

FINE STRUCTURE SEPARATIONS FOR THE  $^2D$  TERMS OF THE Cu ISOELECTRONIC SEQUENCE

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A screening parametrization is used to systematize available data for the 4d and 5d fine structure separations in the copper isoelectronic sequence. Several new results are presented and interpolations between existing measurements and extrapolations to very high  $Z$  are made.

In an earlier study [1] a screening parametrization of the Sommerfeld–Dirac formula [2] was used to interpolate and extrapolate the fine structure separations of the 4p  $^2P$  and 5p  $^2P$  terms for ions in the copper isoelectronic sequence from Ga III to Pb LIV. It was found that these  $^2P$  terms are very well described by the regular doublet law [3]. Ions of the homologous sodium isoelectronic sequence exhibit a similar regularity for  $^2P$  terms [4], but have strong fs perturbations in their  $^2D$  terms [4–6], which provides motivation for a study of the degree of fs regularity in  $^2D$  terms of the copper sequence. At the time of ref. [1] precise data for the  $^2D$  fs separations were not available for a sufficient number of ions in the copper sequence to judge their isoelectronic regularity, but recent spectroscopic investigations [7–9] have improved the range and precision of the available data, and the results of such a study are presented herein.

The formulation of fs data in terms of a screening parametrization [2] is useful for several reasons: it allows interpolations for missing data and extrapolations beyond the range of presently accessible observations; it reveals misidentifications and permits adjustments of less accurate data, and its degree of isoelectronic regularity is a sensitive indicator of perturbing influences [10]. Advantages have also been cited [11] for formulating and presenting theoretical fs calculations directly in terms of screening parameters rather than energy differences. The method uses as a model the theoretical expression for the fs in a hydrogenic atom, with the nuclear charge replaced by an effective

screened charge. By functionally inverting this theoretical expression, each experimental fs splitting is re-expressed as a corresponding screening parameter, with the hope that this quantity will be nearly linear as a function of the reciprocal screened charge.

The fs separation  $\Delta\sigma(nd, Z)$  of a d-state ( $l = 2$ ) doublet of principal quantum number  $n$  and nuclear charge  $Z$  can be written in terms of the Sommerfeld expansion of the Dirac energy [12] with quantum electrodynamic corrections [13] as

$$\Delta\sigma(nd, Z) = \frac{R_\infty \alpha^2 Z_s^4}{6n^3} \left\{ \left[ 1 + \sum_{\beta=1}^{\infty} (\alpha Z_s)^{2\beta} A_\beta(n, 2) \right] \times (1 + m/M_Z)^{-1} + (g_e - 2)(1 - m/M_Z)^2 \right\}. \quad (1)$$

Here  $R_\infty$  and  $\alpha$  are the Rydberg and fs constants,  $g_e$  is the gyromagnetic factor for the electron,  $m$  and  $M_Z$  are the masses of the electron and nucleus and  $Z_s$  is the effective screened charge which eq. (1) serves to define. The Sommerfeld expansion coefficients  $A_\beta(n, l)$  are positive rational fractions which can be expressed [12] as

$$A_\beta(n, 2) = -2n^{-2\beta} \times \sum_{\gamma=0}^{2\beta} (n/6)^\gamma (3\gamma+1 - 2\gamma^2) C_{\beta+2, \gamma+1}, \quad (2)$$

where  $C_{ij}$  is an auxiliary array of rational fractions which are tabulated for  $\beta \leq 7$  in ref. [12]. For  $\beta > 7$

$C_{ij}$  can be computed using a formula given in ref. [12], but higher-order terms can also be taken into account by an alternative evaluation procedure. By numerical computation it can be shown that the ratio of successive coefficients,  $A_\beta/A_{\beta-1}$ , is nearly a constant, which can be approximated by  $A_7/A_6$  for  $\beta > 7$ . Thus all of the remaining terms can be at least partially included by the replacement

$$\sum_{\beta=7}^{\infty} (\alpha Z_s)^{2\beta} A_\beta \approx (\alpha Z_s)^{14} A_7 \sum_{i=0}^{\infty} (\alpha^2 Z_s^2 A_7/A_6)^i \quad (3)$$

$$\approx (\alpha Z_s)^{14} A_7 / (1 - \alpha^2 Z_s^2 A_7/A_6),$$

with the geometric progression summed by use of Euclid's theorem. With this "geometric continuation" the  $l = 2$  Sommerfeld expansion agrees with the exact expression for the Dirac energy to within better than 1 part in  $10^7$  for  $\alpha Z_s \leq 1$ . This exceeds the present precision in the determination of the fs constant, so this expansion can be considered to be computationally equivalent to the exact expression. (Similarly summed expansions can be formed for arbitrary  $l$ . For  $l = 1$  the convergence is slightly less rapid, e.g., at  $Z_s = 92$  the 2p  $^2P$  expansion is in error by 1 part in  $10^5$ .)

Measured fs splittings and their uncertainties were reduced to corresponding values and uncertainties for  $Z_s$  by iterative inversion of eq. (1), as described in ref. [1]. This also determines the screening parameter  $S$ , defined as

$$S(nd, Z) \equiv Z - Z_s. \quad (4)$$

It has been found empirically (e.g., refs. [1,2,4,10]) that  $S$  can often be accurately represented by a power series in the reciprocal screened charge,

$$S(nd, Z) = a_n + b_n/Z_n + \dots \quad (5)$$

The constants  $a_n, b_n, \dots$  can be determined by weighted least-squares adjustment of eq. (5) to the experimental values for  $S$  (ref. [1] describes an iterative adaptation of the least-squares method which takes into account the correlation between  $S$  and  $Z_s$ ). If a linear truncation of eq. (5) suffices, semi-empirical predictions for arbitrary  $Z$  can be obtained from the larger quadratic root of eq. (5),

$$Z_s = [(Z - a_n) + ((Z - a_n)^2 - 4b_n)^{1/2}] / 2, \quad (6)$$

which is substituted into eq. (1). Application to low ionization stages is limited by reality in eq. (6) to  $Z$

$\geq a_n + 2b_n^{1/2}$  (empirically  $\approx 31$  for all  $^2P$  and  $^2D$  terms studied here and in ref. [1]).

The data values used, together with source references, quoted uncertainties and the predictions of the semi-empirical formulation are given in table 1. All data are taken from published sources [7-9,14-18] except for Pd XVIII-In XXI, which result from our own measurements on spectrograms recorded earlier by Edlén [19]. The 4d splittings for Zr XII, Nb XIII and Pd XVIII-In XXI were obtained from  $\Delta J = -1$  4d-5f transition wavelength data, and required correction for the fs of 5f. The 5f splitting is expected to be much smaller than that of the 4d, but is strongly perturbed [20] and inverted [14] for the lower ionization stages. In order to estimate the 5f splitting, single configuration Hartree-Fock calculations [21] were carried out and, to include perturbations, combined with an empirically determined splitting of the opposite character. Following the procedure developed by Edlén [4], this overlaid splitting was modeled as an empirically determined constant ( $\sim 0.8$ ) multiplied by the square of the net core charge. The uncorrected Hartree-Fock results were found to be substantially larger than the corresponding hydrogenic values owing to the collapse of the  $f$  orbitals with increasing nuclear charge (e.g., our HF calculations indicated that  $\bar{r}(4f) < \bar{r}(4d)$  for  $Z > 48$ ), and could not be accurately represented by the  $^2F$  equivalents of eqs. (1) and (5). For purposes of reducing the 4d-5f wavelength data, the 5f fine structure was estimated to be

$$\sigma_{\text{est}}(5f, Z) = R_\infty \alpha^2 (Z - s')^4 / 1500 - 0.8 (Z - 28)^2, \quad (7)$$

where  $s' = 20.87 + 102/(Z - 20)$  is a simplified screening parametrization which recovers the Hartree-Fock values for  $Z = 40-49$ . Although little information concerning the 5f fine structure is presently available, it seems not unreasonable to assume that this procedure can predict their values to within  $\pm 25\%$  in the region  $Z = 40-49$ , and thus adds only a small uncertainty to the relatively larger 4d splittings. The isoelectronic regularity of the 4d screening parameters so obtained lends credence to this assumption, and the validity of eq. (7) can be re-examined when additional 5f data become known for this sequence.

Plots of  $S(nd, Z)$  versus  $1/Z_s$  for  $n = 4$  and  $5$  are shown in fig. 1. Provided the first few ionization stages are excluded, the plots show a striking linearity.

Table 1

Ion	Z	4d <sup>2</sup> D		5d <sup>2</sup> D	
		$\Delta\sigma(\text{exp.})$ ( $\text{cm}^{-1}$ )	$\Delta\sigma(\text{calc.})$	$\Delta\sigma(\text{exp.})$ ( $\text{cm}^{-1}$ )	$\Delta\sigma(\text{calc.})$
Cu I	29	6.857	[14]	3.624	[14]
Zn II	30	50.66	[15]	24.29	[15]
Ga III	31	114.7	[16]	63.4	[16]
Ge IV	32	254(5) a)		80 a)	
As V	33	445(5) b)			190
Se VI	34	679.9(5)	[7]	296.0(5)	[7]
Br VII	35	861 c)			428
Kr VIII	36	1 290(35)	[8]	530(35)	[8]
Rb IX	37				589
Sr X	38				784
Y XI	39				1 017
Zr XII	40	3 507(35) d)			1 291
Nb XIII	41	4 372(50) d)			1 611
Mo XIV	42	5 226(7)	[9]		1 982
Tc XV	43				2 408
Ru XVI	44				2 894
Rh XVII	45				2 894
Pd XVIII	46	10 350(180) e)			3 445
Ag XIX	47	11 870(230) e)			4 067
Cd XX	48	13 540(280) e)			4 765
In XXI	49	15 660(350) e)			5 544
Sn XXII	50				6 411
Sb XXIII	51				7 372
Te XXIV	52				8 433
I XXV	53				9 601
Xe XXVI	54				10 880
Ta XLV	73				12 290
W XLVI	74				13 820
Re XLVII	75				18 630
Os XLVIII	76				78 630
Ir XLIX	77				84 620
Pt L	78				90 950
Au LI	79				97 630
Hg LII	80				104 700
Ti LIII	81				112 100
Pb LIV	82				119 900
U LXIV	92				128 100
					136 800
					145 800
					264 100

a) Lang, cf. ref. [14]. b) Sawyer and Humphreys, cf. ref. [14]. c) Rao and Rao, cf. ref. [14] (excluded from fit).

d) 4d-5f data from ref. [17], reduced using estimated 5f splittings (see text). e) This work, based upon spectrograms from ref. [19], reduced using estimated 5f splittings (see text). f) 4p-5d data from ref. [17], reduced using 4p splittings from ref. [18].

g) This work, based upon spectrograms from ref. [19].

Weighted least-squares fits to eq. (5) were made, and here again, as with the <sup>2</sup>P terms [1], the  $\chi^2$  test indicated that the inclusion of powers of  $1/Z_s$  higher than the first is not justified. The fits yield  $a_4 = 15.376$  and  $b_4 = 59.57$  for 4d and  $a_5 = 16.164$  and  $b_5 = 54.26$  for

5d. For 4d the agreement between fitted and measured values is quite good for all ions above Ga III with the exception of Br VII (the agreement of the Ga III point is only apparent, since its  $Z_s$  value corresponds to an unphysical  $Z$  in eq. (6)). Because of its

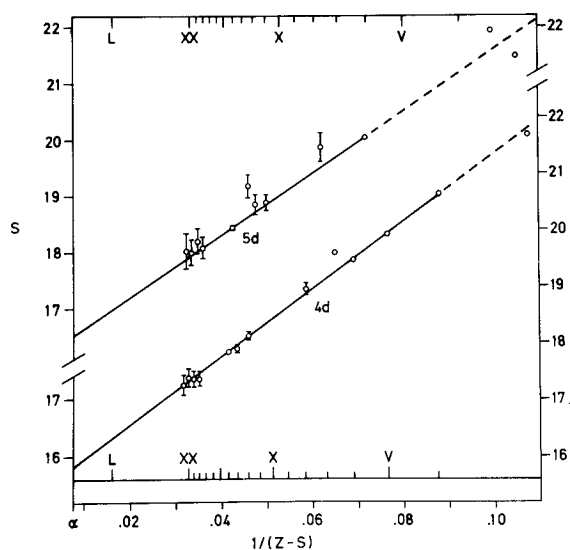


Fig. 1. Plot of the fs screening parameter versus reciprocal screened charge for the 4d and 5d terms in the Cu isoelectronic sequence. The circles represent the available data, and measurement uncertainties are shown when they exceed the circle size. Solid lines indicate weighted linear least-squares fits to the data. Measurements in the dashed line regions were not included in the fit, nor was the Br VII 4d point. The 4d and 5d ordinates are translated from each other slightly to avoid confusion. The two sets of roman numerals denote the stages of ionization ( $Z - 28$ ) for which the abscissae correspond to each of the fitted lines.

clear inconsistency with the other data, the Br VII 4d measurement was assumed to be in error (no uncertainty estimates were given in the source reference) and it was excluded from the fitting process. For 5d the fit is heavily determined by the higher precision Se VI and Mo XIV values, but the results for all ions above Ge IV except Nb XIII are consistent with this fit. One possible explanation for the smaller-than-predicted 5d splitting in Ge IV could be perturbations from the  $3d^9 4s^2 \ ^2D$  term, which, according to published classifications [7,14,16], crosses  $3d^{10} 4d \ ^2D$  near Ga III and  $3d^{10} 5d \ ^2D$  between Ge IV and Se VI. The Nb XIII 5d fs is smaller than the fitted value by nearly three times its quoted uncertainty, but the uncertainty is large and the inclusion of this point had little influence on the fit.

The systematization presented here indicates that, at least to within the accuracy of presently available data, the 4d  $\ ^2D$  and 5d  $\ ^2D$  term fs splittings for the copper isoelectronic sequence can be well represented by the extended regular doublet law for members above the first few stages of ionization. The 4f  $\ ^2F$  and 5f  $\ ^2F$  terms in the copper sequence cannot be so represented, and are perturbed and often inverted for the lower ionization stages. This is in contrast to the sodium isoelectronic sequence, where the  $\ ^2D$  terms are strongly perturbed [4–6], but the  $\ ^2F$  terms are normal and nearly hydrogenic [20].

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