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Ground-state fine structures for the B and F isoelectronic sequences using the extended regular doublet law

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Semiempirical screening parametrizations are used to specify accurately the fine-structure separations of the ^2P ground states in the boron and fluorine isoelectronic sequences.

Magnetic dipole transitions between fine-structure components of the ground-state ^2P multiplets in highly ionized members of the boron and the fluorine isoelectronic sequences have important applications in astrophysics[1] and in high-temperature plasma diagnostics.[2,3] The high-precision requirements for spectroscopic classification of these transition wavelengths can exceed the capabilities of *ab initio* calculations, and Huang *et al.*[4] have suggested that differences between Dirac-Fock calculations and experimental measurements could be semiempirically extrapolated. Such methods are promising for isoelectronic sequences where few data are available, but in systems where a substantial data base exists, very powerful purely empirical methods are applicable.[5] Edlén has used screening parametrizations and the regular doublet law to critically evaluate, interpolate, and enhance the accuracy of the ground-state fine-structure data for the B and F sequences.[1,6] We have utilized and extended these techniques to obtain reliable extrapolations of these fine-structure separations to high stages of ionization, using recent experimental data.

Although presently available *ab initio* methods are sufficiently accurate for many applications, specification of fine-structure intervals offers special problems. For example, theoretical methods that provide reliable predictions for gross energies and oscillator strengths, which derive large contributions from the outer parts of the wave functions, are often much less accurate in predicting fine-structure separations. Compromises between accuracy in the external and internal portions of the wave functions are possible, but the predictions become less than unique. Luc-Koenig[7] and Detrich and Weiss[8] have discussed the relationship between relativistic and nonrelativistic descriptions of alkali-metal-like fine structure and concluded that a single configuration relativistic calculation is equivalent to a multiconfiguration nonrelativistic treatment that includes core polarization. Both approaches are capable of predicting approximate trends in fine-structure separations on a 1% level of accuracy, but both also exhibit systematic discrepancies at higher levels of accuracy.[9,10] In addition, Huang *et al.*[4] have recently pointed out that the relativistic Dirac-Fock method produces spurious contributions from the gross structure that spill over into the fine structure unless special precautions are taken to ensure that configuration interaction and fractional parentage mixtures are forced to converge to the correct nonrelativistic limit.

In the extended regular doublet law the fine structure is described by an effective core charge screening parametrization. Fine-structure separations $\Delta\sigma(Z)$ for a quasihydrogenic $2p$ doublet of nuclear charge Z can be written as a Sommerfeld expansion[11] of the Dirac energy with quantum electrodynamic corrections[12]

$$\Delta\sigma(Z)=\frac{R_\infty\alpha^2Z_S^4}{16(1+\epsilon)}\left[\left(1+\sum_{p=1}A_p(\alpha Z_S)^{2p}\right)\frac{1}{(1+m/M_Z)}-\frac{\alpha}{\pi}(\alpha Z_S)^2\left(\ln\frac{1}{(\alpha Z_S)^2}+\tfrac{11}{24}-5.120\alpha Z_S\right)\right.$$
$$\left.+(g-2)-\frac{(m/M_Z)^2}{(1+m/M_Z)^3}-\frac{\alpha}{\pi}\frac{(m/M_Z)(2+m/M_Z)}{(1+m/M_Z)^2}\right]\,, \qquad (1)$$

where R_∞ is the Rydberg constant, α is the fine-structure constant, g is the gyromagnetic factor for the electron, m is the mass of the active electron, M_Z is the mass of the core, and Z_S is the effective screened charge which Eq. (1) serves to define. The coefficients A_p are a set of rational fractions that are tabulated in Ref. 11. ϵ is a parameter small compared to unity, which can be adjusted to optimize the regularity of the isoelectronic behavior of Z_S. The use of ϵ was suggested by Edlén as a means of empirically accounting for deviations from the one-electron picture due to, for example, configuration interactions. It could also account for many other processes, such as corrections for the relativistic non-

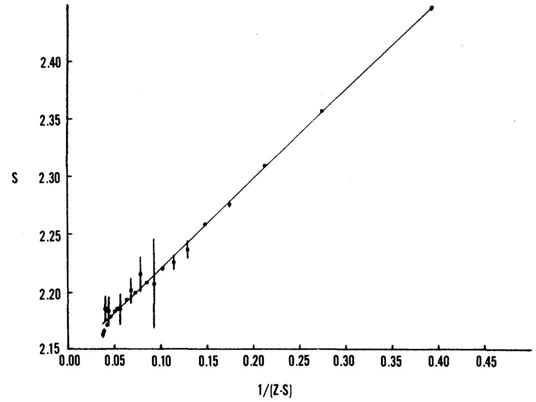

FIG. 1. S vs $1/(Z-S)$ for the $2s^2 2p\ {}^2P$ term in the boron isoelectronic sequence.

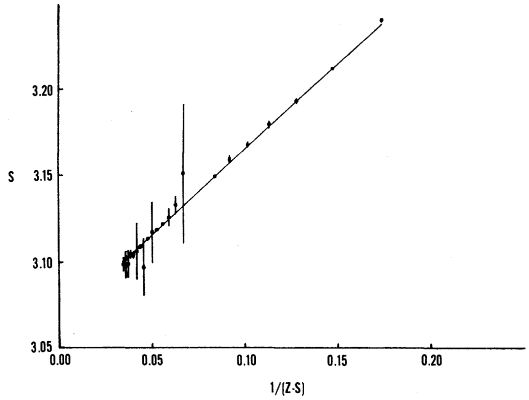

FIG. 2. S vs $1/(Z-S)$ for the $2s^2 2p^5\ {}^2P$ term in the fluorine isoelectronic sequence.

separability of the reduced mass and for higher-order quantum electrodynamical processes.

Through numerical inversion of Eq. (1) the experimental values for $\Delta\sigma(Z)$ are mapped into corresponding values for $Z_S(Z)$ and rewritten as the screening parameter $S(Z)$:

$$S(Z)=Z-Z_S(Z) \ . \tag{2}$$

It has been found that the $S(Z)$ is often very nearly linear as a function of the reciprocal screened charge and, by simultaneous adjustment of the parameter ϵ the data can be very accurately represented by

$$S(Z)=S_0+b/Z_S(Z) \ . \tag{3}$$

Thus there are three fitting parameters: ϵ in Eq. (1) is search-fitted to give the best straight line in the space of Eq. (3), wherein S_0 and b are obtained through a weighted least-squares linear regression. The weights were obtained from the uncertainties quoted in the original data sources.

Results of this analysis applied to the B and F sequences are shown in Figs. 1 and 2. The high degree of linearity of the experimental points when displayed on such a plot is apparent. Although the theoretical basis for this empirically demonstrated relationship is uncertain, it provides great predictive power if it is assumed to persist to very high Z. These linearities were noted by Edlén[1] in 1969. Many additional measurements have become available since that time, most of which seem to verify the persistence of this linearity. There is, however, an apparent inconsistency in the boron sequence. The Fe, Ni, and Cu points (all of quoted accuracies exceeding four parts in 10^4) fall more than three standard deviations below the fitted line, whereas the Sc and Ti points (both of quoted accuracies better than one part in 10^4) fall one to two standard deviations above the fitted line. On the basis of the generally observed behavior of screening parametrizations[5] it is unlikely that these irregularities are real. If the trend of the Cr, Fe, Ni and Cu data from Ref. 40 were separately extrapolated, the predicted fine structure at $Z=42$ would be increased by two parts in 10^4 over that listed in Table II. As additional precise measurements of these splittings for $Z>30$ become available, it should be possible either to verify the linearity, or to incorporate a small curvature into the parametrization, and thus obtain accuracies better than one part in 10^4.

The adjusted values of the three fitting parameters are listed in Table I for each sequence, along with the value of χ-squared per degree of freedom. The predicted fine structures up to $Z=42$ are given in Table II, along with the experimental data used (with source references and quoted uncertainties). The Dirac-Fock predictions of Huang *et al.*[4] are also listed where available. After correction for spurious gross-structure effects, the Dirac-Fock results agree quite

TABLE I. Parameters obtained from weighted least-squares fits.

Sequence	ϵ	S_0	b	χ^2 (reduced)
B	0.017	2.143	0.782	0.98[a], 2.48[b]
F	−0.003	3.066	1.000	0.60

[a] Fe, Ni, and Cr excluded.

[b] All 24 data points included.

TABLE II. Fine-structure separations.

		Boron isoelectronic sequence					Fluorine isoelectronic sequence				
Z		Ion	Expt. (uncert.)	[Ref.]	Fit	Theor.^{a}	Ion	Expt. (uncert.)	[Ref.]	Fit	Theor.^{a}
5	B	0	15.25(5)	[13]	15.25	15.7					
6	C	+1	63.41(5)	[14]	63.41	62.7					
7	N	+2	174.36(2)	[15]	174.36	172.4					
8	O	+3	386.9 (7)	[16]	385.9						
9	F	+4	744.5 (4)	[17]	744.5	0		404.1 (3)	[18]	404.83	399.0
10	Ne	+5	1 310 (5)	[19]	1 305	1 298	+1	780.34(14)	[20]	780.27	774.3
11	Na	+6	2 139 (6)	[17]	2 133	2 124	+2	1 366.3 (10)	[21]	1 366.2	1 359
12	Mg	+7	3 303 (2)	[22]	3 300		+3	2 228 (2)	[23]	2 229	2 221
13	Al	+8	4 903 (70)	[24]	4 888		+4	3 442 (2)	[25]	3 443	
14	Si	+9	6 991 (2)	[22]	6 989	6 968	+5	5 090 (4)	[26]	5 093	5 084
15	P	+10	9 668 (45)	[27]	9 703		+6	7 275 (2)	[28]	7 273	
16	S	+11	13 138.9 (7)	[29]	13 138		+7	10 080 (b)	[30]	10 086	
17	Cl	+12	17 390 (50)	[31]	17 415		+8			13 644	13 636
18	A	+13	22 657 (5)	[29]	22 662	22 612	+9	18 057(130)	[32]	18 069	
19	K	+14			29 016		+10	23 467 (30)	[33]	23 492	
20	Ca	+15	36 643(110)	[34]	36 624		+11	30 049 (35)	[33]	30 056	30 055
21	Sc	+16	45 637 (4)	[35]	45 646		+12	37 908 (3)	[36]	37 911	
22	Ti	+17	56 240 (4)	[37]	56 248		+13	47 219 (4)	[37]	47 219	47 229
23	V	+18	68 610 (b)	[38]	68 608	68 539	+14	58 137(205)	[39]	58 152	
24	Cr	+19	82 926 (14)	[40]	82 915	82 857	+15	70 892 (10)	[40]	70 892	70 919
25	Mn	+20	99 266(220)	[41]	99 368		+16	85 856(260)	[42]	85 632	
26	Fe	+21	118 273 (28)	[40]	118 178	118 117	+17	102 585 (20)	[40]	102 576	102 629
27	Co	+22	139 310(250)	[41]	139 562		+18	121 965(330)	[39]	121 938	
28	Ni	+23	163 961 (55)	[40]	163 756	163 889	+19	143 988 (40)	[40]	143 946	144 038
29	Cu	+25	191 278 (75)	[40]	191 003		+20	168 833 (60)	[40]	168 837	
30	Zn	+26			221 560	221 963	+21	196 980(230)	[43]	196 860	197 006
31	Ga	+27			225 693		+22	228 379(250)	[43]	228 277	
32	Ge	+28			293 683		+23	263 435(140)	[40]	263 363	
33	As	+29			335 824		+24			302 404	
34	Se	+30			382 421		+25			345 700	
35	Br	+31			433 795		+26			393 564	
36	Kr	+32			490 279	492 576	+27			446 323	446 783
37	Rb	+33			552 221		+28			504 318	
38	Sr	+34			619 984		+29	568 360(400)	[44]	567 906	
39	Y	+35			693 945		+30	637 270(500)	[44]	637 535	
40	Zr	+36			774 497		+31			713 452	
41	Nb	+37			862 050		+32			796 001	
42	Mo	+38			957 030	964 352	+33			885 967	887 003

[a] Reference 4.

[b] No uncertainties given in source, not used in fitting.

well for moderate degrees of ionicity, whereas for high *Z* there is a systematic tendency for the Dirac-Fock calculations to slightly (but increasingly) deviate from the splittings. It is possible to empirically parametrize this difference between theory and experiment, but the linearity and the seeming accuracy, and calculational simplicity of the purely empirical approach are compelling.

This method provides a simple, reliable, and generally applicable means of predicting fine-structure separations whenever a substantial body of experimental data is already available. Because of its total reliance on experimental data, it includes all types of processes automatically, and its absolute reliability can be tested as measurements for higher *Z* become available.

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