

Configuration Interaction in Complex Spectra

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The electrostatic interaction is calculated between the terms in Russell-Saunders coupling of the electron configurations $nd^2n's$, nd^3 , $ndn's^2$ and $nd^2n''s$. The first order eigenfunctions, for the terms of these configurations in the LSM_LM_S scheme with $M_L=0$, $M_S=\frac{1}{2}$ are given in terms of the zero order functions of Slater. The matrix elements between the quartets of d^2s and d^3 are found to vanish. The sums over closed shells in non-diagonal matrix elements of electrostatic interaction are found to vanish except when

the two electrons not in closed shells have the same value of l . This sum is evaluated in general and for the configurations $nd^2n's - nd^2n''s$. The matrix elements of magnetic spin orbit interaction are given between the initial states without configuration interaction. The electrostatic energies and magnetic splittings are then calculated for the terms of $nd^2n's$, nd^3 and $ndn's^2$; and compared with the values observed in Ti II and Zr II. Zr II agrees particularly well, especially if the observed 3D terms are rearranged.

THIS paper will treat the electrostatic interaction between the terms in Russell-Saunders coupling of the electron configurations $nd^2n's$, nd^3 , $ndn's^2$ and $nd^2n''s$. The method of treating the interaction of d^2s and d^3 has been outlined by Condon.¹ A previous paper² shows how to calculate the matrix of electrostatic interaction. The matrix elements between the quartets of d^2s and d^3 are found to vanish. Since there is no electrostatic interaction between different kinds of terms, interactions exist between all the doublets and between the quartets of $d^2n's$ and $d^2n''s$. This means that these terms cannot be assigned to any single electron configuration but have eigenfunctions which are linear combinations of those of the terms belonging to each configuration separately. Secular equations are

obtained for the term energies, the order of each equation being equal to the number of terms of the same kind which occur in all the electron configurations. The energies obtained as solutions of these equations still contain integrals over the radial parts of the central field eigenfunctions as parameters. With these energies the eigenfunctions for the new states may be found from the matrix of electrostatic interaction. With these eigenfunctions, the separations of the different levels within a term may be found approximately, since the coupling is Russell-Saunders, by using only the diagonal elements of the spin orbit interaction of each electron.

The energy levels and separations thus found for the configurations d^2s , d^3 and ds^2 are compared with the experimental values from Ti II and Zr II.

1. THE MATRIX OF ELECTROSTATIC INTERACTION

Before giving the matrix elements of electrostatic interaction, it will be necessary to consider in general the sums over closed shells which enter into them.

Slater³ has shown that, in computing the diagonal elements of the matrix of electrostatic interaction, the sum over pairs of electrons, one of which is an outer electron whereas the other runs over the individual electrons in a closed shell, gives the same value for each zero order state. This value has been calculated by Shortley.⁴ Thus these sums do not affect the separation between terms. These sums exist for the non-diagonal matrix elements only when the states differ with respect to the individual sets of quantum numbers of just one electron¹ but can be shown to be zero except where the two electrons not in closed shells have the same value of l . Where these non-diagonal sums

¹ E. U. Condon, Phys. Rev. **36**, 1121 (1930).

³ J. C. Slater, Phys. Rev. **34**, 1293 (1929).

² C. W. Ufford and G. H. Shortley, Phys. Rev. **42**, 167 (1932), referred to as I below.

⁴ G. H. Shortley, Phys. Rev. **40**, 185 (1932).

are different from zero they will affect the separation between terms. To see when these sums vanish and to evaluate them when they do not, the procedure is identical with that used by Shortley⁴ for the diagonal elements, except that the two electrons not in a closed shell have different individual sets of quantum numbers. Following Shortley's calculation and using the orthogonality of the surface spherical harmonics one obtains for the sum over a single closed shell in a non-diagonal matrix element where the states differ only in the individual sets of quantum numbers of one electron:

$$\begin{aligned}
 & \sum_{m'_s} \sum_{m'_l=-l'}^{l'} \delta(m'_s, m_s'') \left[\int \int \bar{v}_1(nlm_l) \bar{v}_2(n'l'm'_l) (e^2/r_{12}) v_1(n''l''m''_l) v_2(n'l'm'_l) d\tau_1 d\tau_2 \right. \\
 & \quad \left. - \delta(m_s, m_s') \int \int \bar{v}_1(nlm_l) \bar{v}_2(n'l'm'_l) (e^2/r_{12}) v_1(n'l'm'_l) v_2(n''l''m''_l) d\tau_1 d\tau_2 \right] \\
 & = \delta(l, l'') \delta(m_l, m_l'') \left[2(2l'+1) \int_0^\infty \int_0^\infty (e^2/r_{>}) R_1(nl) R_1(n'l) R_2^2(n'l') dr_1 dr_2 \right. \\
 & \quad \left. - (2l'+1/2l+1) \sum_k C^l_{l'k} e^2 \int_0^\infty \int_0^\infty (r_{<}^k/r_{>}^{k+1}) R_1(nl) R_1(n'l) R_2(n'l') R_2(n''l) dr_1 dr_2 \right] \\
 & = 2(2l'+1) R^0(nl, n'l'; n''l, n'l') - (2l'+1/2l+1) \sum_k C^l_{l'k} R^k(nl, n'l'; n''l, n'l').
 \end{aligned} \tag{1}$$

This expression reduces to the diagonal value given by Shortley when $n=n''$. The condition $\delta(m_s, m_s'')\delta(m_l, m_l'')$ is always fulfilled since the states differ by only one electron and have the same values of M_L and M_S . This sum over closed shells has the same value whenever it occurs, within a single pair of configurations, since it depends only on the n and l quantum numbers of the electrons.

With this value for the sum over a closed shell, we now return to the matrix of electrostatic interaction for the configurations $nd^2n's$, nd^3 , $ndn's^2$ and $nd^2n''s$ in question. Using first order eigenfunctions in the $LS M_L M_S$ scheme, one obtains the following non-diagonal matrix elements of electrostatic interaction:⁵

$$\begin{aligned}
 & nd^2n's - nd^2n''s \\
 & (nd^2n's_1^4 F | e^2/r_{12} | nd^2n''s_1^4 F) = R_0 - 2''R, \\
 & (nd^2n's_1^4 P | e^2/r_{12} | nd^2n''s_1^4 P) = R_0 - 2''R, \\
 & (nd^2n's_1^2 G | e^2/r_{12} | nd^2n''s_1^2 G) = R_0 - ''R, \\
 & (nd^2n's_1^2 F | e^2/r_{12} | nd^2n''s_1^2 F) = R_0 + ''R, \\
 & (nd^2n's_1^2 D | e^2/r_{12} | nd^2n''s_1^2 D) = R_0 - ''R, \\
 & (nd^2n's_1^2 P | e^2/r_{12} | nd^2n''s_1^2 P) = R_0 + ''R, \\
 & (nd^2n's_1^2 S | e^2/r_{12} | nd^2n''s_1^2 S) = R_0 - ''R,
 \end{aligned} \tag{2}$$

⁵ The order of the eigenfunction is indicated by the subscript on the left. The zero order eigenfunctions are Slater's³ determinants of one-electron central field functions. The first order eigenfunctions are those in which the matrix of electrostatic interaction is diagonal in each configuration

with respect to the different kinds of terms occurring in Russell-Saunders coupling. These may be found from the zero order functions by the methods of Gray and Wills, Wigner or Johnson (cf. I). Second order eigenfunctions are those belonging to terms of the same kind within a con-

where⁶

$$R_0 = (nd^2n's, nd^2n''s) \{ 2R^0(nd, n's; nd, n''s) + \sum_{n'l'l'} [2(2l'+1)R^0(n's, n'l'l'; n''s, n'l'l') - R^0(n's, n'l'l'; n'l'l', n''s)] \}$$

and

$$\begin{aligned} {}''R &= (nd^2n's, nd^2n''s) \frac{1}{5} R^2(nd, n's; n''s, nd), \\ nd^2n's - nd^3 \\ (nd^2n's_1^4F | e^2/r_{12} | nd^3_1^4F) &= 0, \\ (nd^2n's_1^4P | e^2/r_{12} | nd^3_1^4P) &= 0, \\ (nd^2n's_1^2G | e^2/r_{12} | nd^3_1^2G) &= 2\frac{1}{2}5'R_2, \\ (nd^2n's_1^2F | e^2/r_{12} | nd^3_1^2F) &= 10\frac{1}{2}3'R_2, \\ (nd^2n's_1^2D | e^2/r_{12} | nd^3_2^2D^+) &= (5/2)\frac{1}{2}(-3\frac{1}{2}3\alpha_- + 7\frac{1}{2}\alpha_+)R_2, \\ (nd^2n's_1^2D | e^2/r_{12} | nd^3_2^2D^-) &= (5/2)\frac{1}{2}(-7\frac{1}{2}\alpha_- - 3\frac{1}{2}3\alpha_+)R_2, \\ (nd^2n's_1^2P | e^2/r_{12} | nd^3_1^2P) &= (35)\frac{1}{2}3'R_2, \end{aligned} \quad (3)$$

where

$$\begin{aligned} {}'R_2 &= (nd^3, nd^2n's)(1/35)R^2(nd, nd; nd, n's), \\ \alpha_{\pm} &= + \left(\frac{1}{2} \pm \frac{4F_2 + 120F_4}{Ra} \right)^{\frac{1}{2}}, \end{aligned}$$

$$Ra = 2[193F_2^2 - 1650F_2F_4 + 8325F_4^2]^{\frac{1}{2}},$$

and

$$\begin{aligned} F_2 &= (d^3)(1/49)F^2(nd^2), \\ F_4 &= (d^3)(1/441)F^4(nd^2). \end{aligned}$$

$$nd^2n's - ndn's^2 \quad (4)$$

$$(nd^2n's_1^2D | e^2/r_{12} | ndn's^2_1D) = (70)\frac{1}{2}'R_2,$$

figuration in which the matrix of electrostatic interaction for these terms is diagonal. Second order eigenfunctions for the two 2D 's of d^3 have been found in I. Finally third order eigenfunctions are those in which the matrix of electrostatic interaction is diagonal for more than one configuration at a time. Thus, second order functions arise only when more than one term of the same kind occurs in a single configuration and third order eigenfunctions arise only when the non-diagonal elements of electrostatic interaction between terms of the same kind lying in different configurations are not zero. Each order of function can be expressed as a linear combination of the functions of lower order. When only two second or third order functions of the same kind occur it is sometimes convenient to indicate them by plus and minus superscripts on the right. The + and - superscripts on the right indicate the function belonging to the term with higher or lower energy, respectively.

⁶ $\sum_{n'l'l'}$ is the sum over all the closed shells occurring in the atom, l' taking on the values 0, 1, 2, ... for the s, p, d, \dots shells. $n'l'$ distinguishes the different shells with the same value of l' .

In the R 's, the first two electrons in the integral belong to the first configuration in the bracket, and the second two electrons to the second configuration except in $\sum_{n'l'l'}$. In $\sum_{n'l'l'}$ the first two electrons belong to the atom with its electrons outside closed shells in the first configuration given in the bracket and the second two electrons to the atom in the second configuration. In each pair, the electron with l given is outside a closed shell, the electron with $l=l'$ belongs to one of the closed shells.

In the G 's, the first electron in the integral belongs to the first configuration in the bracket and the second electron to the second configuration. In the case of the diagonal elements all the electrons belong to the same configuration which is given in a bracket before the integral.

where

$${}^1R_2 = (nd^2n's, ndn's^2)(1/35)R^2(nd, nd; nd, n's).$$

$$ndn's^2 - nd^3$$

$$(ndn's^2 \text{ } ^2_1D | e^2/r_{12} | nd^3 \text{ } ^2_2D^+) = -2\alpha_+'G_2, \tag{5}$$

where

$$(ndn's^2 \text{ } ^2_1D | e^2/r_{12} | nd^3 \text{ } ^2_2D^-) = 2\alpha_-'G_2,$$

$${}^1G_2 = (nd^3, ndn's^2) \frac{1}{5}G^2(nd, n's)$$

and α_{\pm} is given in Eq. (3). $ndn's^2 - ndn's^2$ gives the diagonal element,

$$(ndn's^2 \text{ } ^2_1D | e^2/r_{12} | ndn's^2 \text{ } ^2_1D) = 2'F_0 + ''F - 'G_2, \tag{6}$$

where

$$'F_0 = (ndn's^2)F^0(nd, n's), \quad ''F = (ndn's^2)F^0(n's^2),$$

and

$${}^1G_2 = (ndn's^2) \frac{1}{5}G^2(nd, n's).$$

The other diagonal elements have been given by Condon and Shortley⁷ and in I. The matrix elements for $nd^2n's$ are obtained from those for $nd^2n's$ by replacing n' by n'' giving different radial integrals.

In order to determine the phases of the first order states required to give these non-diagonal matrix elements, the first order eigenfunctions for d^2s and d^3 in the $LS M_L M_S$ scheme are given in Table I for $M_L=0$ and $M_S=1/2$.

The zero order states $A, B, C \dots$ for d^2s, d^3 and $ndn's^2 \text{ } ^2D_{0,1/2}$ are given in Table II in the notation of I.

The secular equations for the third order energies may now be written and solved in terms of

TABLE I. First order eigenfunctions $M_L=0, M_S=\frac{1}{2}$.

The first order eigenfunctions in the first column on the left in each configuration are linear combinations of the zero order functions $A, B, C \dots$ in the first row, the coefficient of each zero order function appearing in the column below it. The second column from the left gives the normalization factor of the whole linear combination. The zero order functions are normalized separately so that N is the reciprocal of the square root of the sum of the squares of the coefficients appearing in the same row.

$nd^2n's$								nd^3										
N	A	B	C	D	E	F	G	N	A	B	C	D	E	F	G	H		
${}^4_1F_{0, \frac{1}{2}}$	$(15)^{-\frac{1}{2}}$	-1	-1	-1	2	2	2	0	${}^4_1F_{0, \frac{1}{2}}$	$(15)^{-\frac{1}{2}}$	-2	-2	-2	0	0	1	1	1
${}^4_1P_{0, \frac{1}{2}}$	$(15)^{-\frac{1}{2}}$	2	2	2	1	1	1	0	${}^4_1P_{0, \frac{1}{2}}$	$(15)^{-\frac{1}{2}}$	1	1	1	0	0	2	2	2
${}^2_1G_{0, \frac{1}{2}}$	$(70)^{-\frac{1}{2}}$	1	-1	0	-4	4	0	6	${}^2_1H_{0, \frac{1}{2}}$	$(42)^{-\frac{1}{2}}$	-1	2	-1	$-6^{\frac{1}{2}}$	$6^{\frac{1}{2}}$	2	-4	2
${}^2_1F_{0, \frac{1}{2}}$	$(30)^{-\frac{1}{2}}$	-1	-1	2	2	2	-4	0	${}^2_1G_{0, \frac{1}{2}}$	$(14)^{-\frac{1}{2}}$	$-2^{\frac{1}{2}}$	0	$2^{\frac{1}{2}}$	$-3^{\frac{1}{2}}$	$-3^{\frac{1}{2}}$	$2^{\frac{1}{2}}$	0	$-2^{\frac{1}{2}}$
${}^2_1D_{0, \frac{1}{2}}$	$(14)^{-\frac{1}{2}}$	2	-2	0	-1	1	0	-2	${}^2_1F_{0, \frac{1}{2}}$	$(30)^{-\frac{1}{2}}$	$-2^{\frac{1}{2}}$	$8^{\frac{1}{2}}$	$-2^{\frac{1}{2}}$	$-3^{\frac{1}{2}}$	$3^{\frac{1}{2}}$	$-2^{\frac{1}{2}}$	$8^{\frac{1}{2}}$	$-2^{\frac{1}{2}}$
${}^2_1P_{0, \frac{1}{2}}$	$(30)^{-\frac{1}{2}}$	-2	-2	4	-1	-1	2	0	${}^2_1D_{0, \frac{1}{2}}^a$	$(4)^{-\frac{1}{2}}$	-1	0	1	0	0	-1	0	1
${}^2_1S_{0, \frac{1}{2}}$	$(5)^{-\frac{1}{2}}$	1	-1	0	1	-1	0	1	${}^2_1D_{0, \frac{1}{2}}^b$	$(28)^{-\frac{1}{2}}$	$3^{\frac{1}{2}}$	0	$-3^{\frac{1}{2}}$	$-8^{\frac{1}{2}}$	$-8^{\frac{1}{2}}$	$-3^{\frac{1}{2}}$	0	$3^{\frac{1}{2}}$
									${}^2_1P_{0, \frac{1}{2}}$	$(210)^{-\frac{1}{2}}$	-4	8	-4	$54^{\frac{1}{2}}$	$-54^{\frac{1}{2}}$	1	-2	1

⁷ E. U. Condon and G. H. Shortley, Phys. Rev. 37, 1025 (1931).

TABLE II. Zero order eigenfunctions $M_L=0$; $M_S=\frac{1}{2}$.
 $nd\ n's^2\ ^2D_{0, \frac{1}{2}}$ $A\ u_1(0^+)u_2(0_s^+)u_3(0_s^-)$

d^2s		d^3	
A	$A\ u_1(2^+)u_2(-2^-)u_3(0_s^+)$	A	$A\ u_1(2^+)u_2(0^+)u_3(-2^-)$
B	$A\ u_1(2^-)u_2(-2^+)u_3(0_s^+)$	B	$A\ u_1(2^+)u_2(0^-)u_3(-2^+)$
C	$A\ u_1(2^+)u_2(-2^+)u_3(0_s^-)$	C	$A\ u_1(2^-)u_2(0^+)u_3(-2^+)$
D	$A\ u_1(1^+)u_2(-1^-)u_3(0_s^+)$	D	$A\ u_1(2^+)u_2(-1^+)u_3(-1^-)$
E	$A\ u_1(1^-)u_2(-1^+)u_3(0_s^+)$	E	$A\ u_1(1^+)u_2(1^-)u_3(-2^+)$
F	$A\ u_1(1^+)u_2(-1^+)u_3(0_s^-)$	F	$A\ u_1(1^+)u_2(0^+)u_3(-1^-)$
G	$A\ u_1(0^+)u_2(0^-)u_3(0_s^+)$	G	$A\ u_1(1^+)u_2(0^-)u_3(-1^+)$
		H	$A\ u_1(1^-)u_2(0^+)u_3(-1^+)$

the radial integral parameters. One obtains quadratic equations for the 4F 's, 4P 's and 2S 's; cubic equations for the 2G 's, 2F 's and 2P 's; and a quintic equation for the 2D 's.

If nd^2n' 's be omitted, quadratic equations are obtained for the 2G 's, 2F 's and 2P 's; and a quartic equation for the 2D 's.

Next with the energies obtained as solutions of these secular equations, the third order states, in which the matrix of electrostatic interaction for all the configurations is diagonal, may be found by solving the simultaneous equations obtained from the matrix of the secular equation by substituting each energy value successively.

2. SEPARATIONS OF THE ENERGY LEVELS WITHIN TERMS

With the third order states of § 1, it is now possible to calculate the separations of the energy levels within each term approximately as was done for the two $d^3\ ^2D$'s in I. The matrix elements of magnetic interaction calculated from the third order states are given in terms of the matrix elements of magnetic interaction of the first order states. Therefore the latter matrix elements needed in addition to those found for d^3 in Pauling and Goudsmit⁸ and I are given here. For d^2s the diagonal elements of 4F , 4P and 2P are the same as those of d^3 . The others are:

$$\begin{aligned}
 \langle d^2s\ ^2G_{9/2}, 9/2 | v^1 | d^2s\ ^2G_{9/2}, 9/2 \rangle &= 0, \\
 \langle d^2s\ ^2F_{7/2}, 7/2 | v^1 | d^2s\ ^2F_{7/2}, 7/2 \rangle &= d^2s\zeta_{nd}, \\
 \langle d^2s\ ^2D_{5/2}, 5/2 | v^1 | d^2s\ ^2D_{5/2}, 5/2 \rangle &= 0, \\
 \langle ds^2\ ^2D_{5/2}, 5/2 | v^1 | ds^2\ ^2D_{5/2}, 5/2 \rangle &= ds^2\zeta_{nd}.
 \end{aligned}
 \tag{7}$$

The non-diagonal elements, between the first order states of terms of the same kind having the same values of M_L and M_S , vanish for the configurations $nd^2n's$, nd^3 , $ndn's^2$ and nd^2n' 's except that element between the two $d^3\ ^2D$'s which is:

$$\langle d^3\ ^2D_{5/2}^+, 5/2 | v^1 | d^3\ ^2D_{5/2}^-, 5/2 \rangle = -\frac{(21)^{1/2}}{3Ra} (4F_2 + 15F_4)d^3\zeta_{nd},
 \tag{8}$$

where F_2 , F_4 and Ra have the values given in Eq. (3).

If nd^2n' 's be omitted, the matrix elements of magnetic interaction of the quartet levels will be unaffected by the interaction of the configurations, since the non-diagonal elements of electrostatic interaction are zero for the first order quartet eigenfunctions. The elements affected will be those of 2G , 2F , 2D and 2P . As in I, the separations of the energy levels within the term are obtained from the diagonal matrix elements of magnetic interaction by the Landé interval rule.

⁸ L. Pauling and S. Goudsmit, *Structure of Line Spectra*, § 39. The a of this section is ζ_{nd} .

3. COMPARISON WITH EXPERIMENT

The experimental term values of Russell⁹ for Ti II and of Kiess and Kiess¹⁰ for Zr II were the only ones found complete enough to test the calculations.

It was found that the lack of all but a few experimental term values of $d^2n's$, combined with the fact that this configuration lies high compared to $nd^2n's$, nd^3 and $ndn's^2$, made it impossible to determine the three additional radial integral parameters with a reasonable accuracy. Therefore the configuration $d^2n's$ was omitted and only the three configurations $nd^2n's$, nd^3 and $ndn's^2$ compared with experiment.

In order to evaluate the parameters, those radial integrals which contained electrons of identical n and l values were taken as equal, regardless of the fact that these electrons belonged to different configurations.¹¹ Although this introduces some error, it may be expected to give the best values of the parameters which can be obtained without calculating them from the radial eigenfunctions.

The radial integral parameters occurring in the diagonal matrix elements were first evaluated by the method of least squares using the quartet terms, the doublet terms, $nd^2n's^2S$, nd^3^2H , the mean of the 2G 's, and the mean of the 2P 's or 2F 's since these two means are theoretically the same. In Ti II, $nd^2n's^2S$ is not used as it appears to be perturbed and would thus introduce a larger error in the parameters. With these parameters, the interaction parameter $'R_2$ is found by making the sum of the squares of the errors in the calculated values of the three doublet separations, $nd^3^2G - nd^2n's^2G$, $nd^3^2F - nd^2n's^2F$ and $nd^3^2P - nd^2n's^2P$, a minimum. The values of the parameters are listed in Table III. These parameters are then used to solve the quartic equation to find the 2D energy levels.

The results for the energy levels of Ti II and Zr II are given in Fig. 1. In Ti II, d^3^2H and d^3^2P are now separated by the interaction but the

TABLE III. Radial integral parameters $nd^2n's$, nd^3 , and $ndn's^2$, values from experiment.

$F_0 = F^0(nd^3)$. The values of the other parameters in terms of the F 's, G 's and R 's of Slater³ and I are given in Eqs. (3), (4), (5) and (6). In this table, all radial integrals in which the electrons have the same values of n and l are considered equal, even when the electrons belong to different configurations.

	Ti II	Zr II
F_0	6549.	5761.
F_2	938.7	705.7
F_4	68.03	50.44
$'F_0$	2249.	2527.
$''F$	21870.	9562.
$'G_2$	1097.	1873.
$'R_2$	191.8	387.3
α_+	0.8905	0.8888
α_-	0.4550	0.4583
Ra	20340.	15300.

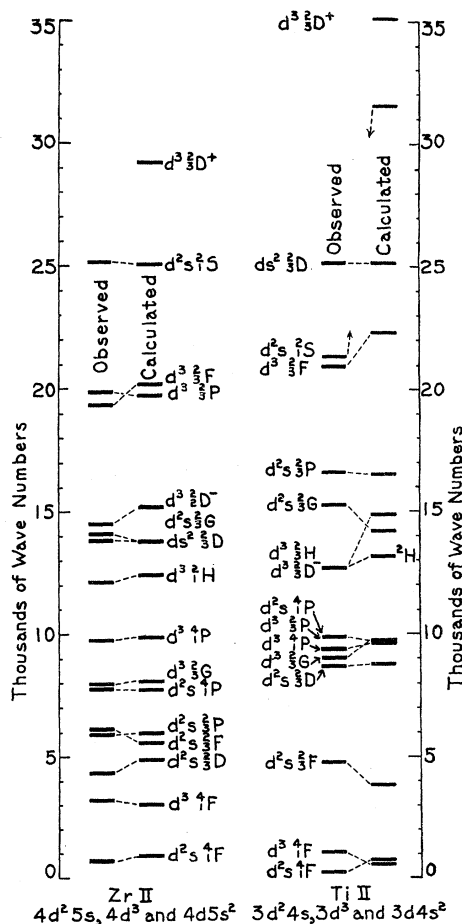


FIG. 1. Term values.

⁹ H. N. Russell, *Astrophys. J.* **66**, 283 (1927).

¹⁰ C. C. Kiess and H. K. Kiess, *Bur. Standards J. Research* **5**, 1210 (1930).

¹¹ I am grateful to Professor D. R. Hartree for pointing out that, while not entirely arbitrary, these integrals are not identical.

TABLE IV. Energy level separations in Ti II and Zr II with interaction between d^2s , d^3 and ds^2 .

Term notation	Ti II		Zr II		Ti II		Zr II		Ti II		Zr II			
$d^3\ ^4F$	† Observed		128.37	458.02	103.41	404.59	75.84	322.84						
	Calculated		<i>133</i>	<i>512</i>	<i>104</i>	<i>398</i>	<i>74.1</i>	<i>284</i>						
$d^2s\ ^4F$			167.75	558.47	131.53	448.77	93.94	314.67						
			<i>170</i>	<i>580</i>	<i>132</i>	<i>451</i>	<i>94.2</i>	<i>322</i>						
$d^3\ ^4P$							122.29	225.85			32.05	189.70		
							<i>74.1</i>	<i>284</i>			<i>44.5</i>	<i>170</i>		
$d^2s\ ^4P$							94.00*	322.14*			57.87	223.35		
							<i>94.2</i>	<i>322</i>			<i>56.5</i>	<i>193</i>		
$d^3\ ^2H$	97.82*	375.20*	$d^3\ ^2G$	120.46	315.06	$d^3\ ^2F$	-59.89	-81.60	$d^3\ ^2D^+$	—	—	$d^3\ ^2P$	125.02	466.76
	<i>97.8</i>	<i>375</i>		<i>108</i>	<i>296</i>		<i>-48.8</i>	<i>-124</i>		<i>-43.6</i>	<i>-164</i>		<i>101</i>	<i>365</i>
			$d^2s\ ^2G$	-8.07	130.69	$d^2s\ ^2F$	268.99	714.69	$d^3\ ^2D^-$	129.38	434.73	$d^2s\ ^2P$	109.46	387.32
				<i>12.2</i>	<i>164</i>		<i>261</i>	<i>828</i>		<i>118</i>	<i>393</i>		<i>101</i>	<i>362</i>
									$d^2s\ ^2D$	33.80	257.20			
										<i>16.8</i>	<i>300</i>			
									$ds^2\ ^2D$	231.70*	734.40*			
										<i>232</i>	<i>734</i>			
11/2 J values	9/2			7/2			5/2			3/2			1/2	

† Observed values are in Roman type, calculated values in italics.

* The observed separations marked with asterisks were used to calculate the following values of ζ_{nd} :

	Ti II	Zr II
$d^3\zeta_{nd}$	88.9	341
$d^2s\zeta_{nd}$	113	386
$ds^2\zeta_{nd}$	99.5	392

agreement is about the same as it was without considering interaction. However, omitting $ds^2\ ^2D$ which has a unique parameter to determine its position, the calculated displacements of the remaining 15 levels from their center of gravity depend now on only 5 instead of 6 radial integral parameters. Thus equally good agreement is obtained for Ti II with one less parameter. The discrepancies still remaining in Ti II might be lessened if the interaction with higher configurations such as $nd^2n's$ could be included. An accurate theoretical evaluation of the radial integral parameters may then be expected to give satisfactory agreement with experiment.

In Zr II, the experimental values of the 2D 's have been reassigned to give a more reasonable agreement with the theory. As no high 2D was observed in d^3 , this term has been omitted from

the experimental list, as was the case in Ti II. The term assigned as the higher 2D of d^3 is considered to be the lower one, $d^3\ ^2D^-$. This means that one of the experimental terms is not a 2D belonging to these configurations. As Kiess and Kiess remark that the assignment of $ndn's^2\ ^2D$ is doubtful, this term is omitted and replaced by the level assigned as the lower 2D of d^3 which is now considered to be $ndn's^2\ ^2D$. As evidence for this change, $d^3\ ^2D^-$ of Kiess and Kiess has its three strongest multiplets with dsp^2PDF so that by changing it to $ds^2\ ^2D$ these become one electron transitions rather than the more improbable two electron jumps. It might be argued that the high lying $d^3\ ^2D^+$, which has been calculated, should be pushed down because of the interaction with 2D 's lying above it. However, as Brillouin¹²

¹² L. Brillouin, J. de Physique 3, 373 (1932).

has shown, it is impossible for such interaction to push it below $ds^2\ ^2D$. Therefore, since in Russell-Saunders coupling the magnetic interaction does not affect the center of gravity of each term, to get even rough agreement, the observed value of $d^3\ ^2D^+$ must lie above $ds^2\ ^2D$.

Now from these third order energies, the third order eigenfunctions may be calculated. The squares of the coefficients, in the linear combination of the first or second order eigenfunctions which must be taken to give the third order eigenfunctions, give the relative weights of the initial states that go to make up the final state. Except for the 2P 's, the original configuration assignment gives the state of greatest weight in the final state after configuration interaction. The final states of 2P are made up of nearly equal weights of the initial states with these weights reversed from the original observed assignment. That configuration interaction should have the greatest effect on the 2P 's is to be expected since they disagreed badly with experiment in the configurations separately.

With the eigenfunctions, the separations of the levels with different J values within the terms can be found in terms of three radial integral

parameters ζ_{nd} , one value coming from each of the configurations d^2s , d^3 , and ds^2 . ζ_{nd} is then found from the observed separation of a term which will give approximately an average value for each configuration. $d^3\zeta_{nd}$ is taken from $d^3\ ^2H$ as was done by Pauling and Goudsmit,⁸ $d^2s\zeta_{nd}$ from $d^2s^4P_{5/2-3/2}$ and $ds^2\zeta_{nd}$ from $ds^2\ ^2D$. The separations calculated with these parameters are compared with the observed values in Table IV.¹³

The separations of the 2D 's in Zr II present another argument in favor of rearranging the 2D 's as has been done here, since there was complete disagreement in the separations of the two 2D 's of d^3 before they were rearranged.

In conclusion it has been seen that the interaction of configurations in Russell-Saunders coupling has improved the calculated energies for the different terms of d^2s , d^3 and ds^2 in Ti II and Zr II. Zr II especially presents a striking effect from configuration interaction. Badly confused before, it comes out in satisfactory agreement with experiment after the interaction has been applied.

¹³ In Ti II, the quartet separations and that for $d^3\ ^2H$ are those given by Pauling and Goudsmit.⁸