativistic configuration interaction (MRCI). This latter study is really courageous even if some clarifications are expected: Zr is considered as a light element. Do these codes, used in this study, give converging data also for high atomic numbers involving heavy elements? Why this study is limited only to two cases: $J = 1/2$ and $J = 3/2$? This work was extended [15] to Zr II Isoelectronic sequences: Hf II, Nb III, Ta III, Mo IV, W IV and La I. He showed that when using Dirac-Fock calculations one has to take into account both correlation and relativistic effects; otherwise calculated hfs constants may have wrong signs.

With more experimental data we have refined our previous parameter values given in [3] and generated predicted A and B hfs constant values for all known levels, inviting experimenters to extend the few existing measurements and hopefully to confirm our calculations.

Appendix A: supplementary data

The complete table of A and B hfs values sorted by angular momentum J and increasing energy levels is presented in supplementary data associated with this paper.

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Table Captions

Table 1: Comparison between experimental and calculated hfs constants A (MHz) and B (MHz) of Zr II

Table 2: Fitted hfs parameter values (MHz) for the model space $(4d + 5s)^3$ given with their standard deviations in parentheses.

Table 3: Fitted hfs parameter values (MHz) for each configuration under study.

Table 4: Variation of a_{ns}^{10}/g_l versus atomic number Z for some singly ionized atoms.

Table 5: Expectation radial integral values (a.u.) computed through different methods

Table 6: Comparison between extracted experimental hfs many-body parameter values (S.E.) and those computed by means of different methods.

	Energy level cm ⁻¹	Aexp [1,4,5] MHz	Error MHz	Acal MHz P.W.	Acal MHz [2]	method
J= 1/2						
	9553.100	459.7553	0.0015	459.24	337.50 98.20 337.55	C.I. D.F. MRCI
	19613.529	-228.7427	0.0040	-224.68	-143.70 -7.90 -150.84	C.I. D.F. MRCI
	25201.570			-3003.44	-2690.31	
J= 3/2						
	0.000	333.3000	0.3000	336.34	273.80	
	2572.210			-274.82	-298.00	
	4248.300	199.2498	0.0020	176.60	190.30 375.10 181.50	C.I. D.F. MRCI
	6111.700	104.91	0.44	111.14	134.30	
	7736.020			-598.84	-534.60	
	9742.800	110.1774	0.0008	109.39	134.00 -56.40 134.10	C.I. D.F. MRCI
	13428.500	10.96	0.88	11.25	-66.80	
	14298.640	-147.20	0.43	-155.00	-114.70	
	20080.301	109.7678	0.0015	111.61	111.50 -76.00 110.30	C.I. D.F. MRCI
	27699.961			-185.74	-190.00	
J= 5/2						
	4505.500	-421.2272	0.0009	-411.86		
	5752.920	-272.6092	0.0006	-269.55		
	9968.650	97.7726	0.0003	92.88		
	14162.900	-312.09	0.54	-344.43		
	14733.370	-63.70	0.98	-54.53		
	19514.840	-139.04	0.46	-141.61		
J= 7/2						
	6467.610	94.5892	0.0004	90.75		
	7837.740	-29.4056	0.0004	-31.13		
	14059.790	86.19	0.47	97.34		
	19433.240	-62.97	0.51	-55.42		
J= 9/2						
	8152.800	-196.1072	0.0004	-198.58		
	11984.460	-145.73	0.92	-143.03		
	14190.450	-291.39	0.81	-306.58		
J= 11/2						
	12359.460	-75.20	8.20	-74.81		

P.W.: present work C.I.: configuration interaction MRCI: Multiconfiguration relativistic cor

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Bexp [1,4,5] MHz	Error MHz	Bcal MHz P.W.	Bcal MHz [2]	method
		0.00		
		0.00		
		0.00		
-14.700	0.800	-14.72	-12.46	
		14.46	11.8	
7.706	0.008	9.99	5.93	C.I.
			17.26	D.F.
			5.82	MRCI
26.600	2.600	18.89	27.23	
		-35.83	-32.86	
34.713	0.003	31.65	27.46	C.I.
			32.18	D.F.
			27.46	MRCI
-32.800	4.600	-31.55	-34.01	
26.500	4.500	19.13	17.08	
33.716	0.007	28.68	28.51	C.I.
			6.98	D.F.
			28.3	MRCI
		-49.28	-46.14	
8.195	0.011	8.92		
-31.307	0.007	-25.35		
-42.969	0.004	-38.95		
-38.000	5.600	-44.60		
34.000	20.000	21.61		
-51.500	3.700	-28.35		
-39.878		-31.75		
-60.181	0.007	-48.44		
-126.700	7.300	-91.65		
-47.300	6.300	-27.64		
-70.336	0.009	-55.27		
-59.000	20.000	-79.65		
-79.000	15.000	-93.77		
		-85.52		

figuration interaction D.F.: Dirac-Fock

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Table 2

hfs parameter	Value (MHz)
a_{5s}^{10}	-2701.6 ± 82.4
a_{4d}^{01}	-139.7 ± 4.6
a_{4d}^{12}	-118.3 ± 7.6
a_{4d}^{10}	73.1 ± 3.2
a_{1C}^{12}	-54.4 ± 0.4
α_1	-43.3 ± 7.9
α_2	-8.4 ± 1.5
α_3	-5.6 ± 1.0
α_9	-372.0 ± 2.9
α_{11}	-1402.2 ± 10.9
$\alpha_4 = \alpha_5 = \alpha_6 = \alpha_7 = \alpha_8 = \alpha_{10}$	0.00 (fixed)

Table 3

Config.	a_{4d}^{01} (MHz)	a_{4d}^{12} (MHz)	a_{4d}^{10} (MHz)	a_{5s}^{10} (MHz)
4d5s ²	-139.73	-118.29	73.07	
4d ² 5s	-122.41	-103.63	221.8	-2701.64
4d ³	-105.08	-88.96	221.8	

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Table 4

Ion	Configuration	a_{ns}^{10}/g_I (MHz/ μ_N)	Z
Sc II [17]	$3d^1 4s$	2457.23	20
Ti II [18]	$3d^2 4s$	2649.92	21
V II [19]	$3d^3 4s$	3072.58	22
Zr II	$4d^2 5s$	5179.8	39
Nb II [20]	$4d^3 5s$	5952.20	40
Mo II [21]	$4d^4 5s$	6321.93	41
Ta II [22]	$5d^3 6s$	18387.08	72

Table 5

Config.	method	$\langle r^{-3} \rangle_{4d}^{01}$	$\langle r^{-3} \rangle_{4d}^{12}$	$\langle r^{-3} \rangle_{4d}^{10}$	$\langle r^{-3} \rangle_{5s}^{10}$	$\langle r^{-3} \rangle_{4d}^{02}$	$\langle r^{-3} \rangle_{4d}^{13}$	$\langle r^{-3} \rangle_{4d}^{11}$
4d ² 5s	HFR (PW)	2.457				2.457		
	HF [10]	2.442	2.589	-0.066	70.79	2.454	0.311	-0.115
	OHFS[10]	2.588	2.741	-0.068	81.93	2.602	0.329	-0.120
4d ³	HFR (PW)	2.146				2.146		
	HF [10]	2.117	2.251	-0.060		2.127	0.277	-0.104
	OHFS[10]	2.195	2.343	-0.067		2.206	0.301	-0.114
4d5s ²	HFR (PW)	2.788				2.788		
	HF [10]	2.782	2.945	-0.073		2.796	0.349	-0.113
	OHFS[10]	3.014	3.172	-0.070		2.303	0.358	-0.124

PW : present work

Table 6

Config.	a_{4d}^{01} S.E.	a_{4d}^{01} HFR	a_{4d}^{01} HF	a_{4d}^{01} OHFS	a_{4d}^{12} S.E.	a_{4d}^{12} HF	a_{4d}^{12} OHFS
$4d^25s$	-118.9	-122.24	-121.97	-128.76	-103.63	-128.81	-136.37
$4d^3$	-103.8	-106.77	-105.33	-109.21	-88.96	-111.99	-116.57
$4d5s^2$	-139.9	-138.71	-138.41	-149.95	-118.29	-146.52	-157.82

Config.	a_{4d}^{10} S.E.	a_{4d}^{10} HF	a_{4d}^{10} OHFS	a_{5s}^{10} S.E.	a_{5s}^{10} HF	a_{5s}^{10} OHFS
$4d^25s$	221.8	3.28	3.38	-2701.64	-2348.22	-2717.75
$4d^3$	221.8	2.98	3.33			
$4d5s^2$	73.07	3.63	3.48			

Config.	b_{4d}^{02} S.E.	b_{4d}^{02} HFR	b_{4d}^{02} HF	b_{4d}^{02} OHFS	b_{4d}^{13} S.E.	b_{4d}^{13} HF	b_{4d}^{13} OHFS
$4d^25s$	-113.50	-118.9	-118.77	-125.94	-17.82	-15.05	-15.92
$4d^3$	-99.01	-103.9	-102.95	-106.77	-15.66	-13.40	-14.57
$4d5s^2$	-125.99	-135.0	-135.33	-159.87	-20.43	-16.89	-17.33

Config.	b_{4d}^{11} S.E.	b_{4d}^{11} HF	b_{4d}^{11} OHFS
$4d^25s$	5.11	5.56	5.8
$4d^3$	4.43	5.03	5.52
$4d5s^2$	5.67	5.45	6.00

S.E. : semi-empirical (experimental)

HF : relativistic Hartree-Fock

OHFS : optimized Hartree-Fock Slater

HFR : pseudo relativistic Hartree-Fock