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RESONANCE SEPARATIONS IN CONFIGURATIONS OF TYPE p^5s and d^9s

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Abstract

Considerations concerning the invariance of the configurations p^5 and d^9 with changing coupling lead to application of Houston's formulas to the cases p^5s and d^9s with negative A and X values. The expressions thus obtained are tested on the separations and g values of numerous spectra. The agreement is satisfactory.

As IS well known the separations of the levels within a configuration depend upon influences of two kinds: firstly those of relativistic origin obeying a $(Z-\sigma)^4$ law and secondly those depending upon the coupling between the electrons. Although through the researches of Goudsmit[1] and Slater[2] the niveau distances are known in the extreme cases of pure Russell-Saunders and of pure $\{jj\}$ coupling, the transition stage has heretofore been investigated only for simple configurations of two electrons one of which is in an s state. The formulas of this case were given by Houston.[3]

For pure $\{LS\}$ coupling such a configuration yields a triplet and a singlet term with inner quantum numbers $l-1$, l, $l+1$ and l; the total separation of the triplet term which is given by the Sommerfeld formula

$$\frac{\Delta\nu}{R} = \frac{\alpha^2(Z-\sigma)^4}{n^3l(l+1)} \tag{1}$$

is small compared with the distance between the two terms. Here A denotes the so-called interval factor, n and l are the quantum numbers of that electron which is not in the s state; Z is the nuclear charge, σ the screening number and $R\alpha^2$ a universal constant with the value 5.82. The position of the middle triplet level is fixed by Landé's interval rule.

In the other extreme case of pure $\{jj\}$ coupling the four levels are arranged in two narrow doublets with the distance (1) from each other. All one knows from elementary considerations about the transition is that the change in coupling will not affect the distance between levels whose inner quantum numbers occur only once, like $l-1$ and $l+1$.

If we define the centroid of the triplet term in the well-known way by

$$\Gamma(J) = \tfrac{1}{2}A(J(J+1) - l(l+1) - 2),$$

then the general formulas of Houston for the transition from $\{LS\}$ to $\{jj\}$ coupling may be written:

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[1] S. Goudsmit. Phys. Rev. **31**, 946 (1928).

[2] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[3] W. V. Houston, Phys. Rev. **33**, 297 (1929).

$$\left.\begin{aligned}
\Gamma_1(l) &= A\left\{\frac{X-1}{2}+\frac{1}{2}((X+1)^2+4l(l+1))^{1/2}\right\}\\
\Gamma(l+1) &= Al\\
\Gamma_2(l) &= A\left\{\frac{X-1}{2}-\frac{1}{2}((X+1)^2+4l(l+1))^{1/2}\right\}\\
\Gamma(l-1) &= -A(l+1)
\end{aligned}\right\}\tag{2}$$

X is the parameter which describes the transition; for $X=\infty$ we obtain pure $\{LS\}$, for $X=0$ pure $\{jj\}$ coupling.

Modification of Houston's Formulas

The application of these formulas to configurations of type p^5s and d^9s suggested itself to the authors for two reasons: firstly the inner quantum numbers are the same as in the cases ps and ds, and secondly it follows from the above mentioned considerations of Goudsmit, that the configurations p^5 and d^9 yield regardless of coupling ^2P and ^2D terms the separation of which is given by (1). The only difference is that these terms possess a negative A value, *i.e.* they are inverted. In (2) a negative A value would mean that (for large X) the singlet lies below the triplet term—which is almost never the case. Upon changing the sign of X also, it is seen however that the singlet term and the middle triplet level change places. Thus a negative X as well as a negative A brings about the desired arrangement with an inverted triplet term and a singlet level above it. If then $-X=X'$ and $-A=A'$ with X', $A'>0$ are introduced into (2) we obtain:

$$\left.\begin{aligned}
\Gamma_2(l) &= A'\left\{\frac{X'+1}{2}+\frac{1}{2}((X'-1)^2+4l(l+1))^{1/2}\right\}\\
\Gamma(l-1) &= A'(l+1)\\
\Gamma_1(l) &= A'\left\{\frac{X'+1}{2}-\frac{1}{2}((X'-1)^2+4l(l+1))^{1/2}\right\}\\
\Gamma(l+1) &= A'l.
\end{aligned}\right\}\tag{3}$$

For positive X' the magnitude of the four Γ values is in the order in which they are given above. It is readily seen that for large or small X' values, that is to say complete $\{LS\}$ or complete $\{jj\}$ coupling, the levels have indeed the position required.

All that has been said about the separations holds *mutatis mutandis* for the g values of the Zeeman effect. Due to the principle of the permanency of the g sums the g values of the outer triplet levels (with inner quantum numbers $l\pm1$) are independent of the coupling. They remain unaltered and thus offer nothing new. The g values of the middle triplet level and the singlet level however are obtained from Houston's expressions by introducing $-X=X'>0$. Thus the following formulas are arrived at:

$$\left.\begin{aligned} g_2(l) &= 1 + \frac{1}{2l(l+1)} + \frac{X' - 1}{2l(l+1)((X'-1)^2 + 4l(l+1))^{1/2}} \\ g_1(l) &= 1 + \frac{1}{2l(l+1)} - \frac{X' - 1}{2l(l+1)((X'-1)^2 + 4l(l+1)]^{1/2}} \end{aligned}\right\} \tag{4}$$

Comparison With Data

A vast amount of spectroscopic material can be interpreted by means of the equations (3), because levels of type p^5s and d^9s occur in a series of well investigated spectra of rare-gas type and of Ni, Pd and Pt type.[4] Fortunately these spectra have lost their Russell-Saunders character almost completely. The comparison with the data was carried out in the following manner. First from the distance $\Gamma(l-1)-\Gamma(l+1)=A'(2l+1)$ the values of A' were obtained. Then by means of the second and fourth equation (3) the position of the centroid was determined. Finally two independant values of X' were calculated from Γ_2 and Γ_1 by means of the formula

$$X'_{1,2} = \frac{\Gamma_{1,2}}{A'} - \frac{l(l+1)}{(\Gamma_{1,2}/A') - 1} \tag{3'}$$

in order to avoid giving preferance to either level. The agreement of these two determinations is a measure for the degree of accuracy with which (3) represent the measured separations.

The following Tables I and II give the numerical values for the levels of type p^5s and d^9s respectively. The first and second columns contain symbols

Table I.

Spectrum	Configuration	$^1P_1-{}^3P_0$	$^3P_0-{}^3P_1$	$^3P_1-{}^3P_2$	A'	X_2	X_1	g_2	g_1
Ne I	$2p^53s$	1070.1	359.3	417.4	258.9	5.75	5.78	1.036	1.464
Ne I	$2p^54s$	153.7	584.0	194.8	259.6	1.33	1.35	1.220	1.280
Ne I	$2p^55s$	50.1	693.6	84.6	259.1	0.53	0.53	1.291	1.209
Ne I	$2p^56s$	21.7	738.6	42.7	260.4	0.24	0.25	1.314	1.186
Ne I	$2p^511s$	3.28	775.5	4.70	260.1	0.04	0.03	1.331	1.169
Na II	$2p^53s$	2481.0	592.0	765.5	452.8	7.17	7.14	1.023	1.477
Mg III	$2p^53s$	3688	977	1216	731	6.86	6.60	1.026	1.464
A I	$3p^54s$	846.2	803.1	606.8	470.0	3.09	3.11	1.101	1.399
A I	$3p^56s$	64.7	1236.5	77.1	471.2	1.56	0.25		
A I	$3p^57s$	9.23	1393.7	48.3	477.7	0.05	0.12		
A I	$3p^58s$	18.5	1452.5	−21.0	473.0	0.13	−0.07		
A I	$3p^59s$	8.61	1420.2	11.1	473.1	0.03	0.08		
K II	$3p^54s$	1312.0	1912.5	730.0	880.8	2.69	1.54	1.16	1.34
K II	$3p^55s$	291.8	1734.1	417.4	716.8	0.99	0.99	1.251	1.249
Ca III	$3p^54s$	1985.0	1681.4	1383.5	1021.7	3.38	3.45	1.087	1.413
Ca III	$3p^55s$	355.9	2462.3	563.4	1041.9	0.85	1.10	1.252	1.248
Kr I	$4p^55s$	655.0	4274.9	945.0	1740.0	0.920	0.915	1.257	1.243
Xe I	$5p^56s$	988.3	8141.6	977.6	3043.1	0.80	0.51	1.281	1.219

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[4] The sources of data on the Ni-, Pd-, and Pt-like spectra are listed in a paper by J. E. Mack, Phys. Rev. **34,** 18 (1929). Other sources are: Cu: G. Kruger; Phys. Rev. **34,** 1122 (1929). Ne: F. Paschen and R. Goetze, Seriengesetze der Linienspektren, 1922. Na: O. Laporte, Nature **121,** June 16 (1928). Mg: J. E. Mack and R. A. Sawyer, Science **68,** 306 (1928). A: K. W. Meissner, Zeits. f. Physik **39,** 172 (1926); **40,** 839 (1926). K, Ca: I. S. Bowen, Phys. Rev. **31,** 497 (1928). Kr: W. F. Meggers, T. L. de Bruin, C. J. Humphreys, B. S. Journ. Res. **3,** 129 (1929).

for the spectra and configurations in question. In the third, fourth and fifth columns the separations of the four levels are given in cm^{-1}. The sixth column contains the values of the interval factor A'. The seventh and eighth columns give the two values of X' as calculated from (3′), and finally in the ninth and tenth columns the g values are listed which were computed from (4) using an average X'.

TABLE II.

Spectrum	Configuration	$^1D_2-{}^3D_1$	$^3D_1-{}^3D_2$	$^3D_2-{}^3D_3$	A'	X_2	X_1	g_2	g_1
Ni I	$3d^94s$	1696.8	833.3	675.0	301.66	7.90	8.12	1.015	1.152
Ni I	$3d^95s$	150.4	1322.2	184.1	301.26	1.06	1.11	1.082	1.085
Cu II	$3d^94s$	2266.0	1151.2	918.5	413.94	7.73	8.02	1.015	1.151
Cu II	$3d^95s$	281.7	1748.7	320.9	413.9	1.44	1.38	1.077	1.090
Cu II	$3d^96s$	95.7	1935.7	133.9	413.9	0.54	0.57	1.091	1.076
Cu II	$3d^97s$	51.1	2001.6	69.6	414.2	0.29	0.29	1.095	1.071
Zn III	$3d^94s$	2650	1576	1178	551	6.93	7.09	1.018	1.148
Ga IV	$3d^94s$	2937	2120	1455	715	6.14	6.26	1.022	1.027
Ge V	$3d^94s$	3180	2796	1740	907	5.42	5.46	1.027	1.139
Pd I	$4d^95s$	1627.8	2338.9	1191.0	706	3.92	4.26	1.051	1.115
Ag II	$4d^95s$	2306.5	3017.7	1557.1	915	4.89	4.32	1.034	1.132
Cd III	$4d^95s$	2652.4	3866.0	1900.1	1153.2	3.91	4.08	1.040	1.127
In IV	$4d^95s$	2871	4912	2196	1422	3.51	3.67	1.044	1.122
Sn V	$4d^95s$	3025	6142	2478	1724	3.15	3.27	1.049	1.117
Pt I	$5d^96s$	3364.3	9356.1	775.9	2026	2.96	0.73		
Au II	$5d^96s$	1855.3	10125.2	2601.5	2545.3	1.53	2.05	1.070	1.096
Hg III	$5d^96s$	2679	12377	3179	3111	1.76	2.05	1.068	1.098
Tl IV	$5d^96s$	2916	15277	3588	3773	1.56	1.87	1.071	1.127

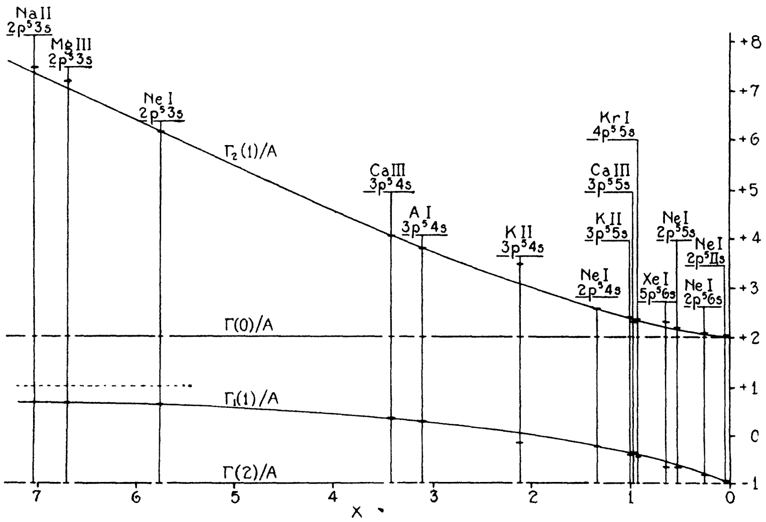

Fig. 1. Values of Γ/A' plotted against X'.

In Fig. 1 and 2 the values of Γ/A' are plotted against X' for the configurations p^5s and d^9s. Obviously by dividing with A' we free ourselves of the dependance upon the spin doublet of the preceding ion and are then in a position to study the dependence of the separations upon X' alone.

The bad agreement in the case of platinum is probably due to the fact that our equations (3) which are only the result of a first order calculation do not hold in the case of very large A' values which are comparable with the ionization potential d^9s-d^9. We thus understand the better agreement for the higher isoelectronic analogues of Pt I, namely Au II, Hg III, etc.

On the other hand the total lack of agreement for the higher series members $3p^56s$ to $3p^59s$ of A I renders doubtful the identifications of the combinations involved. The same might be said of $3p^54s$ of K II.

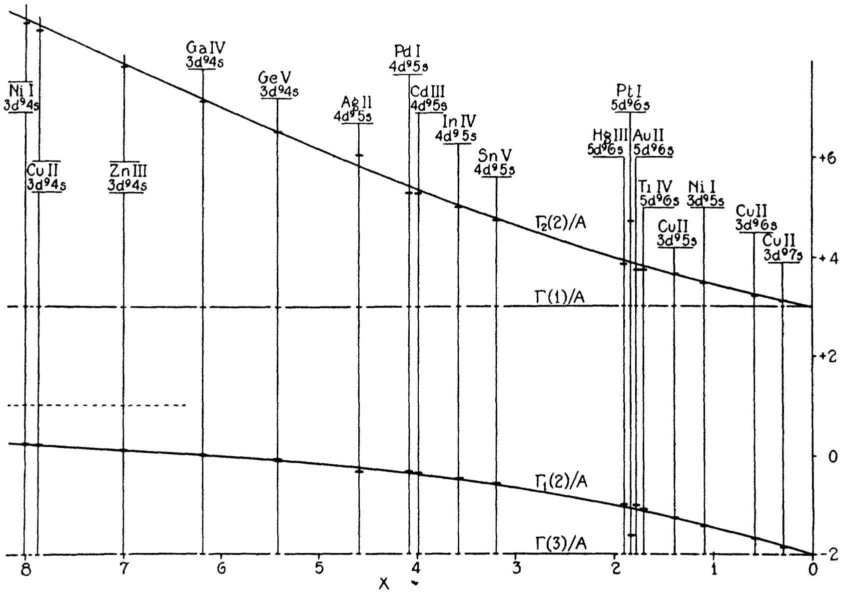

Fig. 2. Values of Γ/A' plotted against X'.

It is interesting to study the dependence of X' upon Z for a group of isoelectronic spectra. It seems that after some initial irregularities X' varies almost linearly with Z.

The only spectrum in which a comparison of the equations (4) with the experiment is possible, is Ne I. In this spectrum the g values of the singlet and the middle triplet level of $2p^53s$ were measured by Back.[5] The following Table III gives the comparison of experimental and theoretical values.

TABLE III.

	observed (Back)	calculated Table II.	calculated $\{LS\}$ coupling	calculated $\{jj\}$ coupling
g_2	1.034	1.036	1.000	1.300
g_1	1.464	1.464	1.500	1.200

The agreement is excellent. Many attempts have been made in the past to compute the g values of these Ne levels, but naturally only the values in limiting cases were obtained.

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[5] E. Back, Ann. d. Physik **76**, 329 (1925).