SINGLET-TRIPLET INTERVAL RATIOS FOR sp, sd, sf, p^5s AND d^9s CONFIGURATIONS*

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Abstract

A systematic comparison of the known data on the singlets and triplets arising from sp, sd, sf, p^5s and d^9s configurations with the theory of Houston shows that the theory gives a good account of the deviations from the Landé interval rule which accompany departure from Russell-Saunders coupling. There are numerous significant discrepancies, however. Writing ${}^1L_l$ and ${}^3L_{l+1}$, ${}^3L_l$, ${}^3L_{l-1}$ with $L=P, D, F$, when $l=1, 2, 3$ for the term values, we plot as abscissa $({}^3L_{l-1}-{}^3L_{l+1})/|{}^3L_l-{}^1L_l|$ and $({}^3L_{l-1}-{}^3L_l)/({}^3L_l-{}^3L_{l+1})$ as ordinate if $({}^3L_l-{}^1L_l)$ is positive, otherwise the reciprocal of this quantity. Houston's equations (12) give functional relations between these interval ratios which are compared with the experimental values.

HOUSTON[1] has worked out an approximate quantum mechanical theory of the relation of the triplet interval ratio to the singlet-triplet interval for two electron configurations in which one of the electrons is in an s state, but the comparison he makes with experimental data gives one very little idea as to just how accurate the theory is. The purpose of the present paper is therefore to make a systematic comparison of the available data with Houston's theory.

If we write the terms of a singlet-triplet system as ${}^1L_l$, ${}^3L_{l+1}$, ${}^3L_l$, ${}^3L_{l-1}$, with $L=P, D, F$, when $l=1, 2, 3$, Houston's equations (12) give the following relative term values in terms of the parameter X, which is the ratio of the exchange perturbation integral to the perturbation theory integral which measures the spin energy. (The first classification applies to $X>0$, the second to $X<0$.):

$$\begin{aligned} {}^1L_l, {}^3L_l &= -\tfrac{1}{2}(X-1) - \tfrac{1}{2}\{(X+1)^2 + 4l(l+1)\}^{1/2} \\ {}^3L_{l+1} &= -l \\ {}^3L_l, {}^1L_l &= -\tfrac{1}{2}(X-1) + \tfrac{1}{2}\{(X+1)^2 + 4l(l+1)\}^{1/2} \\ {}^3L_{l-1} &= l+1. \end{aligned}$$

Fig. 1. illustrates the behavior of these intervals. With X large and positive the triplet has the Landé interval and the singlet is high above the triplet as at a. As X approaches zero the levels approach coincidence in pairs as at b; and with X large and negative we again have the Landé interval with the singlet far below the triplet as at c.

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

The theoretical curves of Figs. 2 and 3 are plotted as follows: For abscissa is used $({}^3L_{l-1}-{}^3L_{l+1})/|{}^3L_l-{}^1L_l|$. For the lower curve, $X>0$, the ordinate is $({}^3L_{l-1}-{}^3L_l)/({}^3L_l-{}^3L_{l+1})$, which goes from $l/(l+1)$ with abscissa zero, to zero with abscissa one. For the upper curve, $X<0$, the ordinate

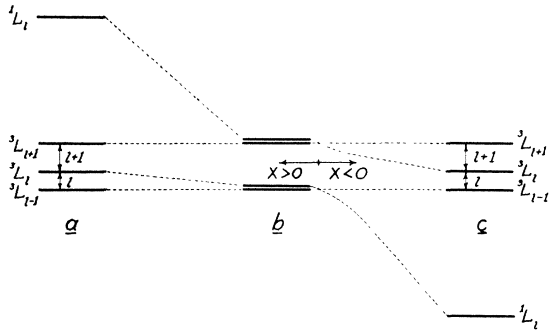

Fig. 1. Diagram illustrating the behavior of the singlet-triplet intervals. (*a*) X large and positive. (*b*) X very small and positive. (*c*) X large and negative.

is the reciprocal of this, $({}^3L_l-{}^3L_{l+1})/({}^3L_{l-1}-{}^3L_l)$, which goes from zero with abscissa one to $(l+1)/l$ with abscissa zero. The fact that the abscissa starts increasing (to $(l+\frac{1}{2})/(l(l+1))^{1/2}$ at $X=-1$) shows that ${}^1L_l-{}^3L_l$ becomes less than the whole spread of the triplet until the ordinate equals $1/2l$ at $X=-2$.

TABLE I. *Coordinates.*

† indicates a point which is not plotted on account of large probable error (see text).
* indicates a point which does not fall within the limit of Figs. 2 and 3.

Elem.	Config.	Abs.	$sp(X>0)$ Ord.	Sources
Al II	$3s3p$	0.0084	0.493	Int. Crit. Tab.
	$4p$	0.0293	0.481	
	$5p$	0.1145	0.445	
Ba I	$6s6p$	0.2301	0.422	Int. Crit. Tab.
	$7p$	0.1410	0.420	
	$8p$	0.1181	0.619	
C I	$3s2p$	0.0527	0.499	Proc. Roy. Soc. **A118,** 43
Ca I	$4s4p$	0.0179	0.494	Int. Crit. Tab.
	$5p$†	0.1253	0.110	
Cd I	$5s5p$	0.1315	0.462	Int. Crit. Tab.
	$6p$	0.1695	0.406	
	$7p$	0.202	0.355	
	$8p$	0.211	0.378	
	$9p$	0.219	0.367	
Ga II	$4s4p$	0.0604	0.478	Phys. Rev. **34,** 714
	$5s4p$	0.1476	0.424	
Ge I	$5s4p$	0.719	0.177	Phys. Rev. **31,** 786
	$6s4p$	0.914	0.095	
Ge III	$4s4p$	0.0818	0.465	Phys. Rev. **34,** 698
	$5p$	0.276	0.366	
Hg I	$6s6p$	0.436	0.382	Int. Crit. Tab.
	$7p$	1.035	0.094	
	$8p$	0.952	0.056	
Mg I	$3s3p$	0.0046	0.487	Int. Crit. Tab.
N II	$3s2p$	0.680	0.235	Proc. Roy. Soc. **A114,** 662
	$4s2p$	0.135	0.437	
	$5s2p$	0.305	0.373	
O III	$3s2p$	0.0658	0.458	Proc. Roy. Soc. **A118,** 43
Pb I	$7s6p$	0.972	0.032	Phys. Rev. **33,** 301
Pb III	$6s6p$	0.600	0.274	Phys. Rev. **34,** 397
Sb IV	$5s5p$	0.278	0.388	Phys. Rev. **34,** 402
Si I	$4s3p$	0.221	0.395	Zeits. f. Phys. **40,** 530
Sn I	$6s5p$	0.918	0.074	Phys. Rev. **30,** 574
Sn III	$5s5p$	0.230	0.407	Int. Crit. Tab.
	$6p$	0.598	0.226	
Sr I	$5s5p$	0.0808	0.474	Int. Crit. Tab.
	$6p$	0.607	0.395	
Te V	$5s5p$	0.323	0.366	Phys. Rev. **34,** 402
Tl II	$6s6p$	0.528	0.316	Phys. Rev. **35,** 236
	$7p$	0.403	0.088	
Zn I	$4s4p$	0.0406	0.489	Int. Crit. Tab.
	$5p$	0.0507	0.475	
	$6p$	0.0589	0.464	
	$7p$	0.0666	0.456	
	$8p$	0.0651	0.464	
	$9p$†	0.0739	0.514	
Yt II	$5s5p$	0.321	0.380	Bur. Stand. Jl. of Res. **2,** 738

Elem.	Config.	Abs.	$sp\ (X<0)$ Ord.	Sources
Al II	$3s6p$*	0.1045	2.193	Int. Crit. Tab.
Ca I	$4s6p$	0.0140	1.950	Int. Crit. Tab.
Hg I	$6s9p$*	0.3935	5.356	Int. Crit. Tab.
	$10p$*	0.1273	7.135	
	$11p$*	0.1131	8.73	
Sr I	$5s7p$*	0.0902	2.100	Int. Crit. Tab.

Elem.	Config.	Abs.	$p^6s\ (X<0)$ Ord.	Sources
A I	$3p^54s$	0.854	0.756	Zeits. f. Phys. **40,** 839
	$6s$	1.008	0.0578	
	$7s$	1.021	0.0282	
	$9s$	1.002	0.0078	
Ca III	$3p^54s$	0.814	0.823	Phys. Rev. **31,** 501
	$5s$*	1.109	0.269	
K II	$3p^54s$	0.819	0.383	Phys. Rev. **31,** 501
	$5s$	1.063	0.241	
Kr I	$4p^55s$	1.058	0.221	B. S. Jl. Res. **3,** 154
Na II	$2p^53s$	0.442	1.293	Phys. Rev. **31,** 967

TABLE I (*continued*)

Ne I	$2p^5 3s$	0.544	1.161	Int. Crit. Tab.
	$5s$	1.047	0.122	
	$6s$	1.027	0.0578	
	$7s$	1.017	0.0322	
	$8s$	1.010	0.0211	
	$9s$	1.006	0.0125	
	$10s$	1.003	0.0084	
	$11s$	1.001	0.0061	
Xe I	$5p^5 6s$	0.999	0.120	B. S. Jl. Res. **3,** 756

sd ($X>0$)

Elem.	Config.	Abs.	Ord.	Sources
Ba I	$6s5d$	0.258	0.476	Int. Crit. Tab.
Ca I	$4s3d$	0.0237	0.640	Int. Crit. Tab.
	$5d$†	0.0258	0.607	
	$7d$†	0.712	0.750	
Cr V	$4s3d$	0.1678	0.525	Phys. Rev. **33,** 542
Lu II	$6s5d$	0.490	0.363	Bul. Am. Ph. Soc. Apr. 10, 1930, 11
[5]Pb III	$6s5d$	0.220	0.466	Phys. Rev. **34,** 397
Sb IV	$5s5d$	0.258	0.628	Phys. Rev. **34,** 402
	$6d$	0.562	0.683	
Sc II	$4s3d$	0.0718	0.616	Sci. Papers, Bur. Stand. **22,** 329
	$5s3d$	0.301	0.483	
Sn III	$5s5d$	0.250	0.659	Int. Crit. Tab.
	$6d$	0.129	0.610	Phys. Rev. **34,** 402
Sr I	$5s4d$	0.083	0.600	Int. Crit. Tab.
	$6d$	0.409	0.398	
Te V	$5s5d$	0.257	0.616	Phys. Rev. **34,** 402
Ti III	$4s3d$	0.1031	0.592	Astro. Jl. **66,** 13
V IV	$4s3d$	0.1335	0.558	Phys. Rev. **33,** 542
Yt II	$5s4d$	0.272	0.506	B. S. Jl. Res. **2,** 738
	$6s4d$	0.996	0.124	

sd ($X<0$)

Elem.	Config.	Abs.	Ord.	Sources
Ba I	$6s6d$	0.0485	1.228	Int. Crit. Tab.
	$7d$	0.0456	0.438	
	$8d$	0.0284	1.190	
	$9d$	0.0746	1.595	
	$10d$†	0.0324	4.61	
Ca I	$4s4d$	0.0207	1.474	Int. Crit. Tab.
	$6d$†	0.0544	1.200	
Cd I	$5s5d$	0.1074	1.555	Int. Crit. Tab.
	$6d$	0.0621	1.414	
	$7d$	0.0553	1.388	
	$8d$†	0.0454	6.000	
Ga II	$4s4d$	0.0096	1.360	Phys. Rev. **34,** 714
	$5s4d$	0.0029	1.416	
	$6s4d$	0.0022	1.125	
Ge III	$4s4d$	0.0099	1.505	Phys. Rev. **34,** 697
Hg I	$6s6d$*	1.510	0.585	Int. Crit. Tab.
	$7d$	1.018	0.923	
	$8d$	0.808	1.051	
	$9d$	0.717	1.438	
	$10d$	0.653	0.556	
[5]Pb III	$6s5d$*	0.250	2.145	Phys. Rev. **34,** 397
Sr I	$5s5d$	0.183	1.520	Int. Crit. Tab.
	$7d$	0.273	1.195	
	$8d$	0.163	1.250	
	$9d$	0.298	1.271	
Tl II	$6s6d$	0.532	1.384	Phys. Rev. **35,** 236
	$7d$	0.237	1.173	
	$8d$*	0.118	1.861	
Zn I	$4s4d$	0.0283	1.618	Int. Crit. Tab.
	$5d$†	0.0128	1.818	
Yt II	$5s5d$	0.0533	1.509	B. S. Jl. Res. **2,** 738

d^9s ($X<0$)

Elem.	Config.	Abs.	Ord.	Sources
Ag II	$4d^9 5s$	0.862	0.526	Phys. Rev. **31,** 317
	$6s$	1.022	0.0896	
Au II	$5d^9 6s$	1.062	0.2569	Phys. Rev. **34,** 19
Cd III	$4d^9 5s$	0.886	0.4916	Phys. Rev. **31,** 778
Cu II	$3d^9 4s$	0.605	0.798	Phys. Rev. **29,** 386
	$5s$	1.018	0.1835	
	$6s$	1.018	0.0692	Phys. Rev. **34,** 1128
	$7s$	1.010	0.0348	
Ga IV	$3d^9 4s$	0.708	0.686	Phys. Rev. **31,** 750
Ge V	$3d^9 4s$	0.759	0.622	Phys. Rev. **31,** 750
Hg III	$5d^9 6s$	1.033	0.2568	Phys. Rev. **34,** 19
In IV	$4d^9 5s$	0.913	0.447	Phys. Rev. **31,** 778
Ni I	$3d^9 4s$	0.596	0.810	Phys. Rev. **29,** 386
	$5s$	1.024	0.1393	
	$6s$	1.016	0.0519	Phys. Rev. **34,** 828
Pd I	$4d^9 5s$	0.890	0.510	Phys. Rev. **29,** 386
	$6s$	1.018	0.065	
Pt I	$5d^9 6s$	0.796	0.0829	Phys. Rev. **34,** 19
	$7s$	1.001	0.0374	Phys. Rev. **34,** 190
Tl IV	$5d^9 6s$	1.042	0.235	Phys. Rev. **34,** 19
Zn III	$3d^9 4s$	0.652	0.748	Phys. Rev. **30,** 381

sf ($X>0$) (not plotted)

Elem.	Config.	Abs.	Ord.	Sources
Al II	$3s4f$†	0.0978	0.750	Int. Crit. Tab.
	$5f$	0.0506	0.783	
	$6f$	0.0573	0.777	
	$7f$	0.0389	0.761	
	$8f$	0.0118	0.657	
	$9f$†	0.0049	0.750	
	$10f$†	0.0030	0.786	
	$11f$†	0.0016	0.667	
	$12f$†	0.0019	0.800	
[6]Ge III	$4s4f$	1.384	0.275	Phys. Rev. **34,** 697
Sn III	$5s4f$	0.0556	0.378	Int. Crit. Tab.
	$5f$	0.0312	0.357	Phys. Rev. **30,** 574
Sr I	$5s4f$†	0.0056	0.630	Int. Crit. Tab.
	$5f$†	0.0113	0.889	
	$6f$†	0.1765	0.049	
	$7f$†	0.314	0.165	

sf ($X<0$) (not plotted)

Elem.	Config.	Abs.	Ord.	Sources
Ba I	$6s4f$	0.0046	1.014	Int. Crit. Tab.
	$5f$	0.0847	4.34	
	$6f$	0.0092	1.594	

[5] S. Smith, Phys. Rev. **34,** 397 (1929) has a question as to which of two singlets belong to this configuration. These are both listed, one for $X>0$, plotted with a question mark and one for $X<0$, which fell off the graph.

[6] The singlet is within the triplet.

A fairly complete search of the literature was made and the points plotted on Figs. 2 and 3. The coordinates are tabulated in the accompanying tables together with a brief reference to the source of the data. No points were plotted for which any of the intervals were less than 2.5 cm^{-1}, since the accuracy of these points did not seem to be sufficient for a fair comparison with the theory. Such points are listed in the table with a dagger (†). Those points

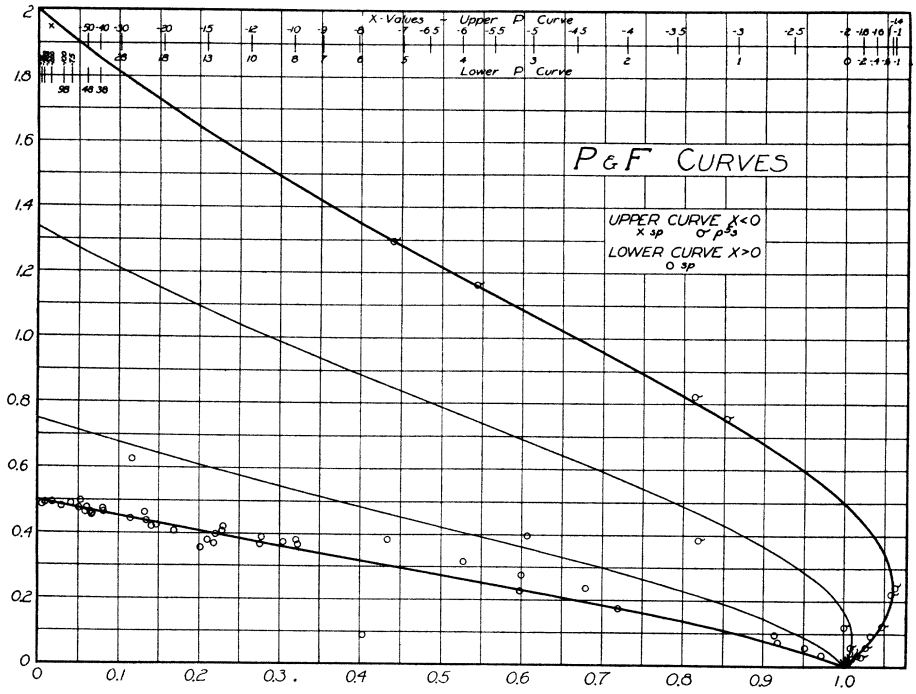

Fig. 2. P and F curves showing sp and p^5s points. (F curve is drawn lightly and no points plotted.)

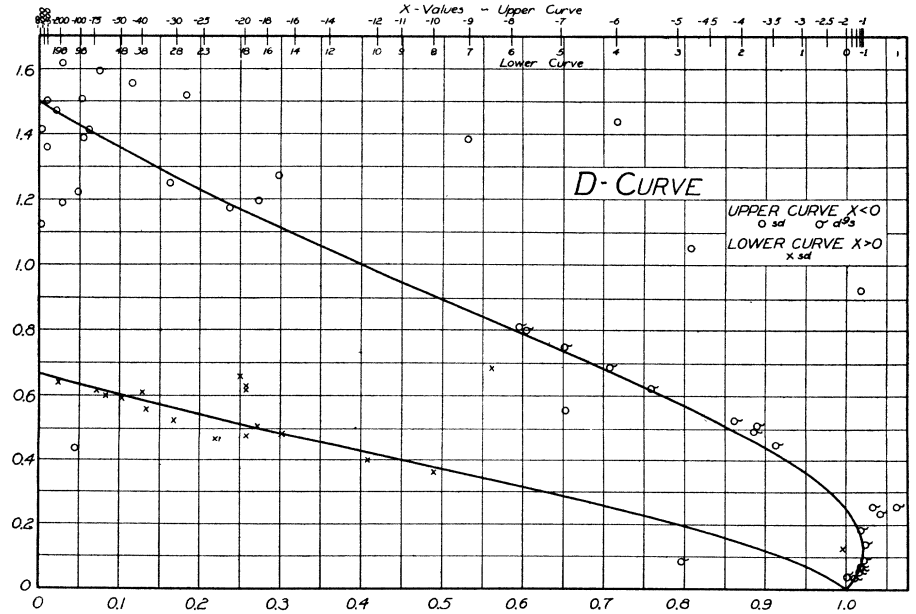

Fig. 3. D curve showing sd and d^9s points.

whose coordinates fell off the graph are listed with an asterisk (*). No *sf* points were plotted because there were just a few clustered near Russell-Saunders coupling.

It is found that the theory works well for p^5s and d^9s configurations, in which we are one p or d electron short of a closed shell, except that the whole system of lines is inverted. These points all fall on the upper curves.

Pb III[2] and Tl II[3] have *sf* configurations in which $^3F_3$ and $^1F_3$ are on opposite sides and outside of the $^3F_2-{}^3F_4$ interval. A similar thing happens in the case of the $3p^5\ 8s$ configuration of A I[4]. These partially inverted triplets might have been plotted with negative ordinates on our graphs.

As to the accuracy with which the points fit the theory, it can be said that in general the d^9s and p^5s fit best, sp and sd for $X>0$ next, and sp and sd for $X<0$ poorest. Also in general, elements of high atomic number show especially pronounced disagreements. The disagreements are to be regarded provisionally as cases in which the second-order perturbations are not negligible rather than as essential defects in the basic theory.

[2] S. Smith, Phys. Rev. **34,** 397 (1929).
[3] S. Smith, Phys. Rev. **35,** 236 (1930).
[4] A. Meissner, Zeits. f. Physik **40.** 839 (1927).