PHYSICAL REVIEW VOLUME 88, NUMBER 3 NOVEMBER 1, 1952

The Configuration Interaction between the Odd Terms in the Iron Group*

NORBERT ROSENZWEIG†
Department of Physics, Cornell University, Ithaca, New York

(Received July 7, 1952)

Using Racah's methods, the matrix components of the electrostatic interaction between the terms of the configurations $d^{n-2}sp$ and $d^{n-1}p$ are expressed as linear combinations of Slater integrals. The result consists of two parts. One part represents the interaction between the terms of the parent configurations. The second part results from the coupling of the p electron to the parent groups and contains the Slater integrals $R^2(sp,dp)$ and $R^1(sp,pd)$. The appropriate linear combinations of these integrals are formed by means on the coefficients of fractional parentage, the Racah coefficients, and a spin-dependent factor. A tabulation of coefficients sufficient for the construction of the matrix components for the entire iron group is given.

I. INTRODUCTION

THE principal lines observed in the spectra of the elements in the iron group arise from the combinations of the levels belonging to the deep even configurations $3d^{n-2}4s^2$, $3d^{n-1}4s$, $3d^n$ with the levels of the deep odd configurations $3d^{n-2}4s4p$ and $3d^{n-1}4p$. Analyses of many of these spectra have been carried out, and assignments of the spectroscopic levels have been made with respect to configuration, spin, and orbital and total angular momenta.[1]

However, whereas the identification of the angular momenta is rather reliable, the specification of the configuration is sometimes not. Under such circumstances it is desirable to settle doubtful assignments by means of theoretical calculations. A twofold attack on this problem is possible[2] namely, the calculation of energy levels and the calculation of line strengths.

This paper deals with the energy level problem[3] and more particularly with the matrix components of the electrostatic interaction which connect different configurations.

If the configurations are well separated, the matrix components of the configuration interaction (CI) are usually small compared to the difference between the diagonal elements which they connect. In such a case these matrix elements have no appreciable effect on the determination of the eigenvalues and they may be neglected. The configuration label then is a set of good quantum numbers to a high degree of accuracy. If, on the other hand, the configurations overlap, the matrix components of CI can frequently not be neglected. In this case the energy eigenfunction may contain more than one configuration to a considerable extent, so that the assignment of a term to only one configuration, if at all meaningful, is a rough approximation.

The configurations of the elements in the iron group overlap considerably. A theoretical study of their term values must therefore include a consideration of CI. The matrix components connecting the even configurations have been derived for d^3, d^2s, and ds^2 by Ufford[4] and for configurations containing many equivalent electrons by Racah.[5] Their results have been applied to specific spectra by various authors.[6]

It is desirable to make available also the matrix components connecting the odd configurations. Rohrlich[2] in his work on the classification of the odd terms of Ti I treated the CI to some extent by considering the interaction between the even parent configurations only. He found that the CI had an appreciable effect on the eigenvalues. Ishidzu and Obi[7] attribute at least partly to the CI, the disagreement between the calculated and observed values of several terms assigned to the configuration d^6p in the spectrum of Fe II. A study[8] of the odd terms of Fe I indicates that CI is even more important in this case than for Ti I or Fe II. This is not surprising in view of the almost complete overlapping of the configurations d^6sp and d^7p and the relatively small energy differences which separate the many like terms.

In this paper we shall obtain the matrix components of the electrostatic interaction which connect the terms of $d^{n-2}sp$ and $d^{n-1}p$. As usual this means we shall express the interaction in the Russell-Saunders scheme in terms of the solutions of the central field problem, i.e., in terms of the Slater integrals R^k. The methods given by Racah[5,9] for dealing with many equivalent electrons will be employed. We refer to his papers for

---

* Based on Sec. V of the author's Ph.D. thesis, Cornell University, 1951, unpublished. Some of the work was carried out at the Argonne National Laboratory.

† Now at Argonne National Laboratory, Chicago, Illinois.

[1] *Atomic Energy Levels*, Vol. I, National Bureau of Standards Circular 467 (1949). Volume II to appear in the near future.

[2] See F. Rohrlich, Phys. Rev. **74**, 1381 (1948).

[3] We are concerned here with the traditional attack on the problem as described by E. U. Condon and W. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935). It consists of constructing the matrix of the electrostatic interaction in the Russell-Saunders scheme. The matrix elements are expressed in terms of the solutions of the approximating central field problem, i.e., in terms of Slater integrals. Extensions which make the theory applicable to configurations containing many equivalent electrons (e.g., filling of the d shill) have been made by G. Racah (see reference 5).

[4] C. W. Ufford, Phys. Rev. **44**, 732 (1933).

[5] G. Racah, Phys. Rev. **63**, 367 (1943), hereafter referred to as RIII.

[6] See, for example, C. W. Ufford (reference 4), Ti II and Zr II; A. Many, Phys. Rev. **70**, 511 (1946), Ti-I and -II, V-II and -III; A. A. Schweizer, Phys. Rev. **80**, 1080 (1950), V I and Cr II; R. E. Trees, Phys. Rev. **83**, 756 (1951), Mn II.

[7] T. Ishidzu and S. Obi, J. Phys. Soc. Japan **5**, 124 (1950).

[8] N. Rosenzweig, thesis, Cornell, 1951, unpublished.

[9] G. Racah, Phys. Rev. **62**, 438 (1942), referred to as RII.

an exposition of the underlying theory as well as for definitions and notation.

II. THE ELECTROSTATIC INTERACTION BETWEEN $d^{n-2}sp$ AND $d^{n-1}p$

In order to be able to distinguish all the observed terms in the configurations $d^{n-1}p$ and $d^{n-2}sp$, the Russell-Saunders scheme must include not only S and L, the spin and orbital angular momenta of the entire configuration, but also the following quantum numbers: $\alpha_1S_1L_1$ representing respectively the seniority number, spin, and orbital angular momenta of the d^{n-2} group; S_2 spin of the parent $d^{n-2}s$; and $\alpha_3S_3L_3$ of the parent d^{n-1}. The matrix elements which are of direct interest are the following:

$$\left[d^{n-2}(\alpha_1S_1L_1)sS_2L_1pSL\left|\sum_{i<j}^{n}\frac{e^2}{r_{ij}}\right|d^{n-1}\alpha_3S_3L_3pSL\right]. \quad (1)$$

However, to begin with, we shall consider the somewhat more general configurations $l^{n-2}l'l''$ and $l^{n-1}l''$. The identification of l, l', and l'' with d, s, and p electrons will not be made until this specialization results in a simplification. Thus, we wish to express

$$C=\left[l^{n-2}(\alpha_1S_1L_1)l'S_2L_2l''SL\left|\sum_{i<j}^{n}\frac{e^2}{r_{ij}}\right|l^{n-1}\alpha_3S_3L_3l''SL\right] \quad (2)$$

in terms of Slater integrals. This can be accomplished because we know, as a result of Racah's work, how to expand the antisymmetric eigenfunctions in the above scheme in terms of one-electron eigenfunctions. The reduction of (2) will, in fact, consist largely of exhibiting explicitly (but only to the extent necessary) the construction of the eigenfunctions and the application of orthogonality conditions.

The following expanded forms of the eigenfunctions will be used:

(A) Explicit antisymmetrization with respect to a particular inequivalent electron.

$$\Psi[l^{n-1}\alpha_3S_3L_3l''SL]=n^{-\frac{1}{2}}\sum_{q=1}^{n}(-1)^Q\Psi[l^{n-1}\alpha_3S_3L_3l_q''SL].$$

Q is the parity of the permutation which exchanges q with n.

(B) Addition of two angular momenta.

$$\psi[l^{n-1}\alpha_3S_3L_3l_q''SL]$$
$$=\sum_{M_{S_3}M_{L_3}}\sum_{m_{s''}m_{l''}}\psi[l^{n-1}\alpha_3S_3L_3M_{S_3}M_{L_3}]\Phi[n''l_q''m_{l''}m_{s''}]$$
$$\times[M_{S_3}M_{L_3}m_{s''}m_{l''}|M_SM_LSL].$$

The coefficients of the transformation are well known. We shall need only the general properties of the unitary transformation.

(C) Expansion in terms of fractional parentage.

$$\psi[l^{n-1}\alpha_3S_3L_3]=\sum_{\alpha_3'S_3'L_3'}\psi[l^{n-2}\alpha_3'S_3'L_3'l_{n-1}S_3L_3]$$
$$\times[l^{n-2}\alpha_3'S_3'L_3'lS_3L_3l^{n-1}\alpha_3S_3L_3].$$

The coefficients in this expansion are the coefficients of fractional parentage as introduced by Racah in RIII. It should be noted that the equivalent l electron which is added to the parent angular momenta in the manner (B) is numbered $n-1$. However, the linear combination is determined in such a way as to make it antisymmetric in all pairs of coordinates.

(D) Transformation between two schemes of coupling three angular momenta.

$$\psi[l^{n-1}\alpha_3'S_3'L_3'l_{n-1}(S_3L_3)l_q''SL]$$
$$=\sum_{S_4L_4}\psi[l^{n-1}\alpha_3'S_3'L_3'l_{n-1}l_q''(S_4L_4)SL]$$
$$\times[S_3'L_3'll''(S_4L_4)SL|S_3'L_3'l(S_3L_3)l''SL].$$

The coefficients of the transformation have been given by Racah in RIII in terms of his W function and are called the Racah coefficients.

Naturally, the eigenfunction

$$\psi[l^{n-2}\alpha_1S_1L_1l'(S_2L_2)l''SL]$$

can also be expanded in the various forms described above. We are now ready to proceed with the reduction of the matrix component (2). In view of the symmetry of the operator and the antisymmetry of the states, we may write

$$C=\tfrac{1}{2}n(n-1)\left[l^{n-2}\alpha_1S_1L_1l'S_2L_2l''SL\times\left|\frac{e^2}{r_{n,\,n-1}}\right|l^{n-1}\alpha_3S_3L_3l''SL\right]. \quad (3)$$

Indicating explicitly the antisymmetrization with respect to the l'' electron in the manner (A), we have

$$C=\tfrac{1}{2}(n-1)\sum_{p,q}(-1)^{P+Q}\left[l^{n-2}\alpha_1S_1L_1l'(S_2L_2)l_p''SL\times\left|\frac{e^2}{r_{n,\,n-1}}\right|l^{n-1}\alpha_3S_3L_3l_q''SL\right]. \quad (4)$$

The expression (4) is a sum of n^2 terms, an advantageous grouping of which is the following:

(a) C': $p=n-1, n$; $q=1, 2\cdots n-2$
and $p=1, 2\cdots n-2$; $q=n-1, n$.
(b) C'': $p=1, 2\cdots n-2$; $q=1, 2\cdots n-2$.
(c) C''': $p=n-1, n$; $q=n-1, n$
and $C=C'+C''+C'''$. (5)

Let us consider one part at a time.

(a) In each term of C' one and only one of l_p'' and l_q'' has the same coordinate as the operator; the other one is orthogonal to the parent eigenfunction. Therefore, each term of C' vanishes.

(b) The coordinates of both l_p'' and l_q'' differ from those of the operator in every term of C''. Therefore, the terms of C'' vanish unless $p=q$. It should be noted that

$$(-1)^{P+Q}=1$$

for every term. There are $n-2$ nonvanishing terms, all of which have the same value. Thus,

$$C''=\tfrac{1}{2}(n-1)(n-2)\left[l^{n-2}\alpha_1S_1L_1l'S_2L_2l_1''SL \right. \\ \left. \times\left|\frac{e^2}{r_{n,\,n-1}}\right|l^{n-1}\alpha_3S_3L_3l_1''SL\right]. \qquad (6)$$

This expression can be simplified by considering the coupling of the electron to its parent angular momenta in the manner (B). Thus,

$$C''=\tfrac{1}{2}(n-1)(n-2)\sum_{M_{S_2}M_{L_2}}\sum_{m'_{l''}m'_{s''}}\sum_{M_{S_3}M_{L_3}}\sum_{m_{l''}m_{s''}} \\ \times\bar{\Phi}[l_1''m_{l''}'m_{s''}'][M_SM_LSL|m_{l''}'m_{s''}'M_{S_2}M_{L_2}] \\ \times\left[l^{n-2}\alpha_1S_1L_1l'S_2L_2M_{S_2}M_{L_2}\right. \\ \left.\times\left|\frac{e^2}{r_{n,\,n-1}}\right|l^{n-1}\alpha_3S_3L_3M_{S_3}M_{L_3}\right] \\ \times[M_{S_3}M_{L_3}m_{s''}m_{l''}|M_SM_LSL]\Phi[l_1''m_{l''}m_{s''}]. \qquad (7)$$

However, the matrix element of the electrostatic interaction is diagonal with respect to $S_2L_2M_{S_2}M_{L_2}$, and its value is independent of $M_{S_2}M_{L_2}$. Hence, the matrix element can be taken outside the summation sign. The summation gives unity. Also, we may make the replacement

$$\tfrac{1}{2}(n-1)(n-2)\frac{e^2}{r_{n,\,n-1}}\longrightarrow\sum_{i<j}^{n-1}\frac{e^2}{r_{ij}}.$$

The result of these considerations is

$$C''=\left[l^{n-2}\alpha_1S_1L_1l'S_2L_2\left|\sum_{i<j}^{n-1}\frac{e^2}{r_{ij}}\right|l^{n-1}\alpha_3S_2L_2\right] \\ \times\delta(S_2S_3)\delta(L_2L_3). \qquad (8)$$

Thus, C'' is precisely the matrix component of the electrostatic interaction between the parent configurations. The reduction of (8) for the configurations $d^{n-2}s$, d^{n-1} is dealt with in RIII. All of these matrix components can be expressed in terms of the single radial integral $R^2(dd,ds)$. The coefficients needed for the left side of the periodic table are tabulated in RIII. In the next section we shall extend these results to the right side of the periodic table. Let us now turn our attention to C'''.

(c) We shall subdivide C''' into two parts as follows:

$$C_1''':\ p=n,\ q=n;\ p=n-1,\ q=n-1;$$
$$C_2''':\ p=n,\ q=n-1;\ p=n-1,\ q=n;$$
$$C'''=C_1'''+C_2'''.$$

Inspection of (4) shows that the two terms comprising C_1''' are equal, and so are the two terms making up C_2'''. However, C_1''' and C_2''' differ in several important respects, as we shall see. We study C_1''' first. Since $(-1)^{P+Q}=1$, we have

$$C_1'''=(n-1)\left[l^{n-2}\alpha_1S_1L_1l'S_2L_2l_n''SL\right. \\ \left.\times\left|\frac{e^2}{r_{n,\,n-1}}\right|l^{n-1}\alpha_3S_3L_3l_n''SL\right]. \qquad (9)$$

Considering the antisymmetrization of the inequivalent electron l' in the manner (A) and its orthogonality to the eigenfunction on the right leads to

$$C_1'''=(n-1)^{\frac{1}{2}}\left[l^{n-2}\alpha_1S_1L_1l_{n-1}'S_2L_2l_n''SL\right. \\ \left.\times\left|\frac{e^2}{r_{n,\,n-1}}\right|l^{n-1}\alpha_3S_3L_3l_n''SL\right]. \qquad (10)$$

We progress in the reduction of (10) by expanding the left eigenfunction in the scheme in which the resultant angular momenta of l_{n-1}' and l_n'' are coupled to the angular momenta of the group of equivalent electrons [see Sec. (D)]. The right eigenfunction can be treated in the same way after it has been expanded in terms of fractional parents [see Sec. (C)]. Thus,

$$C_1'''=\sum_{S_4L_4}\sum_{S_5L_5}\sum_{\alpha_3'S_3'L_3'} \\ \times[S_1L_1l'(S_2L_2)l''SL|S_1L_1l'l''(S_4L_4)SL] \\ \times(n-1)^{\frac{1}{2}}\left[l^{n-2}\alpha_1S_1L_1l_{n-1}'l_n''(S_4L_4)SL\right. \\ \left.\left|\frac{e^2}{r_{n,\,n-1}}\right|l^{n-2}\alpha_3'S_3'L_3'l_{n-1}l_n''(S_5L_5)SL\right] \\ \times[l^{n-2}\alpha_3'S_3'L_3'lS_3L_3|\}l^{n-1}\alpha_3S_3L_3] \\ \times[S_3'L_3'll''(S_5L_5)SL|S_3'L_3'l(S_3L_3)l''SL]. \qquad (11)$$

Next, we observe that the matrix element occurring in (11) is equal to

$$\left[l_1'l_2''S_4L_4\left|\frac{e^2}{r_{12}}\right|l_1l_2''S_4L_4\right] \\ \times\delta(\alpha_1S_1L_1;\alpha_3'S_3'L_3')\delta(S_4L_4;S_5L_5). \qquad (12)$$

Thus, we obtain

$$C_1'''=(n-1)^{\frac{1}{2}}[l^{n-2}\alpha_1S_1L_1lS_3L_3]\!\!|l^{n-1}\alpha_3S_3L_3]$$
$$\times\sum_{S_4L_4}[S_1L_1l'(S_2L_2)l''SL|S_1L_1l'l''(S_4L_4)SL]$$
$$\times\left[l_1'l_2''S_4L_4\left|\frac{e^2}{r_{12}}\right|l_1l_2''S_4L_4\right]$$
$$\times[S_1L_1ll''(S_4L_4)SL|S_1L_1l(S_3L_3)l''SL].\quad(13)$$

It should be noted that the matrix element in expression (13) is actually independent of S_4; it has the same value for singlet and triplet states.

Next we will identify $ll'l''$ with dsp electrons and thereby achieve a considerable simplification of (13) because $L_1=L_2$ and L_4 can be a P state only. Thus,

$$[L_1s(L_1)pL|L_1sp(P)L]=1.$$

The sum over S_4 amounts to

$$\sum_{S_4}[S_1\tfrac{1}{2}(S_2)\tfrac{1}{2}S|S_1\tfrac{1}{2}\tfrac{1}{2}(S_4)S]$$
$$\times[S_1\tfrac{1}{2}\tfrac{1}{2}(S_4)S|S_1\tfrac{1}{2}(S_3)\tfrac{1}{2}S]=\delta(S_2S_3),\quad(14)$$

in accordance with the general property of unitary transformations. Therefore, we have

$$C_1'''=(n-1)^{\frac{1}{2}}[d^{n-2}\alpha_1S_1L_1dS_3L_3]\!\!|d^{n-1}\alpha_3S_3L_3]$$
$$\times[L_1dp(P)L|L_1d(L_3)pL]\delta(S_2S_3)R_d\quad(15)$$

in which we have put

$$R_d=\left[s_1p_2P\left|\frac{e^2}{r_{12}}\right|d_1p_2P\right].\quad(15')$$

By the use of Racah's tensor calculus R_d can readily be expressed in terms of Slater integrals. The result, obtained in Appendix I, is

$$R_d=-(\sqrt{2}/5)R^2(sp,dp).\quad(16)$$

Next we must consider C_2'''. Since $(-1)^{P+Q}=-1$, we have

$$C_2'''=-(n-1)^{\frac{1}{2}}\left[l^{n-2}\alpha_1S_1L_1l'S_2L_2l_n''SL\right.$$
$$\left.\times\left|\frac{e^2}{r_{n,\,n-1}}\right|l^{n-1}\alpha_3S_3L_3l_{n-1}''SL\right].\quad(16')$$

This is treated in the same way as expression (9) for C_1''' and leads to an expression corresponding to (13), *viz.*,

$$C_2'''=-(n-1)^{\frac{1}{2}}[l^{n-2}\alpha_1S_1L_1lS_3L_3]\!\!|l^{n-1}\alpha_3S_3L_3]$$
$$\times\sum_{S_4L_4}[S_1L_1l'(S_2L_2)l''SL|S_1L_1l'l''(S_4L_4)SL]$$
$$\times\left[l_1'l_2''S_4L_4\left|\frac{e^2}{r_{12}}\right|l_2l_1''S_4L_4\right]$$
$$\times[S_1L_1ll''(S_4L_4)SL|S_1L_1l(S_3L_3)l''SL].\quad(17)$$

TABLE I. $[d^7\alpha'S'L'sSL|{}^2/r_{ij}|d\Sigma e^8\alpha SL]$.

d^7s	d^8	H_2
$({}_3^2P)^3P$	${}_2^3P$	$-(210)^{\frac{1}{2}}$
$({}_3^4P)^3P$	${}_2^3P$	0
$({}_1^2D)^1D$	${}_2^1D$	$-(35)^{\frac{1}{2}}$
$({}_3^2D)^1D$	${}_2^1D$	$3(15)^{\frac{1}{2}}$
$({}_3^2F)^3F$	${}_2^3F$	$2(15)^{\frac{1}{2}}$
$({}_3^4F)^3F$	${}_2^3F$	0
$({}_3^2G)^1G$	${}_2^1G$	-10

TABLE II. $[d^6\alpha'S'L'sSL|\Sigma e^2/r_{ij}|d^7\alpha SL]$.

d^6s	d^7	H_2	d^6s	d^7	H_2
$({}_2^3P)^2P$	${}_3^2P$	$(105)^{\frac{1}{2}}$	$({}_4^1F)^2F$	${}_3^2F$	$(15/2)(2)^{\frac{1}{2}}$
$({}_4^3P)^2P$	${}_3^2P$	$-(30)^{\frac{1}{2}}$	$({}_2^3F)^2F$	${}_3^2F$	$-(30)^{\frac{1}{2}}$
$({}_2^3P)^4P$	${}_3^4P$	0	$({}_4^3F)^2F$	${}_3^2F$	$(3/2)(30)^{\frac{1}{2}}$
$({}_4^3P)^4P$	${}_3^4P$	$-(210)^{\frac{1}{2}}$	$({}_2^3F)^4F$	${}_3^4F$	0
$({}_2^1D)^2D$	${}_1^2D$	$(1/2)(210)^{\frac{1}{2}}$	$({}_4^3F)^4F$	${}_3^4F$	$2(15)^{\frac{1}{2}}$
$({}_2^1D)^2D$	${}_3^2D$	$(3/2)(10)^{\frac{1}{2}}$	$({}_2^1G)^2G$	${}_3^2G$	$-(5/3)(6)^{\frac{1}{2}}$
$({}_4^1D)^2D$	${}_3^2D$	$-6(5)^{\frac{1}{2}}$	$({}_4^1G)^2G$	${}_3^2G$	$-(5/6)(66)^{\frac{1}{2}}$
$({}_4^3D)^2D$	${}_3^2D$	$-2(30)^{\frac{1}{2}}$	$({}_4^3G)^2G$	${}_3^2G$	$(3/2)(30)^{\frac{1}{2}}$
			$({}_4^3H)^2H$	${}_3^2H$	$-(30)^{\frac{1}{2}}$

TABLE III. $[d^5\alpha'S'L'sSL|\Sigma e^2/r_{ij}|d^6\alpha SL]$.

d^5s	d^6	H_2	d^5s	d^6	H_2
$({}_5^2S)^1S$	${}_4^1S$	$8(10)^{\frac{1}{2}}$	$({}_5^2F)^1F$	${}_4^1F$	$(7/2)(10)^{\frac{1}{2}}$
$({}_3^2P)^3P$	${}_2^3P$	$-2(35)^{\frac{1}{2}}$	$({}_3^2F)^3F$	${}_4^3F$	$(3/2)(10)^{\frac{1}{2}}$
$({}_3^2P)^3P$	${}_4^3P$	$-(10)^{\frac{1}{2}}$	$({}_3^2F)^3F$	${}_2^3F$	$2(10)^{\frac{1}{2}}$
$({}_3^4P)^3P$	${}_2^3P$	0	$({}_5^2F)^3F$	${}_4^3F$	$-(15/2)(2)^{\frac{1}{2}}$
$({}_3^4P)^3P$	${}_4^3P$	$2(35)^{\frac{1}{2}}$	$({}_3^4F)^3F$	${}_2^3F$	0
$({}_1^2D)^1D$	${}_2^1D$	$-(70)^{\frac{1}{2}}$	$({}_3^4F)^3F$	${}_4^3F$	$-2(10)^{\frac{1}{2}}$
$({}_3^2D)^1D$	${}_2^1D$	$3(10)^{\frac{1}{2}}$	$({}_3^2G)^1G$	${}_2^1G$	$-(10/3)(6)^{\frac{1}{2}}$
$({}_3^2D)^1D$	${}_4^1D$	$6(5)^{\frac{1}{2}}$	$({}_3^2G)^1G$	${}_4^1G$	$(5/6)(66)^{\frac{1}{2}}$
$({}_5^2D)^1D$	${}_4^1D$	$-(10)^{\frac{1}{2}}$	$({}_5^2G)^1G$	${}_4^1G$	$-(9/2)(10)^{\frac{1}{2}}$
$({}_3^2D)^3D$	${}_4^3D$	$-2(10)^{\frac{1}{2}}$	$({}_3^2G)^3G$	${}_4^3G$	$(3/2)(10)^{\frac{1}{2}}$
$({}_5^2D)^3D$	${}_4^3D$	$6(5)^{\frac{1}{2}}$	$({}_5^2G)^3G$	${}_4^3G$	$(5/6)(66)^{\frac{1}{2}}$
$({}_5^4D)^3D$	${}_4^3D$	$-3(10)^{\frac{1}{2}}$	$({}_5^4G)^3G$	${}_4^3G$	$(10/3)(6)^{\frac{1}{2}}$
$({}_5^4D)^5D$	${}_4^5D$	$(70)^{\frac{1}{2}}$	$({}_3^2H)^3H$	${}_4^3H$	$-(10)^{\frac{1}{2}}$
$({}_3^2F)^1F$	${}_4^1F$	$-(15/2)(2)^{\frac{1}{2}}$	$({}_5^2I)^1I$	${}_4^1I$	$(10)^{\frac{1}{2}}$

C_2''' differs from C_1''' in that the direct integral is replaced by the exchange integral with a minus sign. Furthermore, the exchange integral is not independent of spin; the singlet and triplet states differ by a minus sign. Specializing to dsp electrons, we have

$$\left[s_1p_2\,{}^1P\left|\frac{e^2}{r_{12}}\right|d_2p_1\,{}^1P\right]=-\left[s_1p_2P\left|\frac{e^2}{r_{12}}\right|d_2p_1P\right]=-R_e$$
$$\left[s_1p_2\,{}^3P\left|\frac{e^2}{r_{12}}\right|d_2p_1\,{}^3P\right]=\left[s_1p_2P\left|\frac{e^2}{r_{12}}\right|d_2p_1P\right]=R_e.\quad(18)$$

Therefore,

$$C_2'''=(n-1)^{\frac{1}{2}}[d^{n-2}\alpha_1S_1L_1dS_3L_3]\!\!|d^{n-1}\alpha_3S_3L_3]$$
$$\times[L_1dp(P)L|L_1d(L_3)pL]R_e$$
$$\times\sum_{S_4}(-1)^{S_4}[S_1\tfrac{1}{2}(S_2)\tfrac{1}{2}S|S_1\tfrac{1}{2}\tfrac{1}{2}(S_4)S]$$
$$\times[S_1\tfrac{1}{2}\tfrac{1}{2}(S_4)S|S_1\tfrac{1}{2}(S_3)\tfrac{1}{2}S].\quad(18')$$

The sum over S_4 is evaluated in Appendix II:

$$\sum_{S_4} = \delta(S_1S)(-1)^{S_2-S_3}\frac{[(2S_2+1)(2S_3+1)]^{\frac{1}{2}}}{2S+1} - \delta(S_2S_3). \qquad (19)$$

The exchange integral R_e is evaluated in terms of Slater integrals in Appendix I with the result

$$R_e = -(\sqrt{2}/3)R^1(sp,pd). \qquad (20)$$

Finally, we form the desired matrix component from the partial results (5), (8), (15), (18′), and (19), *viz.*,

$$\begin{aligned}
&\left[d^{n-2}\alpha_1S_1L_1s(S_2L_2)pSL\left|\sum_{i<j}^{n}\frac{e^2}{r_{ij}}\right|d^{n-1}\alpha_3S_3L_3pSL\right]\\
&=\left[d^{n-2}\alpha_1S_1L_1sS_2L_2\left|\sum_{i<j}^{n-1}\frac{e^2}{r_{ij}}\right|d^{n-1}\alpha_3S_2L_2\right]\delta(S_2S_3)\delta(L_2L_3)\\
&\quad+(n-1)^{\frac{1}{2}}[d^{n-2}\alpha_1S_1L_1dS_3L_3\rrbracket d^{n-1}\alpha_3S_3L_3]\\
&\quad\times[L_1dp(P)L|L_1d(L_3)pL]\\
&\quad\times[(R_d-R_e)\delta(S_2S_3)+g_eR_e], \qquad (21)
\end{aligned}$$

in which

$$g_e = \delta(S_1S)(-1)^{S_2-S_3}\{[(2S_2+1)(2S_3+1)]^{\frac{1}{2}}/(2S+1)\}.$$

R_d and R_e are given by (16) and (20), respectively.

The result has certain obvious features. If the parent orbital angular momenta are different, the interaction between the parents (first term) vanishes. If, in addition, the parent spins differ, the term containing R_d-R_e also vanishes. Finally, if the grandparent spin S_1 and the total spin are also different, the entire matrix component vanishes.

It should also be noted that the consideration of the configuration interaction introduces three radial integrals, none of which occurs in the part of the matrix labeled by one configuration only. In addition to R_d and R_e, which appear explicitly in formula (21), the integral $R^2(dd,ds)$ arises from the first term of (21) [see Sec. III, part (1) below]. Thus, in the usual procedure of adjusting parameters there will be three more independent parameters. In practice it will be convenient to adopt as independent the combination R_d-R_e and R_e.

TABLE IV. $[d^8\alpha_3S_3L_3\llbracket d^7(\alpha_1S_1L_1)dS_3L_3]$. A particular N is the normalizing factor for the coefficients in its column.

$d^7 \backslash d^8$	${}_0{}^1S$	${}_2{}^3P$	${}_2{}^1D$	${}_2{}^3F$	${}_2{}^1G$
${}_3{}^2P$	0	$-14^{\frac{1}{2}}$	$-126^{\frac{1}{2}}$	4	0
${}_3{}^4P$	0	-8	0	$-56^{\frac{1}{2}}$	0
${}_1{}^2D$	1	$-15^{\frac{1}{2}}$	$-35^{\frac{1}{2}}$	$-35^{\frac{1}{2}}$	$-21^{\frac{1}{2}}$
${}_3{}^2D$	0	$-35^{\frac{1}{2}}$	$135^{\frac{1}{2}}$	$15^{\frac{1}{2}}$	-5
${}_3{}^2F$	0	$-56^{\frac{1}{2}}$	$84^{\frac{1}{2}}$	$-14^{\frac{1}{2}}$	$70^{\frac{1}{2}}$
${}_3{}^4F$	0	$-56^{\frac{1}{2}}$	0	$224^{\frac{1}{2}}$	0
${}_3{}^2G$	0	0	$-180^{\frac{1}{2}}$	$90^{\frac{1}{2}}$	$66^{\frac{1}{2}}$
${}_3{}^2H$	0	0	0	$110^{\frac{1}{2}}$	$-154^{\frac{1}{2}}$
N	1	$240^{-\frac{1}{2}}$	$560^{-\frac{1}{2}}$	$560^{-\frac{1}{2}}$	$336^{-\frac{1}{2}}$

We shall now discuss the quantities in the formula (21).

III. TABULATION OF COEFFICIENTS AND MATRIX COMPONENTS

In this section we shall discuss the availability and tabulation of the matrix elements and coefficients occurring in the result (21). We shall point out that many of these quantities are already listed in RIII; the remaining ones are supplied in this section.

(1) Interaction between the Parent Configurations $d^{n-1}s$ and d^n

The matrix components of the electrostatic interaction between the parent configurations $d^{n-1}s$ and d^n are discussed fully in Sec. 7 of RIII. We merely wish to reiterate certain features of these matrix elements and extend the tabulation given in RIII.

The matrices of the electrostatic interaction are, of course, diagonal with respect to S and L. For the particular matrix components under consideration, we have the additional rule that an element will vanish unless the seniority numbers of d^{n-1} and d^n differ by unity. The nonvanishing matrix elements depend on the single Slater integral $R^2(dd,ds)$. Racah introduces the more convenient parameter $H_2=R^2(dd,ds)/35$. The coefficients of H_2 are given in Tables XX, XXI, and XXII of RIII for the left side of the periodic table ($n=3$, 4, and 5). There is a simple relationship[10] connecting the matrix components of the left and right sides of the periodic table, *viz.*,

$$\begin{aligned}
&\left[d^{n-1}\alpha_1S_1L_1sS_3L_3\left|\sum\frac{e^2}{r_{ij}}\right|d^n\alpha_3S_3L_3\right]\\
&=(-1)^{S+\frac{1}{2}-S'}\left(\frac{2S_1+1}{2S+1}\right)^{\frac{1}{2}}\left[d^{11-n}\alpha_1S_1L_1\right.\\
&\qquad\times\left.\left|\sum\frac{e^2}{r_{ij}}\right|d^{10-n}\alpha_3S_3L_3sS_1L_1\right]. \qquad (22)
\end{aligned}$$

TABLE V. $[d^7\alpha_3S_3L_3\llbracket d^6(\alpha_1S_1L_1)dS_3L_3]$.

$d^6 \backslash d^7$	${}_3{}^2P$	${}_3{}^4P$	${}_1{}^2D$	${}_3{}^2D$	${}_3{}^2F$	${}_3{}^4F$	${}_3{}^2G$	${}_3{}^2H$
${}_0{}^1S$	0	0	$8^{\frac{1}{2}}$	0	0	0	0	0
${}_4{}^1S$	0	0	0	$56^{\frac{1}{2}}$	0	0	0	0
${}_2{}^3P$	$7^{\frac{1}{2}}$	$-16^{\frac{1}{2}}$	$27^{\frac{1}{2}}$	$-49^{\frac{1}{2}}$	$112^{\frac{1}{2}}$	$-14^{\frac{1}{2}}$	0	0
${}_4{}^3P$	$-50^{\frac{1}{2}}$	$-14^{\frac{1}{2}}$	0	$56^{\frac{1}{2}}$	$200^{\frac{1}{2}}$	$16^{\frac{1}{2}}$	0	0
${}_2{}^1D$	$15^{\frac{1}{2}}$	0	$15^{\frac{1}{2}}$	$45^{\frac{1}{2}}$	$-40^{\frac{1}{2}}$	0	$-200^{\frac{1}{2}}$	0
${}_4{}^1D$	$-30^{\frac{1}{2}}$	0	0	$40^{\frac{1}{2}}$	$-180^{\frac{1}{2}}$	0	$100^{\frac{1}{2}}$	0
${}_4{}^3D$	$-20^{\frac{1}{2}}$	$-35^{\frac{1}{2}}$	0	$-240^{\frac{1}{2}}$	$-120^{\frac{1}{2}}$	$15^{\frac{1}{2}}$	$-600^{\frac{1}{2}}$	0
${}_4{}^5D$	0	$75^{\frac{1}{2}}$	0	0	0	$175^{\frac{1}{2}}$	0	0
${}_4{}^1F$	$30^{\frac{1}{2}}$	0	0	$-140^{\frac{1}{2}}$	$-105^{\frac{1}{2}}$	0	$7^{\frac{1}{2}}$	$-33^{\frac{1}{2}}$
${}_2{}^3F$	$-8^{\frac{1}{2}}$	$-14^{\frac{1}{2}}$	$63^{\frac{1}{2}}$	$21^{\frac{1}{2}}$	$28^{\frac{1}{2}}$	$56^{\frac{1}{2}}$	$420^{\frac{1}{2}}$	$-55^{\frac{1}{2}}$
${}_4{}^3F$	$50^{\frac{1}{2}}$	$-56^{\frac{1}{2}}$	0	$84^{\frac{1}{2}}$	$175^{\frac{1}{2}}$	$-14^{\frac{1}{2}}$	$-945^{\frac{1}{2}}$	$-55^{\frac{1}{2}}$
${}_2{}^1G$	0	0	$27^{\frac{1}{2}}$	$-25^{\frac{1}{2}}$	$-100^{\frac{1}{2}}$	0	$220^{\frac{1}{2}}$	$55^{\frac{1}{2}}$
${}_4{}^1G$	0	0	0	$44^{\frac{1}{2}}$	$-275^{\frac{1}{2}}$	0	$-845^{\frac{1}{2}}$	$5^{\frac{1}{2}}$
${}_4{}^3G$	0	0	0	$-180^{\frac{1}{2}}$	$405^{\frac{1}{2}}$	$90^{\frac{1}{2}}$	$-891^{\frac{1}{2}}$	$99^{\frac{1}{2}}$
${}_4{}^3H$	0	0	0	0	$-220^{\frac{1}{2}}$	$110^{\frac{1}{2}}$	$-924^{\frac{1}{2}}$	$-286^{\frac{1}{2}}$
${}_4{}^1I$	0	0	0	0	0	0	$728^{\frac{1}{2}}$	$-182^{\frac{1}{2}}$
N	$210^{-\frac{1}{2}}$	$210^{-\frac{1}{2}}$	$140^{-\frac{1}{2}}$	$980^{-\frac{1}{2}}$	$1960^{-\frac{1}{2}}$	$490^{-\frac{1}{2}}$	$5880^{-\frac{1}{2}}$	$770^{-\frac{1}{2}}$

---

[10] The author is indebted to Professor G. Racah for pointing this out to him.

TABLE VI. $[d^6\alpha_3S_3L_3⟦d^5(\alpha_1S_1L_1)dS_3L_3]$.

d^5 \ d^6	${}_0{}^1S$	${}_4{}^1S$	${}_2{}^3P$	${}_4{}^3P$	${}_2{}^1D$	${}_4{}^1D$	${}_4{}^3D$	${}_4{}^5D$	${}_4{}^1F$	${}_2{}^3F$	${}_4{}^3F$	${}_2{}^1G$	${}_4{}^1G$	${}_4{}^3G$	${}_4{}^3H$	${}_4{}^1I$
${}_5{}^2S$	0	0	0	0	0	$-280^{\frac{1}{2}}$	$42^{\frac{1}{2}}$	0	0	0	0	0	0	0	0	0
${}_5{}^6S$	0	0	0	0	0	0	0	$6^{\frac{1}{2}}$	0	0	0	0	0	0	0	0
${}_3{}^2P$	0	0	$-14^{\frac{1}{2}}$	-5	$-42^{\frac{1}{2}}$	$-210^{\frac{1}{2}}$	$14^{\frac{1}{2}}$	0	$-120^{\frac{1}{2}}$	8	$200^{\frac{1}{2}}$	0	0	0	0	0
${}_3{}^4P$	0	0	-8	$14^{\frac{1}{2}}$	0	0	-7	$-3^{\frac{1}{2}}$	0	$-224^{\frac{1}{2}}$	$448^{\frac{1}{2}}$	0	0	0	0	0
${}_1{}^2D$	1	0	$-45^{\frac{1}{2}}$	0	$-35^{\frac{1}{2}}$	0	0	0	0	$-420^{\frac{1}{2}}$	0	$-63^{\frac{1}{2}}$	0	0	0	0
${}_3{}^2D$	0	-1	$-35^{\frac{1}{2}}$	$-10^{\frac{1}{2}}$	$45^{\frac{1}{2}}$	-10	$-60^{\frac{1}{2}}$	0	$-200^{\frac{1}{2}}$	$60^{\frac{1}{2}}$	-120	-5	$-968^{\frac{1}{2}}$	$-200^{\frac{1}{2}}$	0	0
${}_5{}^2D$	0	$-2^{\frac{1}{2}}$	0	$45^{\frac{1}{2}}$	0	$450^{\frac{1}{2}}$	$-30^{\frac{1}{2}}$	0	-10	0	$540^{\frac{1}{2}}$	0	$4356^{\frac{1}{2}}$	-10	0	0
${}_5{}^4D$	0	0	0	$-90^{\frac{1}{2}}$	0	0	$-135^{\frac{1}{2}}$	$5^{\frac{1}{2}}$	0	0	$480^{\frac{1}{2}}$	0	0	$800^{\frac{1}{2}}$	0	0
${}_3{}^2F$	0	0	$-56^{\frac{1}{2}}$	5	$28^{\frac{1}{2}}$	$-315^{\frac{1}{2}}$	$21^{\frac{1}{2}}$	0	$105^{\frac{1}{2}}$	$-56^{\frac{1}{2}}$	$175^{\frac{1}{2}}$	$70^{\frac{1}{2}}$	$-4235^{\frac{1}{2}}$	$-315^{\frac{1}{2}}$	$-55^{\frac{1}{2}}$	0
${}_5{}^2F$	0	0	0	$-45^{\frac{1}{2}}$	0	$175^{\frac{1}{2}}$	$105^{\frac{1}{2}}$	0	$-525^{\frac{1}{2}}$	0	$315^{\frac{1}{2}}$	0	$-7623^{\frac{1}{2}}$	$-7^{\frac{1}{2}}$	$99^{\frac{1}{2}}$	0
${}_3{}^4F$	0	0	$-56^{\frac{1}{2}}$	-4	0	0	$21^{\frac{1}{2}}$	$-7^{\frac{1}{2}}$	0	$896^{\frac{1}{2}}$	$112^{\frac{1}{2}}$	0	0	$560^{\frac{1}{2}}$	$-220^{\frac{1}{2}}$	0
${}_3{}^2G$	0	0	0	0	$-60^{\frac{1}{2}}$	$-75^{\frac{1}{2}}$	$-45^{\frac{1}{2}}$	0	$3^{\frac{1}{2}}$	$360^{\frac{1}{2}}$	$405^{\frac{1}{2}}$	$66^{\frac{1}{2}}$	$5577^{\frac{1}{2}}$	$-297^{\frac{1}{2}}$	$99^{\frac{1}{2}}$	$-33^{\frac{1}{2}}$
${}_5{}^2G$	0	0	0	0	0	$495^{\frac{1}{2}}$	$-33^{\frac{1}{2}}$	0	$495^{\frac{1}{2}}$	0	$825^{\frac{1}{2}}$	0	$-3645^{\frac{1}{2}}$	$845^{\frac{1}{2}}$	$-15^{\frac{1}{2}}$	$-45^{\frac{1}{2}}$
${}_5{}^4G$	0	0	0	0	0	0	$75^{\frac{1}{2}}$	3	0	0	$1200^{\frac{1}{2}}$	0	0	$-880^{\frac{1}{2}}$	$-660^{\frac{1}{2}}$	0
${}_3{}^2H$	0	0	0	0	0	0	0	0	$132^{\frac{1}{2}}$	$440^{\frac{1}{2}}$	$-220^{\frac{1}{2}}$	$-154^{\frac{1}{2}}$	$308^{\frac{1}{2}}$	$-308^{\frac{1}{2}}$	$-286^{\frac{1}{2}}$	$-77^{\frac{1}{2}}$
${}_5{}^2I$	0	0	0	0	0	0	0	0	0	0	0	0	$-6552^{\frac{1}{2}}$	$-728^{\frac{1}{2}}$	$546^{\frac{1}{2}}$	$-175^{\frac{1}{2}}$
N	1	$3^{-\frac{1}{2}}$	$270^{-\frac{1}{2}}$	$270^{-\frac{1}{2}}$	$210^{-\frac{1}{2}}$	$2100^{-\frac{1}{2}}$	$630^{-\frac{1}{2}}$	$30^{-\frac{1}{2}}$	$1680^{-\frac{1}{2}}$	$2520^{-\frac{1}{2}}$	$5040^{-\frac{1}{2}}$	$378^{-\frac{1}{2}}$	$33264^{-\frac{1}{2}}$	$5040^{-\frac{1}{2}}$	$1980^{-\frac{1}{2}}$	$330^{-\frac{1}{2}}$

This follows directly from (79) in view of (81) of RIII and (74) of RII. We have used Eq. (22) to obtain the results for the right side of the periodic table and have listed these in Tables I, II, and III.

(2) Coefficients of Fractional Percentage

Equation (19) of RIII relates the coefficients of fractional parentage of the left side to the corresponding ones on the right side of the periodic table. For d electrons this relationship is

$$[d^{9-n}(\alpha'S'L')dSL⟦d^{10-n}\alpha SL] = (-1)^{S+S'+L+L'-5/2}\left[\frac{(n+1)(2S'+1)(2L'+1)}{(10-n)(2S+1)(2L+1)}\right]^{\frac{1}{2}} \times[d^n(\alpha SL)dS'L'⟦d^{n+1}\alpha'S'L']. \quad (23)$$

We have applied the above to the results given in Tables II, III, and IV in RIII and have thus obtained the coefficients for the conjugated configurations. The fact that the calculation yielded normalized coefficients served as a valuable check. Our results are given in Tables IV, V, and VI.

(3) Racah Coefficients

The Racah coefficients are given in terms of Racah's W function. Thus Eq. (4) of RIII applied to the Racah coefficient occurring in our equation (21) gives

$$[L_1dp(P)L\,|\,L_1d(L_3)pL] = [3(2L_3+1)]^{\frac{1}{2}}W[L_12L1;L_31]. \quad (24)$$

An explicit algebraic formula for the W function in terms of its six arguments is given in Eq. (36′) of RII. There are altogether fifty-four different coefficients of this type in the entire iron group. We have evaluated these and have listed them in Table VII. The evaluation is best carried out by first reducing the general form of the W function to more specialized expressions.[11] For example, there are six cases of the type in which $L_3=L_1$ and $L=L_1+1$. For this case the Racah coefficient becomes

$$[L_1dp(P)L\,|\,L_1d(L_1)pL_1+1]=\left[\frac{L_1(2L_1-1)}{10(L_1+1)(2L_1+3)}\right]^{\frac{1}{2}}.$$

The fifty-four coefficients listed in Table VII were obtained by means of nine similar formulas.[12]

It should be noted that all the quantities which enter in the configuration interaction (21) are now available in either RIII or this section.

IV. CONCLUDING REMARKS

It need hardly be emphasized that in order to study the term values of a spectrum one must obtain also the matrix components of the electrostatic interaction within configurations. However, it should be pointed out that these matrices are amenable to treatment by the methods given by Racah, and many of these matrices have been obtained by various authors. In RII there are given the matrices of d^2p and d^8p. Rohrlich[13] has calculated the matrices for d^3p, d^7p, and also for d^2sp. Ishidzu and Obi[14] have made available the matrices of d^4p, d^5p, and d^6p. The author has obtained the matrices of d^6ps.[8]

It is expected and hoped that the configuration interaction which we have treated in this paper will be sufficient for an elucidation of the odd terms in the spectra of the iron group. However, the possibility of interactions with other configurations, notably $d^{n-3}s^2p$ and the higher configuration of the type $d^{n-1}n'p$, is by no means ruled out. If we include the word "hope," it is because the matrices are already close to being unmanageably large.

The author wishes to express his gratitude to Dr. F. Rohrlich both for suggesting this work and for many helpful discussions.

---

[11] Compare H. A. Jahn, Proc. Roy. Soc. (London) **A205**, 234 (1951). In this paper there are given a large number of specialized expressions. See also reference 12.

[12] The W function and related coefficients have recently been evaluated and compiled at the Oak Ridge National Laboratory for a wide range of the arguments. The results are contained in Oak Ridge National Laboratory Report ORNL-1098 (April, 1952), by L. C. Biedenharn. We have checked our results (Table VII) against the entries in that collection.

[13] F. Rohrlich, Phys. Rev. **74**, 1372 (1948).

[14] See reference 7. We wish to draw attention to a misprint in that paper. In the ${}^1D$ matrix in Table I, p. 126, the off-diagonal element should be $12(2)^{\frac{1}{2}}B$ instead of $12(12)^{\frac{1}{2}}B$.

TABLE VII. Racah coefficients $[L_1dp(P)L|L_1d(L_3)pL]$.

L_1	L_3	L	Coeff.
0	2	1	1
1	1	0	1
1	1	1	$-\frac{1}{2}$
1	2	1	$\frac{1}{2}[3]^{\frac{1}{2}}$
1	1	2	1/10
1	2	2	$-(1/10)[15]^{\frac{1}{2}}$
1	3	2	$(1/5)[21]^{\frac{1}{2}}$
2	0	1	$(1/5)[5]^{\frac{1}{2}}$
2	1	1	$-(3/10)[5]^{\frac{1}{2}}$
2	2	1	$(1/10)[35]^{\frac{1}{2}}$
2	1	2	(3/10)
2	2	2	$-(1/10)[35]^{\frac{1}{2}}$
2	3	2	$(1/5)[14]^{\frac{1}{2}}$
2	2	3	$(1/35)[35]^{\frac{1}{2}}$
2	3	3	$-(1/5)[5]^{\frac{1}{2}}$
2	4	3	$(3/35)[105]^{\frac{1}{2}}$
3	1	2	3/5
3	2	2	$-(1/5)[10]^{\frac{1}{2}}$
3	3	2	$(1/5)[6]^{\frac{1}{2}}$
3	2	3	$(1/7)[7]^{\frac{1}{2}}$
3	3	3	$-\frac{1}{4}[6]^{\frac{1}{2}}$
3	4	3	$(3/28)[42]^{\frac{1}{2}}$
3	3	4	$(1/12)[6]^{\frac{1}{2}}$
3	4	4	$-(3/20)[10]^{\frac{1}{2}}$
3	5	4	$(1/15)[165]^{\frac{1}{2}}$
4	2	3	$(1/7)[21]^{\frac{1}{2}}$
4	3	3	$-\frac{1}{4}[6]^{\frac{1}{2}}$
4	4	3	$(1/28)[154]^{\frac{1}{2}}$
4	3	4	$(1/20)[70]^{\frac{1}{2}}$
4	4	4	$-(1/20)[154]^{\frac{1}{2}}$
4	5	4	$(1/5)[11]^{\frac{1}{2}}$
4	4	5	$(1/55)[154]^{\frac{1}{2}}$
4	5	5	$-(1/5)[6]^{\frac{1}{2}}$
4	6	5	$(1/55)[2145]^{\frac{1}{2}}$
5	3	4	$(1/15)[105]^{\frac{1}{2}}$
5	4	4	$-(3/5)$
5	5	4	$(1/15)[39]^{\frac{1}{2}}$
5	4	5	$(3/55)[66]^{\frac{1}{2}}$
5	5	5	$-(1/10)[39]^{\frac{1}{2}}$
5	6	5	$(1/110)[5005]^{\frac{1}{2}}$
5	5	6	$(1/26)[39]^{\frac{1}{2}}$
5	6	6	$-\frac{1}{2}$
5	7	6	$(3/13)[13]^{\frac{1}{2}}$
6	4	5	$(3/55)[165]^{\frac{1}{2}}$
6	5	5	$-(1/10)[35]^{\frac{1}{2}}$
6	6	5	$(1/22)[77]^{\frac{1}{2}}$
6	5	6	$(1/26)[143]^{\frac{1}{2}}$
6	6	6	$-(1/14)[77]^{\frac{1}{2}}$
6	7	6	$(6/91)[91]^{\frac{1}{2}}$
6	6	7	$(1/35)[77]^{\frac{1}{2}}$
6	7	7	$-(3/35)[35]^{\frac{1}{2}}$
6	8	7	$(1/5)[17]^{\frac{1}{2}}$

APPENDIX I

We shall express R_d and R_e in terms of Slater integrals R^k. Applying the well-known development

$$\frac{1}{r_{12}}=\sum_{k=0}^{\infty}\frac{r_<{}^k}{r_>{}^{k+1}}P_k(\cos\theta_{12})$$

to R_d gives

$$R_d=\left(s_1p_2P\left|\frac{e^2}{r_{12}}\right|d_1p_2P\right)=\sum_{k=0}^{\infty}\left(s_1p_2P\left|\frac{r_<{}^k}{r_>{}^{k+1}}P_k\right|d_1p_2P\right).$$

The integration over r_1 and r_2 may be separated from the rest giving

$$R_d=\sum_{k=0}^{\infty}R^k(sp,\,dp)(s_1p_2P|P_k|d_1p_2P).$$

The matrix element multiplying R^k differs from zero for only one value of k, *viz.*, $k=2$. This follows from the triangular conditions. Hence,

$$R_d=R^2(sp,dp)(s_1p_2P|P_2|d_1p_2P).$$

Racah's matrix methods for tensor operators enable us to evaluate the coefficient of R^2. P_2 is a scalar product of tensors, and a straightforward application of RII (38) gives

$$(s_1p_2P|P_2|d_1p_2P)=(0\|T^{(2)}\|2)(1\|U^{(2)}\|1)W(0121;12).$$

Using RII (51) and (50′) we find

$$(0\|T^{(2)}\|2)=1,\quad (1\|U^{(2)}\|1)=-(6/5)^{\frac{1}{2}},$$

and for RII (36′) we obtain

$$W(0121;12)=(15)^{-\frac{1}{2}}.$$

Hence,

$$R_d=-(2)^{\frac{1}{2}}/5R^2(sp,dp).$$

Similarly, we have

$$R_e=[s_1p_2P|e^2/r_{12}|d_2p_1P]=R^1(sp,pd)(s_1p_2P|P_1|d_2p_1P),$$

$$(s_1p_2P|P_1|d_2p_1P)$$
$$=-(0\|T^{(1)}\|1)(1\|U^{(1)}\|2)W(0112;11),$$
$$(0\|T^{(1)}\|1)=-1,\quad (1\|U^{(1)}\|2)=-(2)^{\frac{1}{2}},$$
$$W(0112;11)=\tfrac{1}{3},$$

and

$$R_e=-(\sqrt{2}/3)R^1(sp,pd).$$

APPENDIX II

The sum over spin in Eq. (18) is evaluated here. We have

$$\sum_{S_4}=\sum_{S_4}(-1)^{S_4}[S_1\tfrac{1}{2}(S_2)\tfrac{1}{2}S|S_1\tfrac{1}{2}\tfrac{1}{2}(S_4)S]\times[S_1\tfrac{1}{2}\tfrac{1}{2}(S_4)S|S_1\tfrac{1}{2}(S_3)\tfrac{1}{2}S].$$

S_4 assumes the values 0 and 1 corresponding to singlet and triplet states. If the factor $(-1)^{S_4}$ is replaced by unity, the sum becomes simply $\delta(S_2S_3)$. Therefore,

$$\sum_{S_4}=2[S_1\tfrac{1}{2}(S_2)\tfrac{1}{2}S|S_1\tfrac{1}{2}\tfrac{1}{2}(0)S]\times[S_1\tfrac{1}{2}\tfrac{1}{2}(0)S|S_1\tfrac{1}{2}(S_3)\tfrac{1}{2}S]-\delta(S_2S_3).$$

Now let us consider the various possibilities. In the first place, the Racah coefficients occurring in the above vanish unless

$$S_1=S.$$

The only possibilities for S_2 and S_3 are $S+\frac{1}{2}$ or $S-\frac{1}{2}$. Evaluating the Racah coefficients by means of RIII (4) and RII (36′), one finds

$$[S\tfrac{1}{2}(S_2=S+\tfrac{1}{2})\tfrac{1}{2}S|S\tfrac{1}{2}\tfrac{1}{2}(0)S]=[(2S_2+1)/2(2S+1)]^{\frac{1}{2}}$$

and

$$[S\tfrac{1}{2}(S_3=S-\tfrac{1}{2})\tfrac{1}{2}S|S\tfrac{1}{2}\tfrac{1}{2}(0)S]=-[(2S_3+1)/2(2S+1)]^{\frac{1}{2}}.$$

All possibilities for $\sum_{S_4}$ can thus be summarized by

$$\sum_{S_4}=\delta(S_1S)(-1)^{S_2-S_3}[(2S_2+1)(2S_3+1)]^{\frac{1}{2}}/(2S+1)-\delta(S_2S_3).$$