

TERM VALUES IN COMPLEX SPECTRA (COLUMBIUM I & II)

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ABSTRACT. Term values in the case of d^1 and d^3 configurations of Cb II have been calculated from Ostrofsky's and Bowman's formulæ and compared with experimental data due to Meggers and Humphreys. New formulæ are calculated for d^3 configuration of Cb I and the term values estimated from them are found to agree well with the observed data, the positions of the unidentified terms are also predicted.

INTRODUCTION

In a paper on the theory of complex spectra, Slater (1926) first treated atomic multiplets by the method of wave-mechanics and derived (1) Hund's scheme for multiplet classification directly from theory and (2) energy distances of multiplet terms in atomic spectra arising out of a given electronic configuration. Definite formulæ were calculated for the energy values of certain integrals which could be estimated well enough to permit comparison with experiment. A fairly good agreement was shown from typical examples of spectra due to configurations particularly of equivalent p^2 and d^2 electrons.

Condon and Shortley (1931) applied Slater's method to determine formulæ for the relation between the energies of terms for all two electron and several cases of three electron configurations, and in particular extended Slater's table of values for $a^k(lm_l; l'm'_l)$ and $b^k(lm_l; l'm'_l)$ in the case of equivalent f electrons, represented by the spectrum of lanthanum II. Slater's method, however, does not distinguish between terms of the same type occurring more than once in a given configuration, cases of which are very frequent in the more complex spectra, the method gives only their mean energies. But for this deficiency the Slater-Condon formulæ in terms of their F 's and G 's are capable of giving a good agreement with experimental observation.

A different method of treatment of the problem of complex spectra was given by Van Vleck (1931) and extended by Serber (1931). Dirac's vector model was employed by them and Serber was able to obtain also the energy differences between similar terms of the same configuration, which could not be done in the Slater derivation.

The purpose of the present paper is to apply the results of the theoretical work outlined above, to check up the energy values of the multiplet-terms arising out of the d^1 and d^3 configurations in Cb II, the d^3 configuration of Cb I, the structure of which was worked out extensively by Megger and Humphrey (1946). This attempt has led to the calculation of expressions for the d^4 configuration which have not been determined before, and to estimate in the above spectra the values of a few terms which are yet to be identified.

RESULTS

Spectrum of Cb II :—Tables I and II embody the results in the spectrum of Cb II for terms due to the d^1 and d^3s electron configurations respectively. The first column in each table contains the configurations, the second the predicted terms. The experimental data as obtained from the analysis of the spectrum are given in the third column. These values are reduced and expressed with respect to the lowest term which is adopted as zero. Further the mean value of a multiplet term alone is given against each; the individual components cannot be considered here. They involve the question of intervals which were discussed for Cb I and Cb II according to Goudsmit's method, in earlier papers by the author (Rao and Rao, 1948). The fourth column gives the energy values of terms as calculated from the theoretical formulæ quoted in the last column. The formulæ in Table I are due to Ostrofsky (1934) and those mentioned in Table II are taken from Bowman's paper (1941). The derivation of these formulæ was by the methods of Van Vleck and Serber. For the meaning of the parameters F 's and G 's reference may be made to Condon and Shortley's work. For estimating the numerical values of these parameters in the above formulæ the author adopted the method of Normal equations.

TABLE I
Term values of Cb II

Config.	Term	Obs. value	Cal. value	Formula (Ostrofsky)
d^1	$5D$	0	-211.2	$6F_0 - 21F_2 - 189F_4$
	$3H$	9311.3	9556.6	$6F_0 - 17F_2 - 69F_4$
	$3G$	10665.0	10745.4	$6F_0 - 12F_2 - 94F_4$
	$3D$	12692.7	12409.0	$6F_0 - 5F_2 - 129F_4$
	$1I$	14871.2	14442.0	$6F_0 - 15F_2 - 9F_4$
	Mean value of	16710.1	15716.5	$6F_0 - 5F_2 - 7F_4$
	$3F_+$	20557.7	30773.9	$+ \frac{1}{2}(612F_2^2 + 2002F_2F_4 - 4860F_2F_4^2)^{1/2}$
	$3F_-$	12862.4	659.0	—
	Mean value of	16491.0	15716.5	$6F_0 - 5F_2 - 76.5F_4$
	$3P_+$	27168.0	27263.7	$\pm \frac{1}{2}(912F_2 + 38025F_2^2 - 9960F_2F_4)^{1/2}$
	$3P_-$	5813.7	11160.3	—
	Mean value of	21087.6	20126.5	$6F_0 - 5F_2 - 6.5F_4$
	$1G_+$	20109.3	25490.2	$\pm \frac{1}{2}(708F_2^2 + 30825F_2^2 - 6420F_2F_4)^{1/2}$
	$1G_-$	14265.9	14762.8	—
	Mean value of	21139.2	23454.3	$6F_0 + 9F_2 - 76.5F_4$
	$1D_+$	30539.9	86095.2	$\pm \frac{1}{2}(1296F_2^2 + 30825F_2^2 - 10440F_2F_4)^{1/2}$
	$1D_-$	11738.4	-39186.6	—
Mean value of	—	29204.5	$6F_0 + 10F_2 + 6F_4$	
$1S_+$	16777.8	42927.6	$\pm \frac{1}{2}(3088F_2^2 + 133200F_2^2 - 20640F_2F_4)^{1/2}$	
$1S_-$	—	15481.4	—	
$1F$	17983.9	18007.5	$6F_0 - 84F_4$	

$$6F_0 = 23299.5 \quad F_2 = 552.7 \quad F_4 = 63$$

Note —In this and the following tables the suffixes + and - indicate the higher and lower of two similar terms and the corresponding formulæ must be taken with the respective signs.

TABLE II
Term values of Cb II

Config.	Term	Obs. value	Calc. value	Formule (Bowman)
d's	5P	10913.0	8109.6	$F_0 - 117F_1 - 3G_2$
	3P	11655.2	11842.0	$F_0 - 117F_1 + G_2$
	3P	20936.0	18052.0	$F_0 - 6F_2 + 12F_1 - 2G_2$
	1P	20137.6	19918.2	$F_0 - 6F_2 - 12F_1$
	5F	3510.8	-1050.9	$F_0 - 15F_2 - 72F_4 - 3G_2$
	3F	1900	2681.2	$F_0 - 15F_2 - 72F_4 + G_2$
	3F	25378.	27212.5	$F_0 + 9F_2 - 87F_4 - 2G_2$
	1F	31762.3	29078.7	$F_0 + 9F_2 - 87F_4$
	3G	15851.1	14998.5	$F_0 - 11F_2 + 13F_4 - 2G_2$
	1G	16219.0	16861.7	$F_0 - 11F_2 + 13F_4$
	3H	6062.1	18052.0	$F_0 - 6F_2 - 12F_1 - 2G_2$
	1H	21073.1	19918.2	$F_0 - 6F_2 - 12F_1$
	1D ₊	—	16025.1	$F_0 + 5F_2 + 3F_4 - 2G_2$
	1D ₋	21332.9	20412.3	$\pm \frac{1}{2}(193F_2 - 1650F_2F_4 + 8325F_4^2)^{\frac{1}{2}}$
	1D ₊	—	17801.3	$F_0 + 5F_2 + 3F_4$
1D	21332	20278.5	$\pm \frac{1}{2}(193F_2 - 1650F_2F_4 + 8325F_4^2)^{\frac{1}{2}}$	
		$F_0 = 28651.8$	$F_2 = 1214.2$	$F_4 = 129.7$
				$G_2 = 933.1$

The following five expressions are taken and equated to their numerical values as found from the experimental data. Then we have

$$\begin{aligned}
 5D &= 6F_0 - 21F_2 - 189F_4 = 0 \\
 3H &= 6F_0 - 17F_2 - 69F_4 = 9311.3 \\
 3G &= 6F_0 - 12F_2 - 91F_4 = 10065.3 \\
 3D &= 6F_0 - 5F_2 - 129F_4 = 12092.7 \\
 1I &= 6F_0 - 15F_2 - 9F_4 = 11871.2
 \end{aligned}$$

More equations are taken than there are constants to be determined as the latter are not rigid in their values but are adjustable to give maximum satisfaction to the equations. The procedure of finding the values of these constants, which will give the largest measure of agreement with the numerical values, is as detailed below.

If the coefficients of the three constants are respectively a , b , and c , and d is the numerical value of the expression, *i.e.*, the term on the right hand side and λ is the algebraic sum of the a , b , c , and d , then the corresponding values for the five terms for each of the equations are tabulated as below :—

TABLE III

a	b	c	d	λ
1	21	-189	0	-209
1	-17	-69	9511.3	9226.3
1	11	91	10065.3	9960.3
1	5	129	12692.7	12559.7
1	15	-9	14871.2	14818.2
5	-70	-190	46010.5	46385.5

The formation of λ is just to indicate the correctness of the operations conducted. For, λ is equal to the algebraic sum of a , b , c , and d . Then each row is multiplied by the value of ' a ' in that row as shown in the following arrangement :—

aa ab ac ad $a\lambda$

(this arrangement is the same as above, for, all a 's are taken as unity)

Similarly with b and c as follows :—

TABLE IV

ab	bb	bc	bd	$b\lambda$
	111	3969	0	-4389
	289	1173	-158292.1	-156847.1
	111	1128	-120783.6	-119523.6
	25	945	63463.5	-62798.5
	225	135	-223068.0	-222723.0
-70	1124	7050	-565607.2	557503.2

TABLE V

ac	bc	cc	cd	$c\lambda$
		35721	0	39509
		4761	-64479.7	636611.7
		8835	-946138.2	-936268.2
		6641	-1637358.3	-1620201.3
		81	-133840.8	-133633.8
-490	7050	66040	-3359817.0	-3287217.0

The values of the sums of a 's etc. are taken as the coefficients of the respective F 's and the normal equations are formed.

$$\begin{aligned} 5F_0 - 70F_2 - 191F_4 &= 10910.5 \\ -70F_0 + 1124F_2 + 7050F_4 &= -365607.2 \\ -490F_0 + 7050F_2 + 66010F_4 &= -3359817.0 \end{aligned}$$

For each constant there is an equation, and solving the three simultaneous equations, the values of the F 's are obtained. These values give maximum satisfaction to the equations and are given at the foot of each table. Substituting them in the expressions for the terms the term-values are obtained and given in column 4.

SPECTRUM OF Cb I

Table VI gives similar calculations for the terms in the spectrum of Cb I, arising from the electron configuration d^3 . The theoretical formulae for this configuration have thus been obtained by the author.

Van Vleck (1934) has shown that in the case of a configuration of the form sd^k , the energy due to the addition of an s electron to the core a^k , enters in the following manner,

$$W = W(a^k) - \frac{1}{2}K_{a,s} \{k + 2[S(S+1) - S_k(S_k+1) - 3L+4]\} - kJ_{a,s} \dots (1)$$

TABLE VI

Term values of Cb I

Config	Base	Term	Obs. val.	Calc. val. (Ion data)	Calc. val. (Formula)	Formula (author)
d^3	D	6D	0	0	184	$6I_0 - 11I_2 - 189F_4 - 3G_2$
		4D	8311.4	8420	8535.2	$6I_0 - 21I_2 - 189F_4 + 2G_2$
H	H	4H	10612.1	11520	10984.0	$6I_0 - 17I_2 - 69F_4 - 2G_2$
		2H	16879.6	16872	16213.0	$6I_0 - 17F_2 - 69F_4 + G_2$
G	G	4G	11808.5	12271	11712.5	$6I_0 - 12I_2 - 91F_4 - 2G_2$
		2G	16901.6	173.6	16968.5	$6I_0 - 11F_2 - 91F_4 + G_2$
$^3P_+$	$^3P_+$	$^4P_+$	1371.5	18591	2291.9	$6I_0 - 5F_2 - 765I_4 - 2G_2$
		$^2P_+$	—	—	11931.9	$\pm \frac{1}{2}(612I_2^2 + 2002I_4^2 - 4860F_2F_4)^{1/2}$
$^3F_+$	$^3F_+$	$^4F_+$	—	5110	5817.9	$6I_0 - 5F_2 - 65F_4 + G_2$
		$^2F_+$	—	—	17157.9	$\pm \frac{1}{2}(612I_2^2 + 2002I_4^2 - 4860F_2F_4)^{1/2}$
D	D	4D	14839.6	149.1	12841.1	$6F_0 - 5I_2 - 1914 - 2G_2$
		2D	—	10953	1833.1	$6I_0 - 5F_2 - 129F_4 + G_2$
$^3P_+$	$^3P_+$	$^4P_+$	1367.8	18176	19877.5	$6F_0 - 5F_2 - 765I_4 - 2G_2$
		$^2P_+$	—	—	12319.3	$\pm \frac{1}{2}(911F_2^2 + 3802I_4^2 - 9960F_2I_4)^{1/2}$
P	P	4P	—	—	5103.5	$6I_0 - 5I_2 - 765I_4 + G_2$
		2P	—	13288	1757.3	$\pm \frac{1}{2}(911I_2^2 + 3802I_4^2 - 9960F_2I_4)^{1/2}$
H	H	4H	—	—	17439.1	$6I_0 - 15F_2 - 91F_4 - G_2$
		2H	—	—	20047.6	$6I_0 - 5I_2 - 65I_4 - G_2$
$^3G_+$	$^3G_+$	$^4G_+$	—	—	17550.2	$\pm \frac{1}{2}(708F_2^2 + 30825F_4^2 - 612F_2F_4)^{1/2}$
		$^2G_+$	—	—	19711.9	$6F_0 + 9I_2 - 765I_4 - G_2$
D	D	4D	—	—	3739.0	$6I_0 + 9I_2 - 765I_4 - G_2$
		2D	—	—	23856.1	$\pm \frac{1}{2}(1296I_2^2 + 30825F_4^2 - 10110F_2F_4)^{1/2}$
$^3S_+$	$^3S_+$	$^4S_+$	—	—	42242.1	$6I_0 + 10F_2 + 6F_4 - G_2$
		$^2S_+$	—	—	17861.7	$\pm \frac{1}{2}(3088F_2^2 + 133200F_4^2 - 20640F_2F_4)^{1/2}$

$F_0 = 26748.9$ $F_2 = 166.7$ $F_4 = 63$ $G_2 = 1742.0$ $K_{a,s} = 1684$

where W is the energy of sa^k

$W(a^k)$ the energy of a^k alone

K_{as} , the exchange energy between the s electron and core a^k

kJ_{as} , The Coulomb energy

S the resultant spin

S^k The spin of the core a^k . (*i. e.* the base terms)

The core a^k gives rise to a certain set of terms; if we add an s -electron the multiplicity is changed by ± 1 . Thus nd^1 gives a^1D terms, besides some more. Addition of an s -electron gives a^0D and a^1D . From a knowledge of the energy of 3D , we can calculate that of 4D and/or 1D , if K_{as} and J_{as} are determined.

$$\text{But } S = S_k \pm \frac{1}{2}$$

therefore the difference between 1D and 3D is merely given by

$$h\Delta v = 2K_{as} (S_k + \frac{1}{2}) \quad \dots (2)$$

The difference between the two terms that arise out of an addition of an s electron to the core is just proportional to $2(S_k + \frac{1}{2}) = 2S_k + 1$, *i. e.* the multiplicity of the core terms or the bases on which the two terms are formed. Taking the above case we have

$$\begin{aligned} ^0D - ^3D &= h\Delta v = 2(K_{as})(S_k + \frac{1}{2}) \\ &= (2S_k + 1)K_{as} \\ &= 5K_{as} \end{aligned} \quad \dots (3)$$

The difference is equal to 5 times a constant.

Taking again a 2D of d^4 and the resulting 1D , 2D of d^1s we have

$$^1D - ^2D = 3K_{as} \quad \dots (4)$$

Thus the 1D terms computed from eqns. (3) and (4) are obtained separately and we can get different formulae for the two similar terms.

Taking from Ostrofsky's formula the energy value of 1D and substituting this in equation (1) for $W(a_k)$ we have

$$\begin{aligned} W(^0D) &= W(^1D) - \frac{1}{2}K_{as} \{k+2[S(S+1) - S_k(S_k+1) - 3/4]\} + kJ_{as} \\ &= W(^1D) - 4K_{as} + kJ_{as} \end{aligned}$$

Similarly

$$W(^4D) = W(^1D) + K_{as} + kJ_{as}$$

Subtracting $^6D - ^1D$ is $-5K_{as}$, as previously obtained.

Thus in computing the theoretical formula for the 0D , it is seen that the formula differs from the base (1D) only in one respect, it contains an additional term $(-4K_{as})$. (The term kJ_{as} is only a Coulomb term affecting only the absolute level but not the relative separation and so can be neglected from consideration).

Similarly the ⁴D differs only in containing an additional term K_a .

The value for the other ¹D from ³D base is

$$W(^1D) = W(^3D) - 3K_a,$$

which is obviously different from the ⁴D out of the ¹D base. The value for the ²D out of the ³D is $W(^2D) = W(^1D) + 0$

Tabulating the results obtained in the above two typical cases :

TABLE VII

Config	base	config term	formula
d^4	D	⁴ D	$W(^4D) - 4K_a = 6F_0 - 21F_2 - 180F_4 - 4K_a$
		⁴ D	$W(^4D) + K_a = 6F_0 - 21F_2 - 180F_4 + K_a$
	D	¹ D	$W(^1D) - 3K_a = 6F_0 - 5F_2 - 120F_4 - 3K_a$
		² D	$W(^1D) - 0 = 6F_0 - 5F_2 - 120F_4$

This additional term containing the constant K_a , can in fact be denoted by the Slater-Condon's G's for it represents the interaction energy between non-equivalent electrons (d and s). This method can be followed for the derivation of formulae for all other terms of d^4 out of all bases given by the d^4 configuration. In the above method of representation it can be easily seen that the ²D has apparently the same energy as the base D and there is no symmetrical disposition of the formulae in that the ¹D terms have different coefficients for the G's. Bowman in his derivation for d^3 has given the formulae in this fashion. But a more symmetrical and elegant method of representation is seen in Condon and Shortley formulae for the d^2 etc. It is easy to see that all that matters in the formulas is that ⁴D and ¹D must differ by $5G$. So instead of putting $^4D = D - 4G$ and $^1D = D + G$, we may put $^4D = D - 3G$ and $^1D = D + 2G$ which gives $^4D - ^1D = -5G$. Similarly we may put $^1D = ^3D - 2G$ and $^2D = ^3D + G$ which gives $^1D - ^2D = -3G$. The advantage of this representation is that similar terms like 4D and 1D have the same coefficient for G's (varying in sign) and no term appears with the same formula as that of the corresponding base term. It will be relevant to point out a regularity here namely the sextet formulae contain as the coefficient of G, 3; the quartet contains 2, and the doublet 1.

The respective formulae obtained thus are given in the last column of Table VI against each term. The numerical values of the constants are determined by the method of normal equations explained earlier, and are given at the foot of the table and the values of the terms themselves are shown in column 5.

A different method is also adopted to calculate the term values utilising the experimental data of the analysis of Cb II. The procedure, as mentioned previously, is:

$${}^6D - {}^4D = \frac{1}{2}K_{a,s}(S_k + \frac{1}{2})$$

from which $K_{a,s}$ is calculated assuming the observed values of 6D and 4D of d^1 s configuration in Cb I. Substituting this value of $K_{a,s}$ in Van Vleck's equation (1) the values of the terms of d^1 s of Cb I can be determined knowing those of d^1 of Cb II. The value of $kj_{a,s}$ need not be known for reasons already mentioned. It should be noted that the terms of Cb I which can be calculated by this procedure is limited by the known number of terms of d^1 configuration of Cb II. All terms which could thus be calculated are shown in the same Table VI in column 4. These values provide another check on the theoretical formulæ.

A study of the Tables I, II and VI and a comparison of the calculated and observed term values in Cb I and Cb II indicate generally a fairly good agreement. A few exceptions are 3H , 3F and 3F and perhaps 3P of d^1 s configuration of Cb II in which the discrepancies are rather large. It should be noticed that this agreement is approximate and considered as a method for the prediction of unknown terms. It gives us a rough disposition of the region of the multiplets. With this limitation Table VI contains the predicted values of the several terms of Cb I which are yet to be identified. These are expected to be useful in further work on the analysis of the spectrum.

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