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Semi-Empirical Calculations of Fine Structure Splittings and Ionisation Potentials in the MgI Isoelectronic Sequence

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Abstract

A semi-empirical parametrisation of the singlet–triplet and fine structure splittings for available measurements of the $3s3p\ ^{1,3}P$ levels in the Mg I isoelectronic sequence has revealed regularities which are useful for interpolation and extrapolation. By combining an extrapolation of the empirical gross energies, Slater integrals and spin–orbit splitting factors to highly ionised members of this sequence with available measurements for the $3s^2\ ^1S$–$3s3p\ ^1P$ transitions, the positions of the members of the $3s3p\ ^3P$ multiplets and the ionisation potentials can be predicted.

1. Introduction

Highly ionised members of the magnesium isoelectronic sequence such as Kr XXV and Mo XXXI have been observed in tokamak plasma discharges [1]. Valuable information regarding the operation of these devices can be obtained from a study of the resonance transitions and from a knowledge of the ionisation potentials of these highly ionised atoms [2, 3]. The wavelengths of these transitions and the ionisation potentials can be calculated from ab initio procedures [4] or through isoelectronic extrapolations [5]. However, relativistic corrections to these states become large and difficult to reliably estimate in high Z atoms. Predictions for the ionisation potentials have been made [6–9], but agreement among various calculations is not generally of spectroscopic accuracy. For example, the ionisation potential predictions of Carlson et al. [6] and Kelly and Harrison [7] for Fe XV differ by 3%. We have used an extended screening parameter formalism to describe the spin-orbit splitting factor, the gross energy and the Slater integrals representing the direct and exchange part of the electrostatic interaction for the $3s3p$ configuration. Empirical regularities exhibited by these parametrisations permit interpolations and extrapolations and allow us to predict the ionisation potentials for all members of this sequence for which a measurement of the resonance transition $3s^2\ ^1S$–$3s3p\ ^1P$ exists. This also permits accurate estimates of the energies of the ^3P states.

The intermediate coupling equations for the $ns\,n'p\ ^{1,3}P$ states are well established [10]. Using the spectroscopic symbol to represent the excitation energy above the ground state, they are

$$^3P_2 = F_0 - G_1 + \zeta/2 \tag{1}$$

$$^3P_0 = F_0 - G_1 - \zeta \tag{2}$$

$$^3P_1 = F_0 - \zeta/4 - [(G_1 + \zeta/4)^2 + \zeta^2/2]^{1/2} \tag{3}$$

$$^1P_1 = F_0 - \zeta/4 + [(G_1 + \zeta/4)^2 + \zeta^2/2]^{1/2} \tag{4}$$

where F_0 includes the individual electron-nucleus electrostatic energies and the direct electron-electron electrostatic Slater integral, G_1 is the exchange electron-electron electrostatic Slater integral and ζ is the spin–orbit splitting factor. (Although not explicitly denoted here, F_0, G_1 and ζ are a different set of constants for each configuration $ns\,n'p$ for the given ion.) Since there are four energy level components for the configuration and only three theoretical quantities, the latter are overdetermined from eqs. (1)–(4). One set of solutions which is not too sensitive to small uncertainties in the measured energy levels is given by

$$\zeta = 2(^3P_2 - {}^3P_0)/3 \tag{5}$$

$$F_0 = (^1P_1 + {}^3P_1)/2 + (^3P_2 - {}^3P_0)/6 \tag{6}$$

$$G_1 = (^1P_1 + {}^3P_1)/2 - (^3P_2 + {}^3P_0)/2 \tag{7}$$

Our screening parametrisations of ζ and F_0 used, as a model, the theoretical expressions for a single $3p$ electron in a screened Coulomb potential. Since the $3s$ does not contribute to the spin–orbit splitting, the total triplet splitting should be the same as that of a single electron ^2P state.

$$\zeta \equiv R\alpha^2(Z - S_1)^4/81 + \text{higher order.} \tag{8}$$

Assuming the quantity F_0 is dominated by the single electron $3p$ energy,

$$F_0 \equiv IP - R(Z - S_0)^2/9 \tag{9}$$

Here R is the reduced-mass-corrected Rydberg energy ($R_\infty = 109\,737.315\,13\ \text{cm}^{-1}$), α is the fine structure constant ($\alpha = 1/137.036\,02$) and IP is the ionisation potential for the ion in question. S_1 and S_0 are the effective screening parameters (defined by these equations), which are expected to be regular and slowly varying as a function of Z. The higher order corrections to eq. (8) include the Sommerfeld expansion of the Dirac corrections to the Pauli energy, the anomalous magnetic moment of the electron, and radiative corrections.

By inverting the measured energy levels through eqs. (5) and (6) and mapping the results into screening parameter space through eqs. (8) and (9) it was found that the two screening parameters could be well represented by

$$S_1(Z) = a_1 + b_1/[Z - S_1(Z)] \tag{10}$$

$$S_0(Z) = a_0 + b_0/(Z - c_0) \tag{11}$$

The exchange integral G_1 does not have a classical or single electron counterpart, but it was found to be well described by

$$G/R = a_2 + b_2/(Z + c_2) \tag{12}$$

Thus, using the fitting parameters a_i, b_i and c_i, we can predict the positions of the $3s3p\ ^{1,3}P$ term values relative to the ionisation limit for the ions from Mg I through Mo XXXI. For those ions for which an accurate measurement of the $3s^2\ ^1S_0$–$3s3p\ ^1P_1$ resonance transition is available, we have also predicted the ionisation limit.

2. Fine structure splittings

When one of the electrons of a two electron configuration is in an s state the other electron will alone be responsible for the spin–orbit splitting. This gives a total splitting (neglecting spin-spin and spin-other-orbit interactions) for a triplet $ns\,n'p\,^3P$ which is the same as the doublet interval $np\,^2P$, so

$$^3P_2 - {}^3P_0 = {}^2P_{3/2} - {}^2P_{1/2} = 3\zeta/2 \qquad (13)$$

(cf. [5, p. 108]). This triplet splitting was therefore parametrised using the same procedure as has been recently applied to the Li [11], Na [12], Cu [13] single valence electron sequences and to the Be [14] two valence electron sequence. The theoretical expression for the fine structure of a single electron, modified by replacement of the nuclear charge by a single effective screened charge Z_s, was used as a model. The Sommerfeld expansion of the Dirac energy was carried to eighteenth order in αZ_s [15] and corrected to much higher order by a "geometric continuation" [16]. The charge dependences of quantum electrodynamic corrections, such as the anomalous magnetic moment of the electron and the radiative corrections, were also included [17]. In this manner each measured $J = 2$–0 fine structure splitting was reduced to a corresponding value of the screening parameter $S_1(Z)$. It has been found empirically [5] that the screening parameter is often accurately described by a power series expansion in the reciprocal screened charge, as given by eq. (10). The observed data were fitted by a standard weighted polynomial regression. Correlations between the ordinate and abscissa were removed by repeating the fitting process many times, using the fitting parameters from one iteration to compute $1/(Z - S_1)$ for the next until convergence was obtained. The chi-squared test (using estimated uncertainties) indicated that inclusion of powers higher than first order was not justified. A plot of S_1 vs. $1/(Z - S_1)$ for the available data in the Mg I isoelectronic sequence is shown in Fig. 1. An excellent straight line fit was obtained. It was difficult to assess the absolute uncertainties from the original data sources, so estimated uncertainties in the fine structure separations of 1% were used in the fitting. The regression yielded the values $a_1 = 4.777\,69$ and $b_1 = 11.478\,64$ which, through eqs. (10), (8) and (5) can be used to predict the value for $\Delta\sigma$ for any unmeasured ion, as well as to check for inconsistencies in those ions for which measurements have been made. Table I lists the primary data together with our predictions.

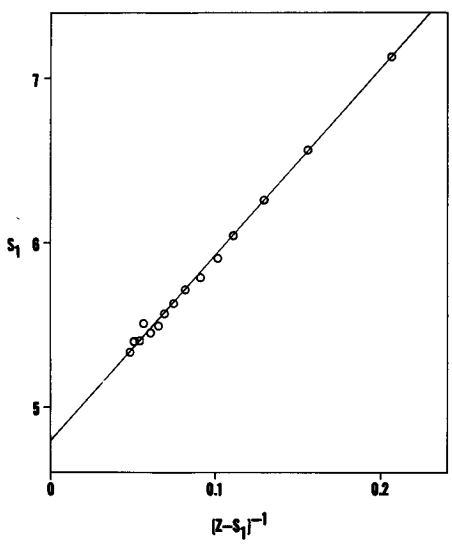

Fig. 1. Plot of the fine structure screening parameter vs. reciprocal screened charge for the $3s3p\,^3P$ terms in the Mg isoelectronic sequence. The circles represent experimental data points and the solid line is the weighted least square fit to the data.

Table I. *Fine structure splitting* $\Delta\sigma = {}^3P_2 - {}^3P_0\,(cm^{-1})$ *for the* $3s3p\,^3P$ *term in the Mg I isoelectronic sequence*

		$3s3p\,^3P_2 - 3s3p\,^3P_0$ cm^{-1}	
Z	Ion	Expt. (ref.)	Present calc.
12	Mg I	60.77 (18)	60.60
13	Al II	184.76 (19)	186.81
14	Si III	390.32 (20)	389.87
15	P IV	697.14 (21)	694.11
16	S V	1 131.16 (22)	1 125.40
17	Cl VI	1 718.0 (23)	1 712.2
18	Ar VII	2 486 (23)	2 486
19	K VIII	3 485 (24)	3 480
20	Ca IX	4 736 (24)	4 732
21	Sc X	6 313 (24)	6 280
22	Ti XI	8 199 (24)	8 169
23	V XII	10 250 (25)	10 443
24	Cr XIII	13 120 (26)	13 151
25	Mn XIV	16 180 (27)	16 344
26	Fe XV	19 870 (28)	20 077
30	Zn XIX		41 620
35	Br XXIV		88 646
36	Kr XXV		101 525
37	Rb XXVI		115 773
38	Sr XXVII		131 487
39	Y XXVIII		148 769
40	Zr XXIX		167 727
41	Nb XXX		188 470
42	Mo XXXI		211 115

3. Gross energy

The quantity $IP - F_0$ includes both the electron-nucleus excitation energy of the p electron and the non-exchange portion of the s–p electron-electron interaction energy. It is this part of the energy which is most likely to resemble a single electron analogue with an effective screened Coulomb potential. Therefore we have examined the quantity

$$S_0(Z) = Z - 3\sqrt{[IP(Z) - F_0(Z)]/R} \qquad (14)$$

in the hope that phenomenological deviations from this very

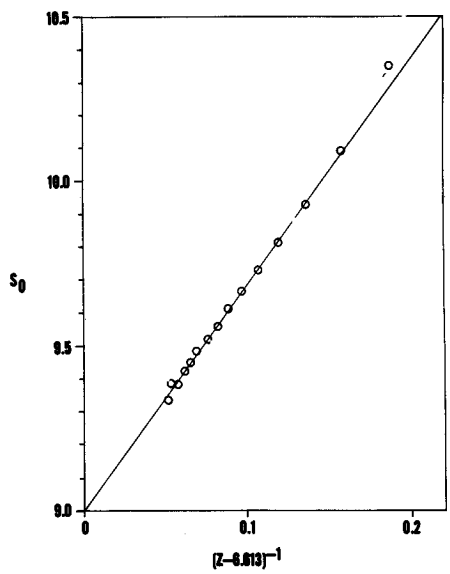

Fig. 2. Plot of $S_0(Z)$ vs. $1/(Z - c_0)$ where $c_0 = 6.613$.

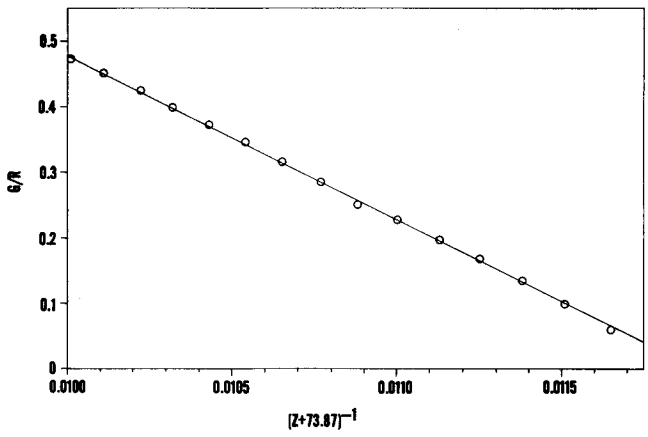

Fig. 3. Plot of G/R vs. $1/(Z + c_2)$ where $c_2 = 78.37$.

simple model would manifest themselves as small and isoelectronically regular variations in the empirical parameter $S_0(Z)$. The ionisation potentials were obtained from spectroscopic observations [18–28]. When the neutral ion is excluded from the fit, the isoelectronic variation of $S_0(Z)$ can be quite accurately described by eq. (11). Figure 2 shows a plot of $S_0(Z)$ vs. $1/(Z - c_0)$, where $c_0 = 6.613$ was least squares search fitted to give the best straight line in this space. The other two parameters of this three-parameter-fit are $a_0 = 8.9957$ and $b_0 = 6.940$. The extrapolation should be of high accuracy, since $S_0(Z)$ is nearly a constant in Z (notice that $S_0(Z)$ varies only from 9.935 to 9.077 between $Z = 13$ and 92).

4. Exchange integral

The exchange integral G_1 is expected to vary smoothly as a function of Z [5]. Although there is no single electron analogue for the dependence of G on Z, we found that the isoelectronic variation of G is well described by eq. (12). Figure 3 shows a plot of G/R as a function of $1/(Z + c_2)$, where $c_2 = 73.87$ was, here again, least squares search-fitted to give the best straight line in this space. The other two parameters in this three-parameter-fit are $a_2 = 2.9795$ and $b_2 = -249.9938$.

Table III. *Experimental and calculated ionisation potentials for the Mg I isoelectronic sequence*

		Ionisation potentials		
Z	Ion	Present values (eV)	Kelly and Harrison [7]	Carlson et al. [6]
13	Al II	18.9	18.828	18.66
14	Si III	33.4	33.492	34.27
15	P IV	51.3	51.37	53.73
16	S V	72.4	72.74	76.74
17	Cl VI	96.7	96.98	103.3
18	Ar VII	124.1	124.319	133.2
19	K VIII	154.8	154.86	166.8
20	Ca IX	188.5	188.54	202.7
21	Sc X	225.3	225.32	239.7
22	Ti XI	265.3	265.23	307.0
23	V XII	308.3	308.25	323.4
24	Cr XIII	354.4	355	364
25	Mn XIV	403.2	404	419.7
26	Fe XV	456.0	457	472.4
29	Cu XVIII	631.6[a]	631	638.3
30	Zn XIX	696.3[a]	696	714.4
31	Ga XX	764.2[a]	764	793.1
32	Ge XXI	835.2[a]	834	873.4
33	As XXII	909.5[a]	908	956.1
34	Se XXIII	986.7[a]	985	1041
36	Kr XXV	1190.2[b]	1147	1219
42	Mo XXXI	1718.7[c]		1805

Using the $3s^2\ ^1S_0$–$3s3p\ ^1P_1$ transitions observed by:
[a] Fawcett and Hayes [29]; [b] Hinnov [1]; [c] Burkhalter et al. [30].

5. Ionisation potentials

From these extrapolations, we can estimate the values of (a) the difference between the ionisation potential and direct electrostatic energy, (b) the exchange integral and (c) the spin-orbit splitting for any Z. If a single transition is known, eq. (4) can be used to obtain F_0, eq. (11) to obtain the ionisation potential, eq. (5) to get the spin–orbit splittings and eqs. (1), (2) and (3) to get the absolute energy levels of the triplet states. Table III shows the results obtained from our calculations and

Table II. *Experimental and calculated energy levels for the $3s3p\ ^3P_0$, $3s3p\ ^3P_1$ and $3s3p\ ^3P_2$ levels in the Mg I isoelectronic sequence*

		$^3P_0$ (cm^{-1})		$^3P_1$ (cm^{-1})		$^3P_2$ (cm^{-1})	
Z	Ion	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
13	Al II	37 393.02	37 325.02	37 453.91	37 389.7	37.577.79	37 511.83
14	Si III	52 724.69	53 088.58	52 853.28	53 217.4	53 115.01	53 478.48
15	P IV	67 918.03	68 057.17	68 146.48	68 285.6	68 615.17	68 751.28
16	S V	83 024.03	83 142.24	83 393.48	83 510.9	84 155.19	84 267.55
17	Cl VI	98 147	97 410.32	98 700	97 968.3	99 865	99 122.6
18	Ar VII	113 095	111 622.69	113 900	112 427.5	115 581	114 108.3
19	K VIII	126 812	127 171.31	127 924	128 289.4	130 297	130 651.2
20	Ca IX	141 612	141 669.8	143 111	143 177.2	146 348	116 401.4
21	Sc X	156 386	156 567.14	158 392	158 548.0	162 699	162 847.5
22	Ti XI	171 274	171 690.86	173 827	174 240.5	179 478	179 861.9
23	V XII	184 460	186 678.82	189 550	189 894.8	196 710	197 121.8
24	Cr XIII	201 810	201 909.8	205 740	206 261.0	214 930	215 420.3
25	Mn XIV	217 610	217 353.71	222 390	222 237.6	233 790	233 697.6
26	Fe XV	233 928	233 045.77	239 663	238 939.8	253 826	253 123

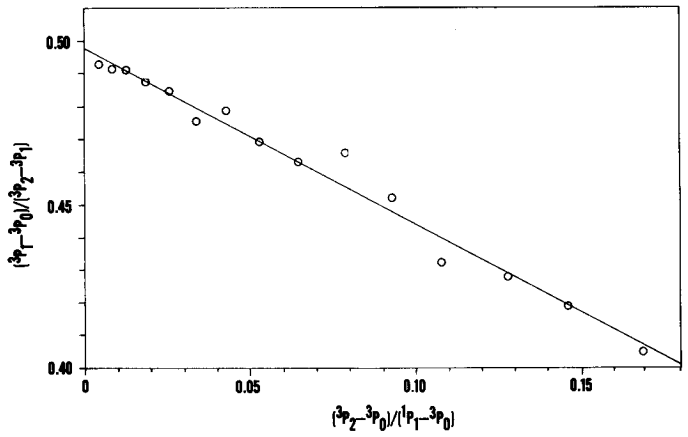

Fig. 4. Plot of $(^3P_1-^3P_0)/(^3P_2-^3P_1)$ vs. $(^3P_2-^3P_0)/(^1P_1-^3P_0)$ for the $3s3p\ ^3P$ members of the Mg isoelectronic sequence.

experimental values. We can predict from these observations the positions of the triplet states and the ionisation potentials and compare them with other values and theoretical calculations. It is seen that this method of extrapolation is as accurate as the theoretical calculations of the ionisation potentials by Carlson et al. [4] and polynomial fits of ionisation potentials made by Kelly and Harrison [5]. The positions of the triplets are compared with experimental values in Table II. It is seen again that excellent agreement is found between the two.

6. Revisions of the absolute energies of the triplet states

For atomic systems obeying intermediate coupling rules without configuration interaction, Condon and Shortley [9] show that a plot of $(^3P_1 - {}^3P_0)/(^3P_2 - {}^3P_1)$ as ordinate against $(^3P_2 - {}^3P_0)/(^1P_1 - {}^3P_0)$ as abscissa is a straight line with a slope of -0.5 and an intercept of 0.5. Figure 4 shows such a plot in the magnesium sequence. From this plot, we believe that the $^3P_0$ energy in Sc X should be increased by about 40 cm^{-1} relative to the $^3P_1$ level; in V XII, the $^3P_0$ must be decreased by about 150 cm^{-1} relative to the $^3P_2$ level and $^3P_1$ be decreased by about 80 cm^{-1} relative to the $^3P_2$ level.

7. Conclusions

From a survey of the recent data on the $3s3p$ states in the Mg I sequence, regularities have been observed in spin–orbit splittings and Slater integrals. By extrapolating these along the sequence, it is shown that reasonably accurate estimates for the fine structure splitting and ionisation potentials for highly ionised members of the sequence can be obtained from an observation of the $3s^2\ ^1S$–$3s3p\ ^1P$ transition alone.

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