

# Isoelectronic Predictions for Ground State $^2P$ Fine Structures Using the Extended Regular Doublet Law

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## Abstract

Screening parametrisations are used to study the fine structure separations of the  $ns^2np$   $^2P$  ground state terms in the Al, Ga, In and Tl isoelectronic sequences, and of the  $ns^2np^5$   $^2P$  ground state terms in the Cl, Br, I and At isoelectronic sequences. Isoelectronic and homologous regularities are exhibited which permit extrapolative predictions of these separations to high states of ionisation.

## 1. Introduction

Isoelectronic sequences which have ground states of the form  $ns^2np$   $^2P$  and  $ns^2np^5$   $^2P$  are useful in plasma diagnostics, since magnetic dipole transitions between the fine structure levels of these multiplets can become strong for high stages of ionisation. Earlier we have used the semiempirical extended regular doublet law to make accurate extrapolations of these transition energies for the  $n = 2$  B and F sequences [1]. Studies of this type were made for the homologous  $n = 3$  splittings in the Al and Cl sequences by Smitt et al. [2] in 1976, but recent Tokamak measurements [3, 4] have yielded wavelengths of a number of very highly ionised members of these sequences which motivate their reexamination. Studies of the screening parameters of all such sequences ( $n = 2-6$ ) were made already in 1964 by Edlén [5], which revealed homologous regularities that could be exploited to improve the reliability of the isoelectronic descriptions. Additional measurements in many of these sequences have subsequently become available, so we have sought to update these studies (the parametrisation of the  $n = 5$  iodine sequence was updated by Epstein and Reader [6] in 1976). As an aid to the identification of these magnetic dipole transitions for plasma diagnostics, we have used the extended regular doublet law to parametrise the available data for the  $n = 3$  Al and Cl sequences, the  $n = 4$  Ga and Br sequences, the  $n = 5$  In and I sequences, and the  $n = 6$  Tl and At sequences. Isoelectronic and homologous trends were quantified and extrapolative predictions of fine structure separations were made which are presented herein.

## 2. Calculational method

The extended regular doublet law provides a precise semiempirical method for parametrising, predicting and verifying fine structure splittings. The procedure employed here is described in detail in [1], and consists of utilising a screened hydrogenic model to convert measured fine structure splittings into screening parameters, which exhibit a much more regular and slowly varying isoelectronic behaviour than do the splittings themselves. In sequences of the type treated here, the empirical regularity has been found to approach an almost exact linearity

between the screening parameter and the reciprocal screened charge.

For an element of nuclear charge  $Z$  in an isoelectronic sequence with  $N_c$  core electrons, the fine structure separation  $\Delta\sigma(N_c, Z)$  of a  $^2P$  term of principal quantum number  $n$  can be mapped into an effective core charge parameter  $Z_s(N_c, Z)$  through the use of the expression for the corresponding fine structure separation in a hydrogenic atom

$$\Delta\sigma(N_c, Z) = \frac{R\alpha^2 Z_s^4}{2(1 + \epsilon)n^3} \left[ \left( 1 + \sum_{p=1} (\alpha Z_s)^{2p} A_{pn} \right) / (1 + m/M_z) - (\alpha Z_s)^2 \frac{4\alpha}{3\pi} (1 - n^{-2}) \{ \ln(\alpha Z_s)^{-2} + C_0 + C_1 \alpha Z_s \} + g - 2 - \frac{3\alpha}{4} (\alpha Z_s)^3 - \frac{2\alpha}{\pi} \frac{m}{M_z} \right] \quad (1)$$

where  $R$  is the Rydberg constant,  $\alpha$  is the fine structure constant,  $g$  is the gyromagnetic factor for the electron, and  $m$  and  $M_z$  are the masses of the electron and nuclear core. The first term is a Sommerfeld expansion [7] of the Dirac energy and the remaining terms are radiative corrections [8, 9]. The coefficients  $A_{pn}$  are a set of rational fractions which are tabulated for  $p < 10$  in [7]. The radiative corrections are written in terms of a formula suggested by Erickson [8], but with constants  $C_0$  and  $C_1$  which we have adjusted to match the recent numerical calculations for  $n = 2$  by Mohr [9]. Erickson's original work was based on low  $Z$  calculations, for which he obtained  $C_0 = 11/24$  and  $C_1 = -7.476$ . The calculations of Mohr are valid through  $Z = 110$ , and are well described through  $Z = 90$  by Erickson's equation with our fitted values  $C_0 = -2.088$  and  $C_1 = 2.786$ .  $\epsilon$  is a parameter which accounts for neglected processes which distort the overall normalisation coefficient. It is adjusted to optimise the isoelectronic regularity of  $Z_s$ , and in practice is small compared to unity. Through numerical inversion of eq. (1) the experimental values for each isoelectronic sequence are thus reduced to corresponding values for  $Z_s(N_c, Z)$ . The screening parameter  $S(N_c, Z)$  is the difference between  $Z$  and  $Z_s(N_c, Z)$ , and is observed to be linear as a function of the reciprocal screened charge.

$$S(N_c, Z) = Z - Z_s(N_c, Z) \rightarrow S_0(N_c) + b(N_c)/Z_s(N_c, Z) \quad (2)$$

For each sequence,  $\epsilon$  is adjusted to give the best fit to eq. (2), and  $S_0$ ,  $b$ , and  $\epsilon$  constitute a three parameter fit which specifies the fine structure splittings for the entire sequence. In a study of these sequences, Edlén [5] has noted an approximate homologous scaling with  $N_c$  which is linear for  $S_0$  and quadratic for  $b$ . We shall therefore consider the quantities  $S_0/N_c$  and  $b/N_c^2$  in the tabulation to follow.

Table I. *Parameters obtained from least squares fits*

	$n$	Sequence	$N_c$	$\epsilon$	$S_0/N_c$	$b/N_c^2$
$ns^2np$	2	B <sup>a</sup>	4	0.017	0.536	0.0489
	3	Al	12	0.016	0.411	0.0906
	4	Ga	30	—	0.338	0.1232
	5	In	48	—	0.325	0.1242
	6	Tl	80	—	(0.320) <sup>b</sup>	0.123
$ns^2np^5$	2	F <sup>a</sup>	8	-0.003	0.383	0.0156
	3	Cl	16	0.011	0.350	0.0692
	4	Br	34	—	0.313	0.1102
	5	I	52	—	0.305	0.1179
	6	At	84	—	(0.300) <sup>b</sup>	0.122

<sup>a</sup> Ref. [1]. <sup>b</sup> Homologous extrapolation.

## 3. Results

The fitted parameters  $\epsilon$ ,  $S_0/N_c$ ,  $b/N_c^2$  are given in Table I for the  $n = 2-6$  series. The values for  $n = 2$  (the B and F sequences) are taken from [1]. The fits for  $n = 3$  (the Al and Cl sequences) utilise new Tokamak measurements [3, 4] not available when the analysis of [2] was performed. The fits for  $n = 4$  (the Ga and Br sequences) and the  $n = 5$  In sequence utilise some measurements which were not yet available when the analysis of [5] was performed, but make no improvement over the analysis of the  $n = 5$  I sequence presented in [6]. Likewise, the fits for  $n = 6$  (the Tl and At sequences) are made on the same (few) data as the analysis of [5]. In both of these  $n = 6$  sequences the value of  $S_0$  was obtained by homologous extrapolation and the value of  $b$  was obtained from a single data point.

The fine structure separations (in  $\text{cm}^{-1}$ ) for the  $n = 3, 4, 5$  and 6 sequences are given in Tables II, III, IV and V, along with the source references [2-6, 10-50] and estimated uncertainties.

Table II. *Fine structure separations of the  $n = 3$  Al and Cl sequences (in  $\text{cm}^{-1}$ )*

$Z$	Aluminium sequence (normal)				Chlorine sequence (inverted)			
	Ion	Exp (uncert)	[Ref.]	Fit	Ion	Exp (uncert)	[Ref.]	Fit
13 Al	0	112 <sup>a</sup>	[10]	(123)				
14 Si	+1	287 <sup>a</sup>	[11]	(299)				
15 P	+2	560 <sup>a</sup>	[12]	(569)				
16 S	+3	951(1)	[2]	958				
17 Cl	+4	1 491(1)	[13]	1 494	0	882 <sup>a</sup>	[14]	(892)
18 A	+5	2 207(1)	[2]	2 207	+1	1 432 <sup>a</sup>	[15]	(1 438)
19 K	+6	3 134(1)	[2]	3 131	+2	2 166(1)	[16]	2 170
20 Ca	+7	4 308(2)	[2]	4 301	+3	3 118(1)	[17]	3 120
21 Sc	+8	5 761(2)	[2]	5 755	+4	4 326(1)	[18]	4 325
22 Ti	+9	7 543(3)	[2]	7 536	+5	5 829(1)	[19]	5 827
23 V	+10	9 696(4)	[2]	9 688	+6	7 668(1)	[2]	7 666
24 Cr	+11	12 261(1)	[20]	12 257	+7	9 892(2)	[2]	9 888
25 Mn	+12	15 295(1)	[20]	15 295	+8	12 546(2)	[2]	12 543
26 Fe	+13	18 851(1)	[20]	18 854	+9	15 683(1)	[21]	15 681
27 Co	+14	22 970(50)	[22]	22 992	+10	19 380(5)	[23]	19 358
28 Ni	+15	27 761(2)	[20]	27 767	+11	23 627(1)	[20]	23 630
29 Cu	+16	33 239(6)	[3]	33 242	+12	28 560(2)	[3]	28 560
30 Zn	+17			39 486	+13			34 211
31 Ga	+18			46 565	+14			40 650
32 Ge	+19	54 564(9)	[4]	54 554	+15	47 944(2)	[4]	47 950
33 As	+20			63 530	+16			56 185
34 Se	+21			73 572	+17	65 454(13)	[4]	65 431
35 Br	+22			84 765	+18			75 773
36 Kr	+23			97 196	+19			87 295
37 Rb	+24			110 958	+20			100 086
38 Sr	+25			126 145	+21			114 240
39 Y	+26			142 859	+22			129 855
40 Zr	+27	161 681(80)	[4]	161 202	+23	147 254(65)	[4]	147 033
41 Nb	+28			181 285	+24			165 879
42 Mo	+29	204 040(125)	[4]	203 220	+25	186 986(105)	[4]	186 503
43 Tc	+30			227 124	+26			209 022
44 Ru	+31			253 121	+27			233 556
45 Rh	+32			281 338	+28			260 228
46 Pd	+33			311 907	+29			289 168
47 Ag	+34			344 968	+30			320 512
48 Cd	+35			380 663	+31			354 400
49 In	+36			419 141	+32			390 979
50 Sn	+37			460 559	+33			430 399
51 Sb	+38			505 076	+34			472 819
52 Te	+39			552 862	+35			518 402
53 I	+40			604 088	+36			567 320
54 Xe	+41			658 938	+37			619 747

<sup>a</sup> Not used in fit.

Table III. Fine structure separations of the  $n = 4$  Ga and Br sequences (in  $\text{cm}^{-1}$ )

Z	Gallium sequence (normal)				Bromine sequence (inverted)			
	Ion	Exp (uncert)	[Ref.]	Fit	Ion	Exp (uncert)	[Ref.]	Fit
31 Ga	0	826 <sup>a</sup>	[24]	<sup>b</sup>				
32 Ge	+1	1 767 <sup>a</sup>	[25]	(1 705)				
33 As	+2	2 940(3)	[26]	2 938				
34 Se	+3	4 376(4)	[27]	4 381				
35 Br	+4	6 089(6)	[28]	6 089	0	3 685 <sup>a</sup>	[29]	(3 621)
36 Kr	+5	8 108(10)	[30]	8 099	+1	5 370 <sup>a</sup>	[31]	(5 347)
37 Rb	+6			10 445	+2	7 375 <sup>a</sup>	[32]	(7 368)
38 Sr	+7			13 160	+3	9 728(1)	[33]	9 727
39 Y	+8	13 700 <sup>a</sup>	[34]	16 278	+4	12 460(1)	[35]	12 460
40 Zr	+9	16 700 <sup>a</sup>	[34]	19 834	+5	15 607(3)	[36]	15 603
41 Nb	+10	20 300 <sup>a</sup>	[34]	23 866	+6	19 191(4)	[37]	19 193
42 Mo	+11	24 400 <sup>a</sup>	[34]	28 411	+7	23 274(10)	[38]	23 269
43 Tc	+12			33 509	+8			27 868
44 Ru	+13			39 202	+9	33 055(30)	[39]	33 031
45 Rh	+14			45 533	+10	38 800(35)	[39]	38 802
46 Pd	+15			52 547	+11	45 180(40)	[39]	45 223
47 Ag	+16			60 290	+12			52 340
48 Cd	+17			68 812	+13			60 202
49 In	+18			78 163	+14			68 857
50 Sn	+19			88 396	+15			78 358
51 Sb	+20			99 566	+16			88 757
52 Te	+21			111 729	+17			100 111
53 I	+22			124 945	+18			112 477
54 Xe	+23			139 276	+19			125 915

<sup>a</sup> Not used in fit. <sup>b</sup> No real solution to eq. (2) for this Z,  $S_0$ , and b.

The first few stages of ionisation have been excluded from the fits. Near the neutral end of a sequence, the fine structure may be affected by configuration interaction and exchange core polarisation (which often behaves as an overscreening and tends to reduce the fine structure from its linearly extrapolated value), leading to a deviation from the regularities exhibited for higher ionisation stages.

In the Al sequence the measured value for the Mo XXX screening parameter falls below the value predicted by the regular doublet law by 0.4%, which greatly exceeds the measurement uncertainty. A similar effect has been noted for the  $4p\ ^2P$  and  $5p\ ^2P$  terms of the Cu I sequence, where the values predicted by this procedure [51] have been found to follow measured values [52] very closely up to 30 times ionised members of the sequence, but thereafter the predictions begin to

slightly underestimate the measured fine structures. At 45 times ionised W this correction is about 1%. Additional measurements are necessary to determine whether such a correction is necessary here.

In the Ga sequence values for Y IX–Mo XII have been obtained through reduction of the  $4s^2 4p\ ^2P_{1/2} - 4s^2 5d\ ^2D_{3/2}$  and  $4s^2 4p\ ^2P_{3/2} - 4s^2 5d\ ^2D_{5/2}$  data of Alexander et al. [34]. We have estimated  $4s^2 5d\ ^2D$  fine structure by a combination of isoelectronic extrapolation, isoionic extrapolation from the Cu sequence, and *ab initio* Hartree–Fock [53] calculation. The three methods agree to within 10% (less than 1% of the  $^2P$  interval) and yield approximate values of 850, 1080, 1360, and  $1690\ \text{cm}^{-1}$  for Y, Zr, Nb, and Mo. Combining these results with the data of [34] yields a  $4s^2 4p\ ^2P$  fine structure substantially smaller than the predictions of the regular doublet law (agree-

 Table IV. Fine structure separations of the  $n = 5$  In and I sequences (in  $\text{cm}^{-1}$ )

Z	Indium sequence (normal)				Iodine sequence (inverted)			
	Ion	Exp (uncert)	[Ref.]	Fit	Ion	Exp (uncert)	[Ref.]	Fit
49 In	0	2 213 <sup>a</sup>	[40]	(2 742)				
50 Sn	+1	4 251 <sup>a</sup>	[41]	(4 055)				
51 Sb	+2	6 576(3)	[42]	6 576				
52 Te	+3	9 224(10)	[43]	9 224				
53 I	+4	12 235(3)	[39]	12 145	0	7 603 <sup>a</sup>	[44]	(7 452)
54 Xe	+5	15 600(100)	[45]	15 399	+1	10 537(10)	[46]	10 510
55 Cs	+6			19 024	+2	13 847(1)	[6]	13 848
56 Ba	+7			23 052	+3	17 549(1)	[6]	17 542
57 La	+8			27 516	+4	21 634(1)	[6]	21 637
58 Ce	+9			32 447	+5	(25 984) <sup>b</sup>	[47]	26 171
59 Pr	+10			37 874	+6			31 177
60 Nd	+11			43 831	+7			36 690

<sup>a</sup> Not included in fit.

<sup>b</sup> Refs. [6] and [47] assert that this term is narrowed by perturbations from  $5p^4\ 4f$ .

Table V. *Fine structure separations of the n = 6 Tl and At sequences (in cm<sup>-1</sup>)*

Z	Thallium sequence (normal)				Astatine sequence (inverted)			
	Ion	Exp (uncert)	[Ref.]	Fit	Ion	Exp (uncert)	[Ref.]	Fit
81 Tl	0	7 793 <sup>a</sup>	[48]	— <sup>b</sup>				
82 Pb	+1	14 081 <sup>a</sup>	[49]	(13 368)				
83 Bi	+2	20 788	[50]					
84 Po	+3			27 647				
85 At	+4			34 718	0			(22 983)
86 Rn	+5			42 200	+1	30 895	[46]	30 895
87 F	+6			50 189	+2			38 936
88 Ra	+7			58 749	+3			47 385
89 Ac	+8			67 932	+4			56 366
90 Th	+9			77 782	+5			65 958
91 Pa	+10			88 341	+6			76 220
92 U	+11			99 649	+7			87 203

<sup>a</sup> Not included in fit.<sup>b</sup> No real solution to eq. (2) for this Z, S, and b.

ment would require the <sup>2</sup>D fine structures to be three times greater than our estimates). This is a serious discrepancy, and motivates a reexamination of these transitions.

#### 4. Conclusions

The various isoelectronic sequences treated here differ greatly in the amount of data which is presently available. Some of the sequences are based upon data for many ions over a large range of charge stages and can be extrapolated with confidence, whereas other sequences are based upon data for only a few member ions and the extrapolation must be considered as somewhat speculative. However, the regularity of the fitting parameters causes the data-rich sequences to reinforce the data-poor sequences, increasing our confidence in all of the predictions. Experimental verification of a few highly ionised predictions could sensitively test the entire predictive procedure.

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