# FINE STRUCTURE SEPARATIONS FOR RESONANCE TRANSITIONS OF THE CU I ISOELECTRONIC SEQUENCE

L.J. CURTIS

*Department of Physics, University of Lund, S-223 62 Lund Sweden*

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A screening parametrization is used to interpret available data for the 4p and 5p fine structure separations in the Cu I isoelectronic sequence. Several new measurements are presented and predictions for very high $Z$ members are made.

Resonance radiation from alkali-like highly ionized metal atoms is frequently observed in Tokamak plasma discharges [1] and provides valuable information concerning these devices [2]. A new generation of Tokamak devices will soon be operable with temperatures capable of stripping Ta, W, Re, Pt and Au atoms down to Cu I-like ions [2]. The wavelengths of the relevant transitions can be predicted either by ab initio theoretical calculations or through isoelectronic extrapolations. However, relativistic modifications to theoretical calculations for these very high $Z$ systems can be severe [3] and extrapolations become highly nonlinear [4] making predictions difficult, although some approximate estimates have been made [3, 5]. In contrast, the isoelectronic behaviour of the fine structure (fs) separations between the levels seems to be extremely regular when expressed in a semi-empirical screening parameter formulation. Therefore this study of the 4p and 5p fs separations of the Cu I isoelectronic sequence was undertaken, systematizing previous results as well as adding several new measurements based upon spectrograms recorded earlier by Edlén [6].

The approach involves an application of the screening parameter formulation described earlier and utilized extensively by Edlén [7]. Here the theoretical expression for the fs in a single electron atom is used as a model, with the nuclear charge replaced throughout by a single effective screened charge. Each measured fs separation can thus be re-expressed as a corresponding screening parameter, which is found empirically to have an isoelectronic behaviour which is nearly linear as a function of the reciprocal screened charge.

Theoretical expressions for the energy levels of one-electron atoms have been given by Garcia and Mack [8]. Using these expressions, the fs separation $\Delta\sigma(n\mathrm{p}, Z)$ of a p state ($l = 1$) multiplet of principal quantum number $n$, nuclear charge $Z$ and effective charge $Z_s$ can be written

$$\Delta\sigma(n\mathrm{p},Z)=\frac{R_\infty\alpha^2Z_s^4}{2n^3}\,[(1+A_nZ_s^2+B_nZ_s^4+C_nZ_s^6)/ \tag{1}$$

$$(1+m/M_Z)+(g_e-2+D_nZ_s^2\ln\alpha^2Z_s^2)(1-m/M_Z)^2]$$

where

$$A_n\equiv\alpha^2(7n^2+18n-24)/16n^2\cdot \tag{2}$$

$$B_n\equiv\alpha^4(31n^4+90n^3+28n^2-360n+240)/128n^4 \tag{3}$$

$$C_n\equiv\alpha^6(635n^6+1890n^5+1488n^4-4800n^3 - 10080n^2+20160n-8960)/4096n^6 \tag{4}$$

$$D_n\equiv 4\alpha^3(1-n^{-2})/3\pi. \tag{5}$$

Here $R_\infty$ and $\alpha$ are the Rydberg and fs constants, $g_e$ is the gyromagnetic factor for the electron, and $m$ and $M_Z$ are the masses of the electron and nucleus. The power series portion of eq. (1) arises from the expansion (to order $(\alpha Z_s)^{10}$) of the Dirac energy, and the remaining terms account for the contributions of the anomalous magnetic moment of the electron and radiative corrections. As a simple empirical model for a multi-electron atom we write $Z_s$ as the nuclear charge modified by an effective screening parameter $S(n\mathrm{p}, Z)$

$$Z_s=Z-S(n\mathrm{p},Z). \tag{6}$$

Thus each measured fs separation $\Delta\sigma(n\mathrm{p}, Z)$ can be reduced to a corresponding screening parameter $S(n\mathrm{p}, Z)$ through the use of eqs. (1)–(6). This can be done effi-

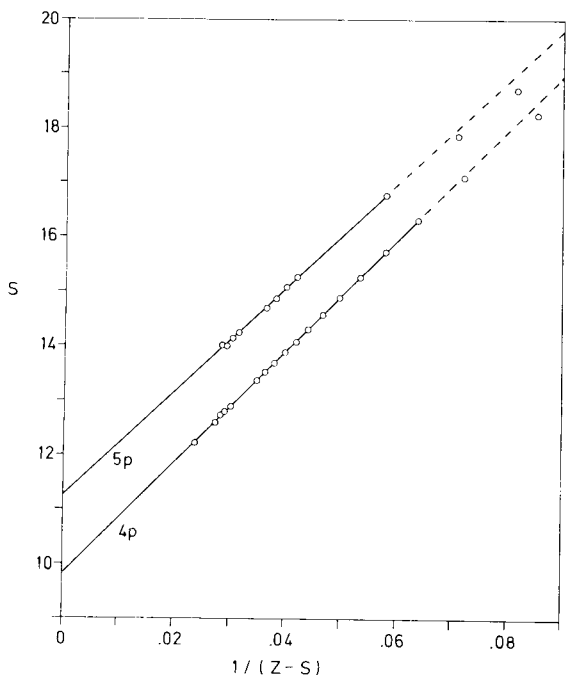


Fig. 1. Plot of $S$ versus $1/(Z\text{-}S)$ as obtained by applying eqs. (1)–(6) to the available measured data for the 4p and 5p fs separations. The solid lines denote weighted least squares fits to eq. (7) (truncated after the linear term). The lines become dashed at the lowest charge stage which was included in the fit.

ciently by isolating the $Z_s^4$ term which is outside of the brackets in eq. (1) on one side of an equation, with the $Z_s$ terms inside the brackets taken into account by successive iteration. Eqs. (1)–(6) can be used in a similar manner to deduce the experimental uncertainty in $S$ from that in $\Delta\sigma$ (i.e., the relative uncertainty in $Z_s$ is essentially 1/4 of that in $\Delta\sigma$).

It has been found empirically [7] that $S$ is often accurately described by a power series expansion in the reciprocal screened charge

$$S = a_n + b_n/(Z - S) + \ldots . \qquad (7)$$

Eq. (7) can be used to describe the data through least squares adjustment of the fitting parameters $a_n$, $b_n$, etc. However, such fitting methods assume a functional relationship between an experimentally uncertain dependent variable and a precisely known independent variable. Such a relationship could be obtained by algebraic solution of eq. (7) for $S$ as a function of $Z$, but the resulting expressions are not linear in the fitting parameters and must be search fitted. Therefore an equivalent but computationally simpler approach was used, treating $1/(Z - S)$ as an error-free independent variable so as to allow eq. (7) to be fitted by a standard polynomial regression, which is then repeated successively using the fitting parameters from one iteration to compute $1/(Z - S)$ for the next until convergence is achieved. Since various experimental determinations vary widely in uncertainty, a weighted least squares minimization was used, with the observed deviations in $S$ normalized to the corresponding experimental uncertainties. The fitting parameters evaluated from the available measured data can then be used to predict $S$ for arbitrary values of $Z$, either by algebraic solution of eq. (7) or by repeated iteration (equivalent to a continued fraction representation) and then used to predict $\Delta\sigma$ through eqs. (1)–(6).

A plot of $S$ versus $1/(Z - S)$ for the available data for the 4p and 5p multiplets is shown in fig. 1. The data were fitted using various polynomial orders in eq. (7) with various lower limits to the stages of ionization included. It was found that a fairly high order polynomial was necessary if the lower ionization stages were to be included (excepting Cu I, which has a highly perturbed spectrum), but that the $\chi^2$ test did not justify using a polynomial higher than linear if the first few ionization stages were excluded. The best results were obtained using first order polynomial fits which began with Ge IV for 4p and with Se VI for 5p. The fitting parameters obtained were $a_4 = 9.810$, $b_4 = 102.13$ and $a_5 = 11.251$, $b_5 = 95.24$. Table 1 lists the primary data and their uncertainties (obtained either from the original sources, or estimated herein, as noted in the table), together with the predictions of this formalism. In addition to the available published data, measurements made as part of this study are also included for the previously unreported fs separations in Pd XVIII, Ag XIX, Cd XX and In XXI. These results were obtained by a remeasurement of spectrograms recorded and published by Edlén [6], and Prof. Edlén is gratefully acknowledged for making his spectrograms available for this study. The interpolated values in table 1 ($Z \leqslant 54$) might be expected to be of similar accuracies as their neighbouring points. The extrapolated values ($Z \geqslant 73$) are, however, based entirely upon the assumption that the linear behaviour seen in fig. 1 persists for substantially higher values of $Z$. Therefore these high $Z$ results should be regarded

Table 1

| Ion | Z | 4p $^2$P | | 5p $^2$P | |
|---|---|---|---|---|---|
| | | $\Delta\sigma$(expt) ($cm^{-1}$) | $\Delta\sigma$(calc) | $\Delta\sigma$(expt) ($cm^{-1}$) | $\Delta\sigma$(calc) |
| Cu I | 29 | 248.384 [9] | | −0.31 [9] | |
| Zn II | 30 | 873.96(7) [10] | | 244.8(3) [10] | |
| Ga III | 31 | 1 717.8(4) [11] | | 534(4) [11] | |
| Ge IV | 32 | 2 788(4) [a, e] | 2 784 | 938(1) [a, e] | |
| As V | 33 | 4 100(4) [b] | 4 119 | | 1 449 [f] |
| Se VI | 34 | 5 700(5) [b] | 5 709 | 2 078(5) [12] [e] | 2 078 |
| Br VII | 35 | 7 580(11) [c, e] | 7 586 | | 2 859 |
| Kr VIII | 36 | 9 779(9) [13] | 9 783 | | 3 783 |
| Rb IX | 37 | 12 334(2) [14] | 12 332 | | 4 865 |
| Sr X | 38 | 15 266(2) [14] | 15 266 | | 6 123 |
| Y XI | 39 | 18 623(3) [14] | 18 619 | 7 560(50) [15] | 7 570 |
| Zr XII | 40 | 22 425(3) [14] | 22 426 | 9 170(70) [15] | 9 230 |
| Nb XIII | 41 | 26 723(4) [14] | 26 725 | 11 130(80) [15] | 11 110 |
| Mo XIV | 42 | 31 547(5) [14] | 31 554 | 13 270(100) [15] | 13 240 |
| Tc XV | 43 | | 36 954 | | 15 630 |
| Ru XVI | 44 | | 42 967 | | 18 300 |
| Rh XVII | 45 | | 49 636 | | 21 280 |
| Pd XVIII | 46 | 57 020(120) [d] | 57 010 | 24 610(200) [d] | 24 590 |
| Ag XIX | 47 | 65 150(140) [d] | 65 130 | 28 250(250) [d] | 28 240 |
| Cd XX | 48 | 73 860(160) [d] | 74 050 | 32 460(300) [d] | 32 270 |
| In XXI | 49 | 84 130(400) [d] | 83 820 | 36 510(700) [d] | 36 700 |
| Sn XXII | 50 | | 94 500 | | 41 550 |
| Sb XXIII | 51 | | 106 100 | | 46 860 |
| Te XXIV | 52 | | 118 800 | | 52 640 |
| I XXV | 53 | | 132 500 | | 58 930 |
| Xe XXVI | 54 | 148 100(2000) [1] | 147 400 | | 65 760 |
| Ta XLV | 73 | | 749 700 | | 347 100 |
| W XLVI | 74 | | 804 900 | | 373 100 |
| Re XLVII | 75 | | 863 300 | | 400 600 |
| Os XLVIII | 76 | | 925 000 | | 429 600 |
| Ir XLIX | 77 | | 990 100 | | 460 300 |
| Pt L | 78 | | 1 059 000 | | 492 800 |
| Au LI | 79 | | 1 131 000 | | 527 000 |
| Pb LIV | 82 | | 1 374 000 | | 641 300 |

[a] Lang, cf ref. [9]. [b] Sawyer and Humphreys, cf ref. [9]. [c] Rao and Rao, cf ref. [9]. [d] This work. [e] Estimated uncertainties. [f] Obtained by a quadratic polynomial fit to eq. (7).

only as a guide for identification purposes, until data become available which either confirm or revise these predictions.

## References


[1] E. Hinnov, Phys. Rev. 14A (1976) 1533.

[2] W.L. Wiese and S.M. Younger, in Proc. Fourth Intern. Beam-foil spectroscopy Conf. (Plenum Press, New York, 1976).

[3] R.D. Cowan, Spectra of highly ionized atoms of Tokamak interest, Los Alamos Report No. LA-6679-MS (Nat. Tech. Infor. Service, Springfield Va, 1977).

[4] Cf. ref. [14], fig. 2.

[5] C. Froese Fischer, J. Phys. B 10 (1977) 1241.

[6] B. Edlén, Physica 13 (1947) 545.

[7] B. Edlén, in Handbuch der Physik XXVII (Springer Verlag, 1964) pp 165–185.

[8] J.D. Garcia and J.E. Mack, J. Opt. Soc. Am. 55 (1965) 654.

[9] Primary references for the older work are given by C.E. Moore in Atomic energy levels, NSRDS NBS 35 (U.S. Gov't. Printing Office, Washington DC, re-issued 1971).

[10] W.C. Martin and V. Kaufman, J. Res. NBS 74A (1970) 11.
[11] Y.N. Joshi, K.S. Bhatia and W.E. Jones, Spectrochimica Acta 28B (1973) 149.
[12] Th.A.M. van Kleef, private communication.
[13] B.C. Fawcett, B.B. Jones and R. Wilson, Proc. Phys. Soc. (London) 78 (1961) 1223.
[14] J. Reader and N. Acquista, Phys. Rev. Lett. 39 (1977) 184.
[15] E. Alexander, M. Even-Zohar, B.S. Fraenkel and S. Goldsmith, J. Opt. Soc. Am. 61 (1971) 508.