An explicit empirical formula for fine-structure separations of $^2P^o$ and ^2D terms for ions in the Cu isoelectronic sequence

L J Curtis

Department of Physics and Astronomy, The University of Toledo, Toledo, Ohio 43606, USA

Abstract. A screened hydrogen-like model has been used to re-express available measurements of fine-structure separations for $^2P^o$ and ^2D terms in the Cu isoelectronic sequence as screening parameters, which are found to be very regular and slowly varying as functions of Z, n and l. These regularities have been quantified by empirical searches for linearising mapping functions, which indicate that the screening parameter S is very well represented by a linear function of the reciprocal screened charge $S = a + b/(Z - S)$, with a slope a and intercept b which follow the relationships $a \propto (n-3)^k$ and $a + 2\sqrt{b} = \text{constant}$. This yields an explicit empirical formula for the fine structure for any value of Z and n for the isoelectronic sequence of these Rydberg series. Predictions for the fine-structure separations for the $n = 4$–8 $^2P^o$ and $n = 4$–6 ^2D terms for all ions from As V to U LXIV are presented.

1. Introduction

An extension of the standard screening parameter formulation of fine-structure data has been developed by which regularities can be studied along both an isoelectronic sequence and a Rydberg series simultaneously. In a comprehensive study of the Cu isoelectronic sequence, linearities have been revealed which permit accurate semi-empirical predictions for the $^2P^o$ and ^2D fine-structure separations for any principal quantum number of any ionisation stage.

The formulation of fine-structure separations in many-electron atoms in the context of a semi-empirical screening parametrisation has long been used to investigate isoelectronic regularities, to interpolate between and extrapolate beyond existing measurements, to reveal misclassifications and to identify perturbing influences. In this approach fine-structure separations in complex atoms are described using the theoretical expression for a single-electron atom with the nuclear charge replaced by an effective screened charge. The first application of this method was to x-ray doublets in neutral atoms (Sommerfeld 1916, 1919), where the screening parameters are nearly independent of atomic number. The method was extended to optical spectra (Goudsmit 1921, Landé 1924, Bowen and Millikan 1924) where the screening parameter exhibited a smooth variation along an isoelectronic sequence, later shown (Edlén 1964) to be well represented by a polynomial in the reciprocal screened charge. Recently, preliminary studies of the Cu isoelectronic sequence (Curtis 1977b, 1979) indicated that a *linear* polynomial is adequate to describe screening parameters for this sequence,

in contrast to the homologous Li and Na sequences, for which higher order polynomials are required (Edlén 1979, 1978). These results for the single valence electron Cu sequence are confirmed, extended and further elucidated by the study reported herein. It is shown that the screening parameters for the $^2P^\circ$ and ^2D terms for all but the lowest charge states can be expressed as explicit empirical functions of the nuclear charge and principal quantum number, permitting predictions both along the Rydberg series and along the isoelectronic sequence.

2. Calculational procedures

The fine-structure separation $\Delta\sigma(n, l, Z)$ for a doublet of principal quantum number n, orbital angular momentum quantum number l and nuclear charge Z can be written as a Sommerfeld expansion (Curtis 1977a) of the Dirac energy with quantum electrodynamic corrections (Garcia and Mack 1965) as

$$\Delta\sigma(n, l, Z) = \frac{R_Z \alpha^2 Z_s^4}{n^3 l(l+1)}\left[\left(1 + \sum_{\beta=1}^{\infty} (\alpha Z_s)^{2\beta} A_\beta(n, l)\right)\right.$$

$$\left. + [g_e - 2 + \delta_{l1}(4\alpha^3/3\pi)(1 - n^{-2})Z_s^2 \ln \alpha^2 Z_s^2](1 - m/M_Z)\right] \tag{1}$$

where R_Z is the reduced-mass-corrected Rydberg constant, α is the fine-structure constant, g_e is the gyromagnetic factor for the electron, m and M_Z are the masses of the electron and the nucleus and Z_s is the effective screened charge which equation (1) serves to define. The Sommerfeld expansion coefficients $A_\beta(n, l)$ are positive rational fractions. Here the Sommerfeld expansion is preferable to the exact expression for the Dirac energy for two reasons. Firstly, the expansion allows the dominant portion of the Z_s dependence to be factored outside the brackets, so that the expression can be easily solved for Z_s by numerical iteration. Secondly, this expansion avoids the severe truncation errors which occur for small values of αZ_s when the exact expression is used and retains accuracy for very high values of αZ_s. (The quadruple nesting of quantities near unity in the exact expression can introduce truncation errors even when very high precision numerical methods are utilised.) For these reasons a special procedure has been developed (Curtis 1979) by which the Sommerfeld expansion is accurate to essentially unlimited order. To do this, the Sommerfeld expansion coefficients can be expressed as (Curtis 1977a)

$$A_\beta(n, l) = -2 \sum_{\gamma=0}^{2\beta} \frac{(l+1)^{\gamma+1} - (l)^{\gamma+1}}{[l(l+1)]^\gamma} n^{\gamma-2\beta} C_{\beta+2,\gamma+1} \tag{2}$$

where C_{ij} is an auxiliary array of rational fractions which has been tabulated for values corresponding to $\beta \leqslant 7$ (Curtis 1977a). The $\beta > 7$ portion of the sum can be taken into account by noting that the ratio $A_\beta/A_{\beta-1}$ becomes nearly a constant for large β and can be replaced by A_7/A_6 for $\beta > 7$. Thus the series approaches a geometric progression which can be summed by Euclid's theorem. The infinite series in equation (1) is therefore quite accurately represented by the finite series summed to $\beta \leqslant 7$ if A_7 is replaced by $\bar{A}_7$, where

$$\bar{A}_7 = A_7/(1 - \alpha^2 Z_s^2 A_7/A_6). \tag{3}$$

With this procedure, numerical calculations indicate that the accuracy of the expansion exceeds the experimental precision for the value of α for all systems studied herein.

Measured values for $\Delta\sigma(n, l, Z)$ and their quoted uncertainties were reduced along the isoelectronic sequence to values and uncertainties for $Z_s(n, l, Z)$ by iterative inversion of equation (1). These were rewritten as a screening parameter $S(n, l, Z)$, defined as

$$S(n, l, Z) = Z - Z_s(n, l, Z) \tag{4}$$

which, following earlier successful empirical analyses (Edlén 1964) as fitted to a power series in the reciprocal screened charge

$$S(n, l, Z) = a(n, l) + b(n, l)/Z_s(n, l, Z) + \ldots \tag{5}$$

by weighted linear least-squares adjustment of the empirical parameters $a(n, l)$, $b(n, l)$, etc. As will be discussed in the next section, if the first few stages of ionisation are excluded, all of the terms studied here were very well described by a linear form of equation (5), so higher order powers will be assumed to be absent in the discussion which follows. Solved simultaneously, equations (4) and (5) yield a quadratic function of S or Z_s which contains a non-physical as well as a physical root. The physical solution for Z_s as a function of Z is given by

$$Z_s = \tfrac{1}{2}\{(Z - a) + [(Z - a)^2 - 4b]^{1/2}\}. \tag{6}$$

It is clear that this formulation breaks down for low ionisation states, since for the square root to be real the following condition must be satisfied

$$Z > z_0 = a + 2\sqrt{b}. \tag{7}$$

In all of the cases treated here z_0 had very nearly the same numerical value and only the first three or four charge states were excluded by the condition of reality of equation (6). Use of equation (5) as a linear fitting function would treat S and $1/Z_s$ as a dependent and an independent variable, when in fact they are correlated by equation (4). A functional relationship between an experimentally uncertain dependent variable and a precisely known independent variable could be obtained by studying S as a function of Z, but this relationship is not linear in the fitting parameters and must be search-fitted. Therefore an equivalent but computationally simpler iterative procedure was used in which equation (5) was adjusted by a standard weighted linear regression, using the experimental value for S and the value for $1/Z_s$ predicted from the previous iteration.

The empirical study was then carried a step further, empirically searching for linearising mapping functions as a means of exploring the dependence of $a(n, l)$ and $b(n, l)$ upon n.

3. Results

The experimental fine-structure data used in this formulation are listed, along with quoted or estimated uncertainties and source references, in table 1. These data were converted to screening parameters using equations (1) and (4). Figure 1 displays a plot of S against $1/(Z - S)$ for the 4p, 5p, 6p, 7p and 4d, 5d and 6d fine-structure separations. The reduced fine-structure separations for the isoelectronic sequence of each term were fitted to a power series in the reciprocal screened charge by weighted

Table 1. Available published values for fine-structure separations (in cm^{-1}) with estimated uncertainties and source references.

Ion	Z	4P	5P	6P	7P	4D	5D	6D[a]	Refs
Ge IV	32	2 788 (4)	938[a]	142[a]	—	254 (5)	80[a]	—	L(29)
As V	33	4 110 (4)	—	—	—	445 (5)	—	—	SH(28)
Se VI	34	5 698 (1)	2 076·7 (40)	1 004 (7)	538 (8)	679·9 (5)	296·0 (5)	—	JV(78)
Br VII	35	7 580 (11)	—	—	—	861[a]	—	—	RR(34)
Kr VIII	36	9 779 (9)	3 740 (40)	—	—	1 290 (35)[a]	530 (35)	—	F(61), L(80)
Rb IX	37	12 334 (2)	—	—	—	—	—	—	RA(77)
Sr X	38	15 266 (2)	—	—	—	—	1 015 (10)	—	RA(77), R(80)
Y XI	39	18 622 (4)	7 541 (8)	3 840 (24)	—	2 868 (5)	1 285 (38)	658 (62)	RA(79b)
Zr XII	40	22 425 (2)	9 208 (4)	4 723 (16)	—	3 567 (2)	1 609 (14)	813 (40)[b]	RA(79c)
Nb XIII	41	26 720 (4)	11 080 (8)	5 723 (20)	3 237 (34)	4 368 (6)	1 960 (20)	1 051 (50)	RA(80)
Mo XIV	42	31 547 (5)	13 218 (20)	6 776 (25)	3 880 (500)	5 266 (8)	2 417 (12)	—	RA(79a), CE(77)
Pd XVIII	46	57 020 (120)	24 610 (200)	—	—	10 350 (180)	4 780 (140)	—	C(77, 79)
Ag XIX	47	65 150 (140)	28 250 (250)	—	—	11 870 (230)	5 420 (170)	—	C(77, 79)
Cd XX	48	73 860 (160)	32 460 (300)	—	—	13 540 (280)	6 390 (200)	—	C(77, 79)
In XXI	49	84 130 (400)	36 510 (700)	—	—	15 660 (350)	7 250 (300)	—	C(77, 79)
Xe XXVI	54	148 060 (1900)	—	—	—	—	—	—	H(76)

[a] Not used in the fitting.
[b] Blended.

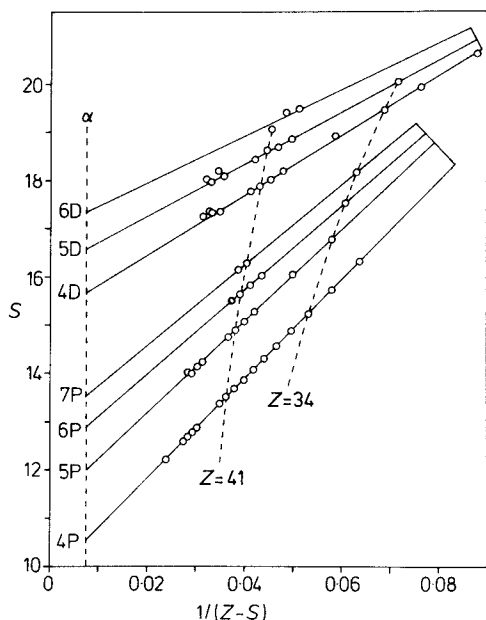|	
C(77, 79)	Curtis (1977b, 1979).
CE(77)	Curtis et al (1977).
F(61)	Fawcett et al (1961).
H(76)	Hinnov (1976).
JV(78)	Joshi and van Kleef (1978).
L(29)	Lang (1929).
L(80)	Livingston et al (1980).
RR(34)	Rao and Rao (1934).
RA(77)	Reader and Acquista (1977).
RA(79)	Reader and Acquista (1979a, b, c).
RA(80)	Reader and Acquista (1980).
R(80)	Reader (1980, private communication).
SH(28)	Sawyer and Humphreys (1928).

Figure 1. S versus $1/(Z-S)$ for the $^2P^\circ$ and ^2D terms of the copper sequence. Circles represent measured data and full curves denote weighted least-squares fits for all but 6d, which is extrapolated using equations (8) and (9). In order to provide a guide to the identity of the data points broken curves connect the selenium ($Z = 34$) and niobium ($Z = 41$) points and mark $Z - S = \alpha$ where the Sommerfeld expansion breaks down.

linear least-squares adjustment of the parameters $a(n, l)$, $b(n, l)$ etc in equation (5). The points were weighted according to the uncertainties in table 1, transformed into screening parameter space, and the iterative procedure described in the previous section was utilised to account for the correlation between the variables S and $1/(Z - S)$. If the first few ionisation stages were excluded, the χ^2 test indicated that the inclusion of powers of $1/(Z - S)$ higher than the first is not justified. For all except 6d (for which only two unblended data points are available) the fitted curves are also plotted in figure 1. For 6d the curve drawn is extrapolated from the 4d and 5d data. The high degree of linearity is clearly manifested by this plot. The fitted values for $a(n, l)$ and $b(n, l)$ are listed in table 2.

Table 2. Isoelectronic fits to equation (5) and values for equation (7).

n	l	a	b	z_0
4	1	9·80	102·4	30·0
5	1	11·28	94·8	30·8
6	1	12·19	87·9	30·9
7	1	12·94	82·9	31·2
8	1	(13·53)[a]	(75·5)[a]	
4	2	15·23	61·6	30·9
5	2	16·17	54·2	30·9
6	2	(16·74)[a]	(50·1)[a]	

[a] Predicted using equations (8) and (9).

These fits were used to predict S, and therefore $\Delta\sigma$, as a function of Z. Estimates of the uncertainties in these predictions were also obtained as a function of Z from the error matrix of the fit, but such estimates include only a propagation of the errors in the

Table 3. Predicted fine-structure separations (in cm^{-1}; AEB denotes $A \times 10^{B}$).

Ion	Z	4P	5P	6P	7P	8P	4D	5D	6D
As V	33	0·4110E4	0·1423E4	0·6748E3	0·3523E3	0·2290E3	0·4418E3	0·1906E3	0·9785E2
Se VI	34	0·5701E4	0·2075E4	0·1006E4	0·5380E3	0·3449E3	0·6800E3	0·2960E3	0·1533E3
Br VII	35	0·7579E4	0·2854E4	0·1404E4	0·7629E3	0·4859E3	0·9743E3	0·4275E3	0·2229E3
Kr VIII	36	0·9777E4	0·3775E4	0·1878E4	0·1032E4	0·6555E3	0·1333E4	0·5888E3	0·3088E3
Rb IX	37	0·1233E5	0·4855E4	0·2437E4	0·1352E4	0·8569E3	0·1763E4	0·7838E3	0·4131E3
Sr X	38	0·1526E5	0·6109E4	0·3089E4	0·1726E4	0·1094E4	0·2272E4	0·1016E4	0·5380E3
Y XI	39	0·1862E5	0·7553E4	0·3844E4	0·2161E4	0·1369E4	0·2870E4	0·1290E4	0·6858E3
Zr XII	40	0·2243E5	0·9206E4	0·4711E4	0·2663E4	0·1687E4	0·3565E4	0·1611E4	0·8589E3
Nb XIII	41	0·2673E5	0·1108E5	0·5700E4	0·3237E4	0·2052E4	0·4366E4	0·1981E4	0·1060E4
Mo XIV	42	0·3156E5	0·1320E5	0·6821E4	0·3890E4	0·2467E4	0·5283E4	0·2407E4	0·1291E4
Tc XV	43	0·3696E5	0·1559E5	0·8085E4	0·4628E4	0·2937E4	0·6325E4	0·2893E4	0·1556E4
Ru XVI	44	0·4298E5	0·1826E5	0·9503E4	0·5457E4	0·3466E4	0·7503E4	0·3444E4	0·1857E4
Rh XVII	45	0·4965E5	0·2123E5	0·1109E5	0·6386E4	0·4059E4	0·8828E4	0·4065E4	0·2197E4
Pd XVIII	46	0·5703E5	0·2453E5	0·1285E5	0·7422E4	0·4721E4	0·1031E5	0·4762E4	0·2579E4
Ag XIX	47	0·6515E5	0·2818E5	0·1480E5	0·8572E4	0·5456E4	0·1196E5	0·5541E4	0·3007E4
Cd XX	48	0·7408E5	0·3220E5	0·1696E5	0·9844E4	0·6271E4	0·1380E5	0·6408E4	0·3484E4
In XXI	49	0·8386E5	0·3662E5	0·1933E5	0·1125E5	0·7169E4	0·1582E5	0·7369E4	0·4013E4
Sn XXII	50	0·9454E5	0·4146E5	0·2194E5	0·1279E5	0·8158E4	0·1806E5	0·8429E4	0·4598E4
Sb XXIII	51	0·1062E6	0·4676E5	0·2479E5	0·1448E5	0·9244E4	0·2051E5	0·9597E4	0·5243E4
Te XXIV	52	0·1188E6	0·5253E5	0·2790E5	0·1633E5	0·1043E5	0·2320E5	0·1088E5	0·5951E4
I XXV	53	0·1326E6	0·5880E5	0·3130E5	0·1834E5	0·1173E5	0·2614E5	0·1228E5	0·6727E4
Xe XXVI	54	0·1475E6	0·6562E5	0·3498E5	0·2054E5	0·1314E5	0·2933E5	0·1381E5	0·7575E4
Cs XXVII	55	0·1635E6	0·7300E5	0·3898E5	0·2292E5	0·1467E5	0·3281E5	0·1547E5	0·8499E4
Ba XXVIII	56	0·1809E6	0·8098E5	0·4331E5	0·2550E5	0·1633E5	0·3658E5	0·1728E5	0·9503E4
La XXIX	57	0·1996E6	0·8960E5	0·4799E5	0·2829E5	0·1813E5	0·4065E5	0·1924E5	0·1059E5
Ce XXX	58	0·2197E6	0·9888E5	0·5304E5	0·3130E5	0·2007E5	0·4506E5	0·2136E5	0·1177E5
Pr XXXI	59	0·2413E6	0·1089E6	0·5847E5	0·3455E5	0·2217E5	0·4980E5	0·2365E5	0·1304E5
Nd XXXII	60	0·2645E6	0·1196E6	0·6431E5	0·3805E5	0·2443E5	0·5491E5	0·2611E5	0·1442E5

Pm XXXIII	61	0·2893E6	0·1311E6	0·7059E5	0·4180E5	0·2685E5	0·6039E5	0·2876E5	0·1589E5
Sm XXXIV	62	0·3159E6	0·1434E6	0·7731E5	0·4583E5	0·2945E5	0·6627E5	0·3160E5	0·1748E5
Eu XXXV	63	0·3443E6	0·1566E6	0·8451E5	0·5015E5	0·3224E5	0·7256E5	0·3465E5	0·1918E5
Gd XXXVI	64	0·3746E6	0·1708E6	0·9222E5	0·5477E5	0·3523E5	0·7929E5	0·3791E5	0·2100E5
Tb XXXVII	65	0·4069E6	0·1858E6	0·1004E6	0·5971E5	0·3842E5	0·8647E5	0·4139E5	0·2295E5
Dy XXXVIII	66	0·4413E6	0·2019E6	0·1092E6	0·6498E5	0·4183E5	0·9412E5	0·4511E5	0·2503E5
Ho XXXIX	67	0·4779E6	0·2190E6	0·1186E6	0·7060E5	0·4547E5	0·1023E6	0·4907E5	0·2725E5
Er XL	68	0·5168E6	0·2372E6	0·1285E6	0·7659E5	0·4934E5	0·1109E6	0·5329E5	0·2961E5
Tm XLI	69	0·5582E6	0·2565E6	0·1391E6	0·8296E5	0·5347E5	0·1201E6	0·5778E5	0·3213E5
Yb XLII	70	0·6021E6	0·2771E6	0·1504E6	0·8974E5	0·5786E5	0·1299E6	0·6254E5	0·3480E5
Lu XLIII	71	0·6487E6	0·2989E6	0·1624E6	0·9693E5	0·6252E5	0·1403E6	0·6759E5	0·3763E5
Hf XLIV	72	0·6980E6	0·3220E6	0·1751E6	0·1046E6	0·6747E5	0·1512E6	0·7294E5	0·4063E5
Ta XLV	73	0·7503E6	0·3466E6	0·1885E6	0·1127E6	0·7271E5	0·1628E6	0·7860E5	0·4381E5
W XLVI	74	0·8056E6	0·3725E6	0·2028E6	0·1213E6	0·7828E5	0·1751E6	0·8459E5	0·4718E5
Re XLVII	75	0·8641E6	0·4000E6	0·2178E6	0·1303E6	0·8417E5	0·1880E6	0·9092E5	0·5073E5
Os XLVIII	76	0·9259E6	0·4291E6	0·2338E6	0·1400E6	0·9040E5	0·2016E6	0·9759E5	0·5449E5
Ir XLIX	77	0·9912E6	0·4598E6	0·2507E6	0·1501E6	0·9699E5	0·2160E6	0·1046E6	0·5845E5
Pt L	78	0·1060E7	0·4922E6	0·2685E6	0·1609E6	0·1040E6	0·2311E6	0·1121E6	0·6262E5
Au LI	79	0·1133E7	0·5265E6	0·2873E6	0·1722E6	0·1113E6	0·2471E6	0·1199E6	0·6702E5
Hg LII	80	0·1210E7	0·5626E6	0·3071E6	0·1842E6	0·1191E6	0·2638E6	0·1281E6	0·7165E5
Tl LIII	81	0·1290E7	0·6007E6	0·3280E6	0·1968E6	0·1273E6	0·2814E6	0·1367E6	0·7652E5
Pb LIV	82	0·1376E7	0·6408E6	0·3501E6	0·2101E6	0·1359E6	0·2999E6	0·1458E6	0·8163E5
Bi LV	83	0·1465E7	0·6831E6	0·3733E6	0·2241E6	0·1450E6	0·3192E6	0·1553E6	0·8700E5
Po LVI	84	0·1560E7	0·7276E6	0·3978E6	0·2389E6	0·1546E6	0·3395E6	0·1653E6	0·9263E5
At LVII	85	0·1659E7	0·7745E6	0·4236E6	0·2544E6	0·1646E6	0·3608E6	0·1758E6	0·9854E5
Rn LVIII	86	0·1764E7	0·8238E6	0·4507E6	0·2708E6	0·1752E6	0·3831E6	0·1868E6	0·1047E6
Fr LIX	87	0·1874E7	0·8756E6	0·4791E6	0·2880E6	0·1864E6	0·4064E6	0·1983E6	0·1112E6
Ra LX	88	0·1989E7	0·9301E6	0·5091E6	0·3060E6	0·1981E6	0·4308E6	0·2103E6	0·1180E6
Ac LXI	89	0·2111E7	0·9874E6	0·5406E6	0·3250E6	0·2104E6	0·4563E6	0·2229E6	0·1251E6
Th LXII	90	0·2238E7	0·1048E7	0·5736E6	0·3450E6	0·2234E6	0·4829E6	0·2360E6	0·1325E6
Pa LXIII	91	0·2372E7	0·1111E7	0·6084E6	0·3659E6	0·2370E6	0·5107E6	0·2497E6	0·1403E6
U LXIV	92	0·2513E7	0·1177E7	0·6448E6	0·3879E6	0·2512E6	0·5398E6	0·2641E6	0·1484E6

experimental data and neglect, for example, errors in the assumed form of the fitting function. Thus these estimates are unrealistically small (e.g., the fitting uncertainty for the 4p fine-structure separation for $Z = 92$ is less than one part in 10^4) in view of the empirical nature of the observed linearity. However, these predictions would be very useful in classifying highly ionised spectra even if their accuracy were in the per cent range.

In order to attempt extrapolations to higher n values, the empirical systematics of $a(n, l)$ and $b(n, l)$ were also examined using various mapping functions, displayed and least-squares fitted on a computer graphics terminal. Of the many mapping functions attempted, there was one which stood out because of the linearity of its relationship. This is shown in figure 2, in which $a(n, l)$ is plotted against $(n - 3)$ $(n - 3$ being the difference between the principal quantum number of the valence electron and that of the highest core electrons). For the $^2P^\circ$ terms, the points fall along a straight line to within 0·2% of $a(n, l)$ implying a relationship
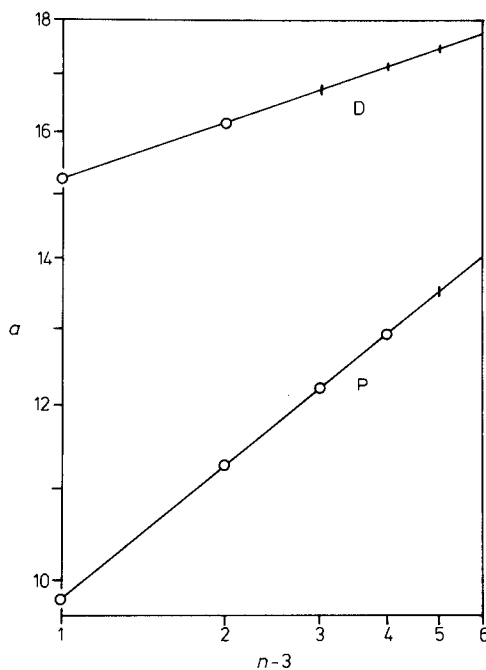
$$a(n, l) = p(l)(n - 3)^{k(l)}. \tag{8}$$

Figure 2. a plotted against $n - 3$ for the ^2P and ^2D terms of the copper sequence. Circles represent the values of the intercepts and corresponding quantum numbers of the fitted lines in figure 1.

Least-squares adjustment of equation (8) to the $^2P^\circ$ data yields $p(1) = 9·80$ and $k(1) = 0·20$, while a similar adjustment for the ^2D data yields $p(2) = 15·2$ and $k(2) = 0·09$. Further, it was noted that the slopes of the fitted lines decrease as the intercepts increase. This trend can be made quantitative by noting that equation (7), the condition for the square root in equation (6) to be real, yields essentially the same numerical value

for all the Rydberg series studied here. Thus the slope and intercept are related by

$$z_0 = a + 2\sqrt{b} \simeq 30\cdot9. \tag{9}$$

To display the validity of this relationship, the values of z_0 are also listed in table 2.

The relationships expressed in equations (8) and (9) permit the extrapolation of known fine-structure separations not only to higher charge states of the isoelectronic sequence, but also to higher members of the individual Rydberg series, through their substitution into equation (6) and its subsequent substitution into equation (1). Estimates of $a(n, l)$ and $b(n, l)$ for the 8p and 6d terms are listed in table 2 and, if the results are borne out by future measurements, the extrapolations could be made for much higher principal quantum numbers. The prediction for 6d is particularly important to verify experimentally, since the ^{2}D fit in figure 2 is based upon only two points, and thus does not check the validity of equation (8) for ^{2}D. The predictions for the fine-structure separations for the terms $n = 4$–8 ^{2}P$^\circ$ and $n = 4$–6 ^{2}D for all ions from As v through U LXIV are given in table 3.

4. Conclusion

The results presented in table 2 make clear predictions for the fine-structure separations for many ^{2}P$^\circ$ and ^{2}D terms in the Cu isoelectronic sequence which have not yet been measured. These predictions can be useful in future spectroscopic analyses and possibly in the identification of Cu-like heavy-metal ions which are sometimes observed as impurities in high-temperature plasmas in controlled fusion devices (e.g. Hinnov 1976). This study also motivates additional fine-structure measurements for highly ionised members of this sequence since they would verify whether the high degree of linearity observed is actually retained to very high stages of ionisation. Additional measurements would be particularly valuable for the 6d ^{2}D terms, since they could confirm or refute the validity of equation (8) for $l = 2$. Finally, the linearities which have been revealed here empirically must have fundamental theoretical significance, which could possibly be explored if the assumptions necessary to duplicate it using *ab initio* theories were known.

Acknowledgments

References

Bowen I S and Millikan R A 1924 *Phys. Rev.* **24** 209–22
Curtis L J 1977a *J. Phys. B: Atom. Molec. Phys.* **10** L641–5
—— 1977b *Phys. Lett.* **64A** 43–6
—— 1979 *Phys. Lett.* **72A** 427–30
Curtis L J, Lindgård A, Edlén B, Martinson I and Nielsen S E 1977 *Phys. Scr.* **16** 72–6

Edlén B 1964 *Handb. der Phys.* vol 22 (Berlin: Springer) pp 165–85
—— 1978 *Phys. Scr.* **17** 565–74
—— 1979 *Phys. Scr.* **19** 255–66
Fawcett B C, Jones B B and Wilson R 1961 *Proc. Phys. Soc.* **78** 1223–6
Garcia J D and Mack J E 1965 *J. Opt. Soc. Am.* **55** 654–85
Goudsmit S 1921 *Naturwiss* **9** 995
Hinnov E 1976 *Phys. Rev.* A **14** 1533–41
Joshi Y N and van Kleef Th A M 1978 *Physica* **94C** 270–4
Landé A 1924 *Z. Phys.* **25** 46–57
Lang R J 1929 *Phys. Rev.* **34** 697–711
Livingston A E, Curtis L J, Schectman R M and Berry H G 1980 *Phys. Rev.* **21** 771–81
Rao A S and Rao K R 1934 *Proc. Phys. Soc.* **46** 163–8
Reader J and Acquista N 1977 *Phys. Rev. Lett.* **39** 184–7
—— 1979a *J. Opt. Soc. Am.* **69** 144–9 (Erratum on 6p in press)
—— 1979b *J. Opt. Soc. Am.* **69** 1285–8
—— 1979c *J. Opt. Soc. Am.* **69** 1659–62
—— 1980 *J. Opt. Soc. Am.* **70** 317–21
Sawyer R A and Humphreys C J 1928 *Phys. Rev.* **32** 583–92
Sommerfeld A 1916 *Ann. Phys., Lpz* **51** 1–94, 125–67
—— 1919 *Atombau und Spectrallinien* (Braunschweig: Viewig)