

On the Configurations $ll's$

GIULIO RACAH

The Hebrew University, Jerusalem, Palestine

(Received October 14, 1942)

The spectra of the configurations $ll's$ are calculated by using Dirac's vector model. A comparison is made with the experimental data of Sc I, Y I, and Cu I.

THEORY

THE configurations $ll's$ are of the simplest instances of configurations in which a term of a particular kind occurs more than once, so that the diagonal-sum method does not suffice to give complete formulas for the electrostatic energies of the different terms. We shall show that with Dirac's vector model we can reduce this question to a simple three-vector problem which may be solved without writing energy matrices.

The interaction between the electrons l and s is¹

$$W_{ls} = F_0 \pm G_l, \quad (1)$$

where the upper sign holds when the spins are antiparallel and the lower sign when the spins are parallel. Following Dirac's vector model we may substitute the operator²

$$P_{ls} = -\frac{1}{2}[1 + (\boldsymbol{\sigma}_l \cdot \boldsymbol{\sigma}_s)] \quad (2)$$

for the double sign, and write

$$W_{ls} = F_0 + P_{ls}G_l. \quad (3)$$

In the same way the interaction between the electrons l and l' may be written

$$W_{ll'} = \Phi_L + P_{ll'}\Gamma_L, \quad (4)$$

where Φ_L and Γ_L are linear combinations of Slater's $F^k(nl, n'l')$ and $G^k(nl, n'l')$; the coefficients of these linear combinations are functions of l , l' , and L , and their general formulas were given in a previous paper.³

The electrostatic energies of the configuration $ll's$ are the eigenvalues of the operator

$$W = F_0(nl, n'l's) + F_0(n'l', n'l's) + \Phi_L + (P_{ls}G_l + P_{l's}G_{l'} + P_{ll'}\Gamma_L). \quad (5)$$

In the quartet terms every P_{ab} equals -1 , and, therefore,

$$W(^4L) = F_0 + F_0' + \Phi_L - G_l - G_{l'} - \Gamma_L. \quad (6)$$

In order to obtain the eigenvalues of (5) for the doublet terms it suffices to calculate the square of the operator in brackets: we take into account the identities⁴

$$(\boldsymbol{\sigma}_a \cdot \boldsymbol{\sigma}_b)^2 = 3 - 2(\boldsymbol{\sigma}_a \cdot \boldsymbol{\sigma}_b) \quad (7)$$

and⁵

$$(\boldsymbol{\sigma}_a \cdot \boldsymbol{\sigma}_b)(\boldsymbol{\sigma}_a \cdot \boldsymbol{\sigma}_c) + (\boldsymbol{\sigma}_a \cdot \boldsymbol{\sigma}_c)(\boldsymbol{\sigma}_a \cdot \boldsymbol{\sigma}_b) = 2(\boldsymbol{\sigma}_b \cdot \boldsymbol{\sigma}_c); \quad (8)$$

we obtain

$$\begin{aligned} & (P_{ls}G_l + P_{l's}G_{l'} + P_{ll'}\Gamma_L)^2 \\ & = G_l^2 + G_{l'}^2 + \Gamma_L^2 + \frac{1}{2}[1 + (\boldsymbol{\sigma}_l \cdot \boldsymbol{\sigma}_s) + (\boldsymbol{\sigma}_{l'} \cdot \boldsymbol{\sigma}_s) \\ & \quad + (\boldsymbol{\sigma}_l \cdot \boldsymbol{\sigma}_{l'})](G_lG_{l'} + G_l\Gamma_L + G_{l'}\Gamma_L); \quad (9) \end{aligned}$$

owing to the relation⁶

$$2(\boldsymbol{\sigma}_l \cdot \boldsymbol{\sigma}_s) + 2(\boldsymbol{\sigma}_{l'} \cdot \boldsymbol{\sigma}_s) + 2(\boldsymbol{\sigma}_l \cdot \boldsymbol{\sigma}_{l'}) = 4S(S+1) - 9 \quad (10)$$

and to the fact that for doublets

$$S(S+1) = 3/4,$$

our result reduces to

$$\begin{aligned} & (P_{ls}G_l + P_{l's}G_{l'} + P_{ll'}\Gamma_L)^2 \\ & = G_l^2 + G_{l'}^2 + \Gamma_L^2 - G_lG_{l'} - G_l\Gamma_L - G_{l'}\Gamma_L \quad (11) \end{aligned}$$

TABLE I. The configuration $4s4p3d$ of Sc I. ($F_2=315$, $G_p=4041$, $G_d=1340$, $G_1=375$, $G_3=26.6$.)

Term	Obs.	Calc.	Diff.
$sp(^3P)d \ ^4F^0$	15877	15718	+159
$\quad \quad \quad \ ^2D^0$	16052	16223	-171
$\quad \quad \quad \ ^4D^0$	16132	16099	+33
$\quad \quad \quad \ ^4P^0$	18542	18636	-94
$\quad \quad \quad \ ^2F^0$	21063	21001	+62
$sp(^1P)d \ ^2D^0$	24955	24859	+96
$\quad \quad \quad \ ^2F^0$	25665	25751	-86
$\quad \quad \quad \ z \ ^2P^0$	18808	22026	
$\quad \quad \quad \ y \ ^2P^0$	24955	24859	
$\quad \quad \quad \ x \ ^2P^0$	30662	27876	

¹ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge, 1935), (which we shall denote by TAS), p. 197; the index of G is, however, incorrect.

² P. A. M. Dirac, *Quantum Mechanics* (Oxford, 1935), Section 61, Eq. (35).

³ G. Racah, *Phys. Rev.* **61**, 186 (1942).

⁴ See reference 2, Section 61, Eq. (33).

⁵ This identity follows readily from reference 2, Section 19, Eqs. (54) and (55).

⁶ See reference 2, p. 227.

and then

$$W(^2L) = F_0 + F_0' + \Phi_L \pm (G_i^2 + G_{i'}^2 + \Gamma_L^2 - G_i G_{i'} - G_i \Gamma_L - G_{i'} \Gamma_L)^{\frac{1}{2}}. \quad (12)$$

For the particular case of the configuration pds the formulas are

$$\begin{aligned} {}^4P &= F_0 + 7F_2 - G_p - G_d - G_1 - 21G_3, \\ {}^2P &= F_0 + 7F_2 \pm [G_p^2 + G_d^2 + (G_1 + 21G_3)^2 - G_p G_d - (G_p + G_d)(G_1 + 21G_3)]^{\frac{1}{2}}, \\ {}^4D &= F_0 - 7F_2 - G_p - G_d + 3G_1 - 7G_3, \\ {}^2D &= F_0 - 7F_2 \pm [G_p^2 + G_d^2 + (3G_1 - 7G_3)^2 - G_p G_d + (G_p + G_d)(3G_1 - 7G_3)]^{\frac{1}{2}}, \\ {}^4F &= F_0 + 2F_2 - G_p - G_d - 6G_1 - G_3, \\ {}^2F &= F_0 + 2F_2 \pm [G_p^2 + G_d^2 + (6G_1 + G_3)^2 - G_p G_d - (G_p + G_d)(6G_1 + G_3)]^{\frac{1}{2}}, \end{aligned} \quad (13)$$

where⁷

$$\begin{aligned} F_0 &= F^0(n\bar{p}, n''s) + F^0(n'd, n''s) + F^0(n\bar{p}, n'd), \\ F_2 &= F^2(n\bar{p}, n'd)/35, \\ G_p &= G^1(n\bar{p}, n''s)/3, \quad G_d = G^2(n'd, n''s)/5, \\ G_1 &= G^1(n\bar{p}, n'd)/15, \quad G_3 = 3G^3(n\bar{p}, n'd)/245. \end{aligned} \quad (14)$$

We calculated also in the same way the term energies of the configuration d^3sp and obtained the following results:

$$\begin{aligned} {}^4P &= F_0 - 7F_2 - G_p, \\ {}^2P &= F_0 - 7F_2 + G_d + 10G_1 \pm [G_p^2 + G_d^2 + 100G_1^2 - G_p G_d - 10(G_p + G_d)G_1]^{\frac{1}{2}}, \\ {}^4D &= F_0 + 7F_2 - G_p, \\ {}^2D &= F_0 + 7F_2 + G_d \pm [G_p^2 + G_d^2 - G_p G_d]^{\frac{1}{2}}, \\ {}^4F &= F_0 - 2F_2 - G_p, \\ {}^2F &= F_0 - 2F_2 + G_d + 15G_3 \pm [G_p^2 + G_d^2 + 225G_3^2 - G_p G_d - 15(G_p + G_d)G_3]^{\frac{1}{2}}. \end{aligned} \quad (15)$$

COMPARISON WITH EXPERIMENTAL DATA⁸

Sc I

If we except the doublets 2P , the remaining terms fit very well to the theoretical formulas and

	$sp(^3P)d$	s^2p	$sp(^1P)d$	
$W(^2P^0) =$	$sp(^3P)d$	$F_0 + 7F_2 - G_p + \frac{1}{2}(G_d + G_1 + 21G_3)$	$\frac{1}{5}R''\sqrt{3}$	$\frac{1}{2}(G_d - G_1 - 21G_3)\sqrt{3}$
	s^2p	$\frac{1}{5}R''\sqrt{3}$	X	$\frac{1}{5}R'' - \frac{2}{3}R'$
	$sp(^1P)d$	$\frac{1}{2}(G_d - G_1 - 21G_3)\sqrt{3}$	$\frac{1}{5}R'' - \frac{2}{3}R'$	$F_0 + 7F_2 + G_p - \frac{1}{2}(G_d + G_1 + 21G_3)$

(16)

where X is the unperturbed value of $4s^24p\ ^2P^0$ and $R' = R^1(4s4p, 4p3d)$, $R'' = R^2(4s4p, 3d4p)$, (17) R^k being defined by TAS 8⁶⁸.

⁷ This definition of G_3 differs by a factor 3 from that of TAS, but agrees with reference 3, Eq. (50).

⁸ All experimental data are taken from R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932).

TABLE II. Sharing of the eigenfunctions between the low ${}^2P^0$ terms of Sc I.

Term	$sp(^3P)d$	s^2p	$sp(^1P)d$
$z\ ^2P^0$	53%	42%	5%
$y\ ^2P^0$	39%	24%	37%
$x\ ^2P^0$	8%	34%	58%

the values of the interaction parameters obtained by least squares from these seven terms are in good agreement with the corresponding values of Ti II.⁹ The results are given in Table I; the doublets of the same kind are there distinguished by the resultant spin of the electrons $4s$ and $4p$ instead of that of $4s$ and $3d$, since G_p is much greater than G_d and Γ_L and, therefore, the spin coupling of $4s$ and $4p$ outweighs that of $4s$ and $3d$. The purity of our correlation is about 95 percent, whilst the purity of the correlation to the states $3d4s$ of Sc II is only 89 percent for 2F and 53 percent for 2D .

The calculated values of the two 2P terms fall almost exactly in the centers of the intervals between the three experimental ${}^2P^0$ terms which are in that region of the spectrum, so that it is even impossible to say which of these terms belong to $3d4s4p$. The classification of the remaining term as $3d^2(^1S)4p\ ^2P^0$ cannot be accepted, since this term must be the highest of the configuration $3d^24p$ and not the lowest;⁹ owing to its position, it may be assigned without difficulty to $4s^24p$.

In order to see if the proximity of $4s^24p\ ^2P^0$ may produce displacements of about 3000 cm^{-1} in the ${}^2P^0$ terms of $3d4s4p$, we calculated the configuration interaction between these terms. The resulting matrix is

Introducing the values of the known parameters we have

$$W(^2P^0) = \begin{vmatrix} 22047 & \frac{1}{5}R''\sqrt{3} & 203\sqrt{3} \\ \frac{1}{5}R''\sqrt{3} & X & \frac{1}{5}R'' - \frac{2}{3}R' \\ 203\sqrt{3} & \frac{1}{5}R'' - \frac{2}{3}R' & 27855 \end{vmatrix}, \quad (16')$$

⁹ G. Racah, Phys. Rev. **62**, 438 (1942). Section 9.

and the requirement that the three eigenvalues of this matrix should agree with the three experimental doublets ${}^2P^0$ gives us three equations for X , R' , and R'' ; the resolution of this system gives $X = 24223$ and

$$R' = -2015, \quad R'' = 10831, \quad (18a)$$

or

$$R' = 8764, \quad R'' = 9535. \quad (18b)$$

The linear combination

$$S = \alpha^2 R^1(sp, ps) + R^1(dp, pd) + 2\alpha R^1(sp, pd) \quad (19)$$

may be considered as the integral G^1 for the p electron and an electron which has the radial eigenfunction $\alpha R(s) + R(d)$; S must, therefore, be positive for every value of α ,¹⁰ and this gives us the theoretical limitation

$$|R'| \leq [G^1(4s, 4p) \cdot G^1(3d, 4p)]^{\frac{1}{2}} \\ = [45G_p G_1]^{\frac{1}{2}} = 8528; \quad (20)$$

the value (18b) of R' must therefore be rejected. The analogous limitation for R'' is

$$|R''| \leq [F^2(4s, 4p) \cdot F^2(3d, 4p)]^{\frac{1}{2}}; \quad (21)$$

unfortunately $F^2(4s, 4p)$ does not appear in the formulas of the term energies, but it is reasonable to assume that it must be greater than $F^2(3d, 4p)$; since the value (18a) of R'' does not reach $F^2(3d, 4p) = 35F_2$, we have no reason for rejecting it, and the deviations of the ${}^2P^0$ terms from the theoretical formulas (13) may be considered as explained.

It is interesting to consider the sharing of the eigenfunctions between the three doublets ${}^2P^0$; we calculated it with the parameters (18a) and the results are given in Table II. We see that the sharing is so strong that it has no physical

TABLE III. The configuration $4d5s5p$ of Y I. ($F_2 = 399$, $G_p = 3287$, $G_d = 1716$, $G_1 = 550$, $G_3 = 45.5$.)

Term	Obs.	Calc.	Diff.
$ds\ p \ ^4F^0$	15690	15498	+192
$ds\ p \ ^4D^0$	16855	16583	+272
$ds\ p \ ^4P^0$	19079	19333	-254
$ds(^1D)p \ ^2F^0$	21750	22245	-495
$ds(^3D)p \ ^2F^0$	24736	25447	-711
$dp(^1D)s \ ^2D^0$	16098	16188	-90
$dp(^3D)s \ ^2D^0$	24500	24322	+178
$sp(^3P)d \ ^2P^0$	24553	24155	+398
$sp(^1P)d \ ^2P^0$	28035	27527	+508

¹⁰ See reference 9, Section 10.

TABLE IV. The configuration $3d^94s4p$ of Cu I. ($F_2 = 315.5$, $G_p = 6906$, $G_d = 901$, $G_1 = 391.5$, $G_3 = 95$.)

Term	Obs.	Calc.	Diff.
$sp(^3P)d^9 \ ^4P^0$	22603	22589	-14
$\ ^4F^0$	20990	21012	+22
$\ ^4D^0$	18180	18172	-8
$\ ^2F^0$	17875	17541	-334
$\ ^2P^0$	16448	16067	-381
$\ ^2D^0$	15880	16867	+987
$sp(^1P)d^9 \ ^2F^0$	5383	6019	+636
$\ ^2P^0$	5290	5667	+377
$\ ^2D^0$	4841	3863	-978

meaning to assign the different doublets to a definite configuration; it is also remarkable that the term $y \ ^2P^0$, the value of which differs very little from the unperturbed value of $4s^24p \ ^2P^0$, shares only 24 percent of its eigenfunction.

Ti II

Two terms of $3d4s4p$ are unknown; the remaining do not fit to the formulas, since the order of 2P and 4P is inverted.

Y I

The parameters were calculated by least squares and the comparison with the experimental data is given in Table III. It is remarkable that in this case the parameters of the spin coupling are of the same order of magnitude, so that the coupling of the spins is different for every value of L ; the purities of the given spin couplings are 100 percent for 2F and 2P and 97 percent for 2D .

Zr II

The terms of $4d5s5p$ are so mixed with those of $4d^25p$ that it is impossible to fit them to the theoretical formulas without considering the two configurations together, and also their interaction.

Cu I

The intervals between the quartets have almost exactly the theoretical ratio, but the doublets are perturbed by the terms of the normal series and fit only roughly to the formulas (15). Owing to this fact, we calculated at first $F_0 - G_p$ and F_2 from the quartets, and then the G^k from the doublets. The results are shown in Table IV.