Theory of Complex Spectra. II

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The spectra of two-electron configurations in (jj) and (jl) coupling and of the configurations d^n, f^3, d^2p, and d^8p in (LS) coupling are calculated with tensor operators. The agreement with the odd terms of Ti II and Ni II is satisfactory. It is also proved that $G^k/(2k+1)$ is a positive decreasing function of k.

§1. INTRODUCTION

IN a first paper on this matter[1] a general formula was given for the coefficients of Slater's integrals for the two-electron configurations in (LS) coupling. It was also shown that this formula gives the possibility of calculating the terms of more complex configurations, and some simple examples were given. But the method used for the configurations p^2l still necessitates for d^3 very long calculations, because we must calculate the fourth power of the matrix of the scalar product of two angular momenta. It appeared therefore more convenient to develop a new method, based on tensor operators.

The algebra of tensor operators is developed in analogy to the treatment of Chapter III of TAS[2] for the vector operators. With this method some group-theoretical results of Wigner and of Kramers are obtained by a direct algebraical way, and in some cases also in a more simple and general form.

Expressing the coefficients of Slater's integrals as scalar products of tensors, we give a direct demonstration of Eq. (12′) I, and obtain also its extension to (jj) and (jl) coupling. This new method is more suitable for calculations of many-electron spectra, and applications are made to the configurations d^n, f^3, d^2p, and d^8p.

Since the whole method is based on Wigner's[3] transformation formula for vector addition (TAS 14[35]), we shall begin with a direct algebraical derivation of this formula, without the use of the theory of groups.

§2. THE ALGEBRAIC CALCULATION OF $(j_1j_2m_1m_2|j_1j_2jm)$

It is shown in §14[3] of TAS that the transformation coefficients $(m_1m_2|jm)$ for the addition of two angular momenta are defined by the relation

$$\psi(\gamma j_1 j_2 jm)=\sum_{m_1m_2}\phi(\gamma j_1 j_2 m_1 m_2)(m_1m_2|jm) \tag{1}$$

and are completely determined by the initial condition

$$(j_1j_2|j_1+j_2\,j_1+j_2)=1 \tag{2}$$

and by the two recursion formulas

$$[(j+m)(j-m+1)]^{\frac{1}{2}}(m_1m_2|jm-1)=[(j_1+m_1+1)(j_1-m_1)]^{\frac{1}{2}}(m_1+1\,m_2|jm)$$
$$+[(j_2+m_2+1)(j_2-m_2)]^{\frac{1}{2}}(m_1m_2+1|jm) \tag{3}$$

and

$$[(j-m)(j+m)]^{\frac{1}{2}}(j-1\vdots J_1\vdots j)(m_1m_2|j-1m)$$
$$=[m_1-m(j\vdots J_1\vdots j)](m_1m_2|jm)-[(j-m+1)(j+m+1)]^{\frac{1}{2}}(j+1\vdots J_1\vdots j)(m_1m_2|j+1m). \tag{4}$$

[1] G. Racah, Phys. Rev. **61**, 186 (1942), which will be referred to as I.
[2] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge, 1935). We refer to this book (TAS) and to I for definitions, notations, and bibliographical indications.
[3] E. Wigner, *Gruppentheorie* (Vieweg, 1931), Chapter 17, Eq. (27).

But it is also pointed out there that a general formula for such coefficients is very difficult to obtain from these relations.

The calculation is however much simplified if we add a third recursion formula, which follows also, as (3), from TAS $3^3 3$ if we take the upper sign instead of the lower:

$$[(j-m)(j+m+1)]^{\frac{1}{2}}(m_1m_2|jm+1)$$
$$=[(j_1-m_1+1)(j_1+m_1)]^{\frac{1}{2}}(m_1-1m_2|jm)+[(j_2-m_2+1)(j_2+m_2)]^{\frac{1}{2}}(m_1m_2-1|jm). \quad (5)$$

In order to avoid the irrational factors we put

$$(m_1m_2|jm)=(-1)^{j_1-m_1}f(m_1m_2;\, jm)[(j_1+m_1)!(j_2+m_2)!(j+m)!]^{\frac{1}{2}}/[(j_1-m_1)!(j_2-m_2)!(j-m)!]^{\frac{1}{2}}, \quad (6)$$

and obtain from (3) and (5)

$$f(m_1m_2;\, jm-1)=(j_2+m_2+1)(j_2-m_2)f(m_1m_2+1;\, jm)-(j_1+m_1+1)(j_1-m_1)f(m_1+1m_2;\, jm) \quad (3')$$

and

$$(j-m)(j+m+1)f(m_1m_2;\, jm+1)=f(m_1m_2-1;\, jm)-f(m_1-1m_2;\, jm). \quad (5')$$

Putting $m=j$ in (5'), we see that $f(m_1m_2;\, jj)$ is independent of m_1 and m_2 and we may write

$$f(m_1m_2;\, jj)=A_j. \quad (7)$$

From (7) and (3') we get

$$f(m_1m_2;\, jj-1)=[(j_2+m_2+1)(j_2-m_2)-(j_1+m_1+1)(j_1-m_1)]A_j; \quad (7')$$

from (7') and (3') we get

$$f(m_1m_2;\, jj-2)=[(j_2+m_2+1)(j_2+m_2+2)(j_2-m_2)(j_2-m_2-1)$$
$$-2(j_2+m_2+1)(j_2-m_2)(j_1+m_1+1)(j_1-m_1)+(j_1+m_1+1)(j_1+m_1+2)(j_1-m_1)(j_1-m_1-1)]A_j \quad (7'')$$

and we see that the general formula will be

$$f(m_1m_2;\, jj-u)=A_j\sum_t(-1)^t\binom{u}{t}\frac{(j_1+m_1+t)!(j_1-m_1)!(j_2+m_2+u-t)!(j_2-m_2)!}{(j_1+m_1)!(j_1-m_1-t)!(j_2+m_2)!(j_2-m_2-u+t)!}, \quad (8)$$

where, as in all formulas of this paper, the summation parameter takes on all integral values consistent with the factorial notation, the factorial of a negative number being meaningless. To demonstrate (8) it suffices to verify that it satisfies (3'); this verification is very simple and will be omitted for brevity.

Introducing (8) in (6) and remembering that

$$m=m_1+m_2, \quad (9)$$

we obtain the dependence of $(m_1m_2|jm)$ on m_1, m_2, and m:

$$(m_1m_2|jm)=\delta(m_1+m_2,\, m)A_j\left[\frac{(j_1-m_1)!(j_2-m_2)!(j-m)!(j+m)!}{(j_1+m_1)!(j_2+m_2)!}\right]^{\frac{1}{2}}\sum_t(-1)^{j_1-m_1+t}$$
$$\times\frac{(j_1+m_1+t)!(j+j_2-m_1-t)!}{t!(j-m-t)!(j_1-m_1-t)(j_2-j+m_1+t)!}. \quad (10)$$

In order to obtain from (4) the dependence of A_j on j, we calculate at first from (10) the expression of $(m_1m_2|j+1j)$: owing to the δ factor and to the expression of $(j\frac{1}{2}J_1\frac{1}{2}j)$ (TAS $10^3 2a$), we have

$$(m_1m_2|j+1j)=\delta(m_1+m_2,\, j)(-1)^{j_1-m_1}A_{j+1}\left[\frac{(j_1+m_1)!(j_2+m_2)!(2j+1)!}{(j_1-m_1)!(j_2-m_2)!}\right]^{\frac{1}{2}}2(j+1)[m_1-j(j\tfrac{1}{2}J_1\tfrac{1}{2}j)]. \quad (11)$$

The left side of (4) vanishes for $m=j$; introducing (7) and (11) and eliminating the common factors, we get

$$0=A_j-2(j+1)(2j+1)(j+1\,|\,J_1\,|\,j)A_{j+1},$$

and owing to the expression of $(j+1\,|\,J_1\,|\,j)$ (TAS 10^3 2b), this becomes

$$A_j=[(j_1+j_2+j+2)(j_1+j_2-j)(j+j_1-j_2+1)(j+j_2-j_1+1)(2j+1)/(2j+3)]^{\frac{1}{2}}A_{j+1} \tag{12}$$

and is satisfied by

$$A_j=B[(2j+1)(j_1+j_2-j)!]^{\frac{1}{2}}/[(j_1+j_2+j+1)!(j+j_1-j_2)!(j+j_2-j_1)!]^{\frac{1}{2}}, \tag{13}$$

where B is also independent of j.

It follows from (2) that

$$B=1; \tag{14}$$

and collecting (10), (13), and (14) we have at last

$$(m_1m_2|jm)=\delta(m_1+m_2, m)\left[\frac{(2j+1)(j_1+j_2-j)!(j_1-m_1)!(j_2-m_2)!(j-m)!(j+m)!}{(j_1+j_2+j+1)!(j+j_1-j_2)!(j+j_2-j_1)!(j_1+m_1)!(j_2+m_2)!}\right]^{\frac{1}{2}}$$
$$\times\sum_t(-1)^{j_1-m_1+t}\frac{(j_1+m_1+t)!(j+j_2-m_1-t)!}{t!(j-m-t)!(j_1-m_1-t)!(j_2-j+m_1+t)!}. \tag{15}$$

This formula is similar to Wigner's formula (TAS 14^35), and is, also, unsymmetrical and unpractical for the use; it is, however, possible to obtain a more symmetrical and useful form, by transforming it with the methods shown in the appendix of I: using (52) I and (55′) I we have

$$\sum_t(-1)^{j_1-m_1+t}\frac{(j_1+m_1+t)!(j+j_2-m_1-t)!}{t!(j-m-t)!(j_1-m_1-t)!(j_2-j+m_1+t)!}$$
$$=\sum_{tu}(-1)^{j_1-m_1+t}\frac{(j_1+m_1+t)!}{t!(j_2-j+m_1+t)!}\cdot\frac{(j_2+m_2)!(j+j_2-j_1)!}{(j_2+m_2-u)!(j+j_2-j_1-u)!(j_1-j_2-m-t+u)!u!}$$
$$=\sum_u(-1)^{j_2+m_2-u}\frac{(j_1+m_1)!(j+j_1-j_2)!(j_2+m_2)!(j+j_2-j_1)!}{(j_1-j_2-m+u)!(j_1-j-m_2+u)!(j+m-u)!(j_2+m_2-u)!(j+j_2-j_1-u)!u!},$$

and putting $z=j_2+m_2-u$ we get

$$(j_1j_2m_1m_2|j_1j_2jm)=\delta(m_1+m_2, m)[(2j+1)(j_1+j_2-j)!(j+j_1-j_2)!(j+j_2-j_1)!/(j_1+j_2+j+1)!]^{\frac{1}{2}}$$
$$\cdot\sum_z(-1)^z\frac{[(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j+m)!(j-m)!]^{\frac{1}{2}}}{z!(j_1+j_2-j-z)!(j_1-m_1-z)!(j_2+m_2-z)!(j-j_2+m_1+z)!(j-j_1-m_2+z)!}. \tag{16}$$

We might also transform TAS 14^35 in the same way, and the result would of course be the same.

For further use it is convenient to introduce the abbreviations

$$v(abc;\alpha\beta\gamma)=\delta(\alpha+\beta+\gamma, 0)\sum_z(-1)^{c-\gamma+z}$$
$$\times\frac{[(a+\alpha)!(a-\alpha)!(b+\beta)!(b-\beta)!(c+\gamma)!(c-\gamma)!]^{\frac{1}{2}}}{z!(a+b-c-z)!(a-\alpha-z)!(b+\beta-z)!(c-b+\alpha+z)!(c-a-\beta+z)!} \tag{17}$$

and

$$V(abc;\alpha\beta\gamma)=[(a+b-c)!(a+c-b)!(b+c-a)!/(a+b+c+1)!]^{\frac{1}{2}}v(abc;\alpha\beta\gamma) \tag{17′}$$

and to write

$$(j_1j_2m_1m_2|j_1j_2jm)=(-1)^{j+m}(2j+1)^{\frac{1}{2}}V(j_1j_2j;\, m_1m_2-m). \tag{16′}$$

The functions v and V are defined for integral and half-integral values of the arguments, with the limitation that $a-\alpha$, $b-\beta$, $c-\gamma$ must be integers; it follows from this limitation and from the factor $\delta(\alpha+\beta+\gamma, 0)$ that all the nine numbers

$$a+\alpha, \quad a-\alpha, \quad b+\beta, \quad b-\beta, \quad c+\gamma, \quad c-\gamma, \quad a+b-c, \quad a+c-b, \quad b+c-a \tag{18}$$

must be integers.

Since in (17) z takes on only such integral values for which the argument of every factorial is not negative, the number of terms in this sum is one more than the *smallest* of the nine numbers (18) (and not only of four of them, as in (15) or in TAS 14[35]); therefore V vanishes if one of the numbers (18) is negative, and the summation reduces to one term if one of these numbers vanishes.

Assuming the argument of one of the five other factorials instead of z as summation parameter in (17), we obtain some symmetry properties for v and V:

$$V(abc;\alpha\beta\gamma)=(-1)^{a+b-c}V(bac;\beta\alpha\gamma)=(-1)^{a+b+c}V(acb;\alpha\gamma\beta)=(-1)^{a-b+c}V(cba;\gamma\beta\alpha)$$
$$=(-1)^{2b}V(cab;\gamma\alpha\beta)=(-1)^{2c}V(bca;\beta\gamma\alpha). \tag{19a}$$

Interchanging in (17) a with b and α with $-\beta$, we have

$$V(abc;\alpha\beta\gamma)=(-1)^{2\gamma}V(bac;\,-\beta-\alpha-\gamma);$$

and owing to the first of (19a) and to the fact that $2(c-\gamma)$ is even, we get also

$$V(abc;\alpha\beta\gamma)=(-1)^{a+b+c}V(abc;\,-\alpha-\beta-\gamma). \tag{19b}$$

Since the transformation matrix $(j_1j_2m_1m_2|j_1j_2jm)$ is a unitary one, it follows from (16′) that the real function V must satisfy the orthogonality relations

$$\sum_{\alpha\beta} V(abc;\alpha\beta\gamma)\,V(abc';\alpha\beta\gamma')=\delta(c,c')\delta(\gamma,\gamma')/(2c+1) \quad (a+b\geqslant c\geqslant|a-b|,\ c\geqslant|\gamma|), \tag{20a}$$

and

$$\sum_{c\gamma}(2c+1)\,V(abc;\alpha\beta\gamma)\,V(abc;\alpha'\beta'\gamma)=\delta(\alpha,\alpha')\delta(\beta,\beta') \quad (a\geqslant|\alpha|,\ b\geqslant|\beta|); \tag{20b}$$

if the inequalities in parentheses are not satisfied, the left side vanishes.

The sum in (17) cannot generally be transformed into a closed form; it is, however, possible to do so for the particular case $\alpha=\beta=\gamma=0$ (a, b, c integers!): if $a+b+c$ is odd, it follows from (19b) that $V(abc;000)$ vanishes; if

$$a+b+c=2g \tag{21}$$

with g integer, it is shown in Appendix A that

$$v(abc;000)=(-1)^g g!/[(g-a)!(g-b)!(g-c)!] \tag{22}$$

and therefore

$$\begin{cases} V(abc;000)=(-1)^g\left[\dfrac{(a+b-c)!(a+c-b)!(b+c-a)!}{(a+b+c+1)!}\right]^{\frac{1}{2}}\dfrac{g!}{(g-a)!(g-b)!(g-c)!}, & (a+b+c \text{ even}) \\ V(abc;000)=0, & (a+b+c \text{ odd}). \end{cases} \tag{22′}$$

§3. THE ALGEBRA OF TENSOR OPERATORS

(1) Definition of Tensor Operator

It is shown in §8[6] of TAS that the matrix components of the electrostatic interaction between two electrons depend on the matrix elements of the spherical harmonics $\Theta(km)\Phi(m)$; in this case the spherical harmonics play the role of operators and not of eigenfunctions, and it appears convenient to consider in a general way the algebra of such operators.

In Chapter III of TAS the algebra of vector operators was developed from the sole assumption that their components satisfy the commutation rule 8³2 with respect to **J**; this assumption is indeed equivalent to the definition of a vector, because the operators J_x, J_y, and J_z are proportional to the rotation operators,[4] and therefore the commutation law with respect to **J** determines completely the transformation law of each quantity considered for a rotation of the axes; since 8³2 holds for x, y, and z, each group of three quantities which satisfies 8³2 has the same transformation law as x, y, and z, and is therefore a vector.

It is shown in the theory of tensors that by means of symmetrizations and contractions each tensor may be decomposed in parts which transform themselves independently for a rotation of the axes, the transformation law of each irreducible part being the same as that of the spherical harmonics of a determinate degree. We may therefore define as "irreducible tensor operator of the degree k" each operator $\mathbf{T}^{(k)}$ whose $2k+1$ components $T_q^{(k)}$ $(q=-k, -k+1, \cdots, k-1, k)$ satisfy the same commutation rule with respect to **J** as the spherical-harmonic operators $\Theta(kq)\Phi(q)$; this commutation rule is easily derived from §§3³ and 4³ of TAS, and is

$$[(J_x \pm iJ_y), T_q^{(k)}] = [(k \mp q)(k \pm q + 1)]^{\frac{1}{2}} T_{q\pm 1}^{(k)}, \tag{23a}$$

$$[J_z, T_q^{(k)}] = qT_q^{(k)}. \tag{23b}$$

It is easily seen that for $k=1$ (23) reduce to TAS 8³2, if we put

$$T_1^{(1)} = -(T_x + iT_y)/(2)^{\frac{1}{2}}, \quad T_0^{(1)} = T_z, \quad T_{-1}^{(1)} = (T_x - iT_y)/(2)^{\frac{1}{2}}. \tag{24}$$

In view of TAS 4³18 we shall say that an irreducible tensor operator is Hermitian, if

$$T_q^{(k)\dagger} = (-1)^q T_{-q}^{(k)}. \tag{25}$$

(2) Dependence of the Matrix of $T^{(k)}$ on m

The dependence on m of the matrix elements of $T_q^{(k)}$ in the jm scheme will readily be derived from (23). The relation (23b) gives us in the usual manner the selection rule: the only non-vanishing elements of $(\alpha jm|T_q^{(k)}|\alpha' j'm')$ are those for which

$$m' = m - q. \tag{26}$$

The two relations (23a), written for a general non-vanishing element, give

$$\begin{aligned}
[(j+m)(j-m+1)]^{\frac{1}{2}}(\alpha jm-1|T_q^{(k)}|\alpha' j'm-q-1) &= [(j'+m-q)(j'-m+q+1)]^{\frac{1}{2}}(\alpha jm|T_q^{(k)}|\alpha' j'm-q) \\
&\quad + [(k-q)(k+q+1)]^{\frac{1}{2}}(\alpha jm|T_{q+1}^{(k)}|\alpha' j'm-q-1), \\
[(j-m)(j+m+1)]^{\frac{1}{2}}(\alpha jm+1|T_q^{(k)}|\alpha' j'm-q+1) &= [(j'-m+q)(j'+m-q+1)]^{\frac{1}{2}} \\
&\quad \times (\alpha jm|T_q^{(k)}|\alpha' j'm-q) + [(k+q)(k-q+1)]^{\frac{1}{2}}(\alpha jm|T_{q-1}^{(k)}|\alpha' j'm-q+1).
\end{aligned} \tag{27}$$

We observe now that if we replace $(\alpha jm|T_q^{(k)}|\alpha' j'm')$ by $(j'km'q|j'kjm)$, (27), we reduce exactly to (3) and (5); since we saw that these equations were sufficient to determine the dependence of $(j_1j_2m_1m_2|j_1j_2jm)$ on m_1, m_2, and m, it follows that

$$(\alpha jm|T_q^{(k)}|\alpha' j'm') = A(j'km'q|j'kjm), \tag{28}$$

where A is independent of m, m', and q.[5] Owing to (16′) and (19), we write

$$(\alpha jm|T_q^{(k)}|\alpha' j'm') = (-1)^{j+m}(\alpha j\|T^{(k)}\|\alpha' j')\, V(jj'k\,; -mm'q). \tag{29}$$

[4] P. A. M. Dirac, *Quantum Mechanics* (Oxford, 1935), §29.

[5] This relation was already given by Wigner, Reference 3, Chapter 21, Eq. (19), with group-theoretical methods.

This formula is the tensorial extension of TAS 9^3 II; in order to avoid mistakes we wrote the quantities which are independent of m, m', and q with $\|$ instead of $\vdots$, since for $k=1$ these quantities differ from the analogous quantities defined in §9^3 of TAS; it is easy to see that they are related by the following relations:

$$\begin{aligned}(\alpha j\|T^{(1)}\|\alpha' j)&=[j(j+1)(2j+1)]^{\frac{1}{2}}(\alpha j\vdots T\vdots\alpha' j),\\ (\alpha j\|T^{(1)}\|\alpha' j-1)&=[j(2j-1)(2j+1)]^{\frac{1}{2}}(\alpha j\vdots T\vdots\alpha' j-1),\\ (\alpha j\|T^{(1)}\|\alpha' j+1)&=-[(j+1)(2j+1)(2j+3)]^{\frac{1}{2}}(\alpha j\vdots T\vdots\alpha' j+1).\end{aligned}\tag{30}$$

It must also be observed that for a Hermitian tensor $\mathbf{T}^{(k)}$ the matrix $(\alpha j\|T^{(k)}\|\alpha' j')$ is not Hermitian, but satisfies the relation

$$(\alpha j\|T^{(k)}\|\alpha' j')=(-1)^{j-j'}\overline{(\alpha' j'\|T^{(k)}\|\alpha j)};\tag{31}$$

the general relation for any tensor is

$$(\alpha j\|T^{(k)}\|\alpha' j')=(-1)^{j-j'}\overline{(\alpha' j'\|T^{(k)\dagger}\|\alpha j)}.\tag{31'}$$

The reasons which brought us to this choice of phases are similar to those which fixed the phases in TAS $4^3$17.

(3) Scalar Product of Tensors

If two irreducible tensors of the same degree are given, we consider the quantity

$$Q=\sum_q(-1)^q T_q^{(k)}U_{-q}^{(k)};\tag{32}$$

owing to (29), (19), and (20a), the matrix elements of Q are

$$(\alpha jm|Q|\alpha' j'm')=\sum_{\alpha'' j''}(-1)^{j-j''}(\alpha j\|T^{(k)}\|\alpha'' j'')(\alpha'' j''\|U^{(k)}\|\alpha' j')\delta(j,j')\delta(m,m')/(2j+1).\tag{33}$$

The matrix of Q is then diagonal with respect to j and m, and entirely independent of m; it follows that Q commutes with $\mathbf{J}$, and is therefore a scalar. Since, owing to (24), Q is for $k=1$ the scalar product of the two vectors, we shall in general name Q the scalar product of $\mathbf{T}^{(k)}$ and $\mathbf{U}^{(k)}$, and write

$$Q=(\mathbf{T}^{(k)}\cdot\mathbf{U}^{(k)})=\sum_q(-1)^q T_q^{(k)}U_{-q}^{(k)}.\tag{32'}$$

The most important example of such scalar products is given by the spherical-harmonic addition theorem (TAS $4^3$22).

The tensorial extension of TAS $12^3$2 may be obtained by a direct use of (16') and (29). If $\mathbf{T}^{(k)}$ and $\mathbf{U}^{(k)}$ are of such a character that, when a resolution of the type TAS $6^3$5 is made of the states in question, $\mathbf{T}^{(k)}$ operates only on ϕ_1 and $\mathbf{U}^{(k)}$ only on ϕ_2, the matrix elements of Q will be

$$\begin{aligned}&(\gamma j_1j_2jm|(\mathbf{T}^{(k)}\cdot\mathbf{U}^{(k)})|\gamma' j'_1j'_2j'm')=\sum_{\gamma'' q m_1m_2m'_1m'_2}(-1)^q(j_1j_2jm|j_1j_2m_1m_2)(\gamma j_1m_1|T_q^{(k)}|\gamma'' j_1'm'_1)\\ &\times(\gamma'' j_2m_2|U_{-q}^{(k)}|\gamma' j'_2m'_2)(j'_1j'_2m'_1m'_2|j'_1j'_2j'm')=(-1)^{j_1+j_2-j-j'-m}[(2j+1)(2j'+1)]^{\frac{1}{2}}\\ &\times\sum_{\gamma''}(\gamma j_1\|T^{(k)}\|\gamma'' j'_1)(\gamma'' j_2\|U^{(k)}\|\gamma' j'_2)\sum(-1)^q V(j_1j_2j;m_1m_2-m)V(j_1j'_1k;-m_1m'_1q)\\ &\qquad\times V(j_2j'_2k;-m_2m'_2-q)V(j'_1j'_2j';m'_1m'_2-m').\end{aligned}\tag{34}$$

The last sum is very difficult to evaluate for general values of the parameters; but, owing to (33), it suffices to calculate it for the particular case $j=j'=m=m'$. It is shown in Appendix B that

$$\begin{aligned}&\sum_{\alpha\beta\gamma\delta\varphi}(-1)^{f+\varphi}v(abe;\alpha\beta-e)v(acf;-\alpha\gamma\varphi)v(bdf;-\beta\delta-\varphi)v(cde;\gamma\delta-e)\\ &\qquad=(-1)^{2e+f+d-b}w(abcd;ef)/(2e+1),\end{aligned}\tag{35}$$

where

$$w(abcd\,;ef)=\sum_z(-1)^z\frac{(a+b+c+d+1-z)!}{(a+b-e-z)!(c+d-e-z)!(a+c-f-z)!}\times(b+d-f-z)!z!(e+f-a-d+z)!(e+f-b-c+z)!}. \tag{36}$$

Putting also

$$W(abcd\,;ef)=\left[\frac{(a+b-e)!(a+e-b)!(b+e-a)!(c+d-e)!(c+e-d)!(d+e-c)!}{\cdot(a+c-f)!(a+f-c)!(c+f-a)!(b+d-f)!(b+f-d)!(d+f-b)!}{(a+b+e+1)!(c+d+e+1)!(a+c+f+1)!(b+d+f+1)!}\right]^{\frac{1}{2}}w(abcd\,;ef), \tag{36'}$$

we have

$$\sum_{\alpha\beta\gamma\delta\varphi}(-1)^{f+\varphi}V(abe\,;\alpha\beta-e)\,V(acf\,;-\alpha\gamma\,\varphi)\,V(bdf\,;-\beta\delta-\varphi)\,V(cde\,;\gamma\delta-e)$$
$$=(-1)^{2e+f+d-b}W(abcd\,;ef)/(2e+1)\,; \tag{35'}$$

and owing to (34) and (33) we get

$$\sum_{\alpha\beta\gamma\delta\varphi}(-1)^{f+\varphi}V(abe\,;\alpha\beta-\epsilon)\,V(acf\,;-\alpha\gamma\,\varphi)\,V(bdf\,;-\beta\delta-\varphi)\,V(cdg\,;\gamma\delta-\eta)$$
$$=(-1)^{e+\epsilon+f+d-b}W(abcd\,;ef)\delta(e,g)\delta(\epsilon,\eta)/(2e+1) \tag{37}$$

and

$$(\gamma j_1j_2jm|(\mathbf{T}^{(k)}\cdot\mathbf{U}^{(k)})|\gamma'j'_1j'_2jm)$$
$$=(-1)^{j_1+j'_2-j}\sum_{\gamma''}(\gamma j_1\|T^{(k)}\|\gamma''j'_1)(\gamma''j_2\|U^{(k)}\|\gamma'j'_2)W(j_1j_2j'_1j'_2\,;jk), \tag{38}$$

which is the tensorial extension of TAS 12[3]2.[6]

(4) Properties of W

The functions w and W are defined for integral and half-integral values of the parameters, with the limitation that each of the four triads

$$(a,b,e),\quad(c,d,e),\quad(a,c,f),\quad(b,d,f) \tag{39}$$

has an integral sum. Since in (36) z takes on only such integral values for which the argument of every factorial is not negative, W vanishes unless the elements of each triad (39) satisfy the triangular inequalities; if one of these triangles reduces to a segment, the summation reduces to one term.

It follows from the symmetry of (36) and (36′) that

$$W(abcd;ef)=W(badc;ef)=W(cdab;ef)=W(acbd;fe)\,; \tag{40a}$$

assuming the argument of one of the two last factorials instead of z as summation parameter in (36), we obtain other symmetry properties of W:

$$W(abcd\,;ef)=(-1)^{e+f-a-d}W(ebcf\,;ad)=(-1)^{e+f-b-c}W(aefd\,;bc)\,; \tag{40b}$$

combining (40a) and (40b) we obtain 24 different permutations of the parameters of W, which correspond to all possible permutations between the four triads (39).

Since (33) and (34) have a meaning only for integral values of k, our demonstration of (37) holds only for integral values of f; but it follows from the symmetry properties of V and W that (37) holds also for half-integral values of f.

[6] For the diagonal elements of this matrix an equivalent formula was given by H. A. Kramers, Proc. Amst. Akad. Sci. **34**, 965 (1931).

If we multiply the two sides of (37) by $(2g+1)V(cdg;\gamma'\delta'-\eta)$ and extend a summation over all possible values of g and η, we obtain, owing to (20b),

$$\sum_{\alpha\beta\varphi}(-1)^{f+\varphi}V(abe;\alpha\beta-\epsilon)V(acf;-\alpha\gamma'\varphi)V(bdf;-\beta\delta'-\varphi)=(-1)^{e+\epsilon+f+d-b}W(abcd;ef)V(cde;\gamma'\delta'-\epsilon),$$

or, owing to (19) and (40) and omitting the dashes,

$$\sum_{\alpha\beta\varphi}(-1)^{f+\varphi}V(abe;\alpha\beta-\epsilon)V(afc;-\alpha\varphi\gamma)V(fbd;\varphi\beta-\delta)$$
$$=(-1)^{b+c-a-d+e+\epsilon}W(aefd;bc)V(edc;-\epsilon\delta\gamma). \quad (41)$$

We rewrite (41) with slightly different parameters,

$$\sum_{\alpha'\beta'\eta}(-1)^{g+\eta}V(abe;\alpha'\beta'-\epsilon)V(agc;-\alpha'\eta\gamma)V(gbd;\eta\beta'-\delta)$$
$$=(-1)^{b+c-a-d+e+\epsilon}W(aegd;bc)V(edc;-\epsilon\delta\gamma), \quad (41')$$

and multiply the two sides by the two sides of (41) and by $(2d+1)(2e+1)$; extending a summation over all possible values of γ, ϵ, and e, and owing to (20), we obtain an orthogonality relation between the W:

$$\textstyle\sum_e(2e+1)W(aefd;bc)W(aegd;bc)=\delta(f,g)/(2f+1). \quad (42)$$

Interchanging a with b and α' with β' in (41') and operating as before, we obtain another useful relation between the W:

$$\textstyle\sum_e(-1)^{a+b+c+d+e+f+g}(2e+1)W(acbd;fe)W(abdc;eg)=W(acdb;fg). \quad (43)$$

(5) Matrix of a Tensor $T^{(k)}$ Which Commutes with J_2 or with J_1

From (16'), (29), and (41) we have

$$(\gamma j_1j_2jm|T_q^{(k)}|\gamma'j'_1j'_2j'm')=\sum_{m_1m'_1m_2}(j_1j_2jm|j_1j_2m_1m_2)(\gamma j_1m_1|T_q^{(k)}|\gamma'j'_1m'_1)(j'_1j_2m'_1m_2|j'_1j_2j'm')$$
$$=(-1)^{j_2+k-j'_1+m}[(2j+1)(2j'+1)]^{\frac{1}{2}}(\gamma j_1\|T^{(k)}\|\gamma'j'_1)W(j_1jj'_1j';j_2k)V(jj'k;-mm'q),$$

and owing again to (29) we get

$$(\gamma j_1j_2j\|T^{(k)}\|\gamma'j'_1j_2j')=(-1)^{j_2+k-j'_1-j}(\gamma j_1\|T^{(k)}\|\gamma'j'_1)[(2j+1)(2j'+1)]^{\frac{1}{2}}W(j_1jj'_1j';j_2k), \quad (44a)$$

which is the tensorial extension of TAS 11[3]8. In the same way we obtain also

$$(\gamma j_1j_2j\|U^{(k)}\|\gamma'j_1j'_2j')=(-1)^{j_1+k-j_2-j'}(\gamma j_2\|U^{(k)}\|\gamma'j'_2)[(2j+1)(2j'+1)]^{\frac{1}{2}}W(j_2jj'_2j';j_1k). \quad (44b)$$

§4. THE ELECTROSTATIC INTERACTION BETWEEN TWO ELECTRONS

It was shown in I that the coefficients of Slater's integrals F^k and G^k in the two-electron configurations are the matrix elements of $P_\kappa(\cos\omega)$, where ω is the angle between the radii vectors of the two electrons. It follows from (32') and from the spherical-harmonic addition theorem (TAS 4[3]22) that

$$P_k(\cos\omega)=(\mathbf{C}_1^{(k)}\cdot\mathbf{C}_2^{(k)}), \quad (45)$$

where $\mathbf{C}^{(c)}$ is the tensor operator defined by

$$C_q^{(k)}=[4\pi/(2k+1)]^{\frac{1}{2}}\Theta(kq)\Phi(q); \quad (46)$$

we see from TAS 8[6]6 that the non-vanishing matrix elements of $C_q^{(k)}$ are the c^k of Condon and Shortley.

Confronting the expressions TAS 9[6]8 and (29) of $(l0\|C_0^{(k)}\|l'0)$, we obtain

$$(-1)^l(l\|C^{(k)}\|l')V(ll'k;000)=\tfrac{1}{2}[(2l+1)(2l'+1)]^{\frac{1}{2}}C_{lkl'}, \quad (47)$$

where (TAS 9[6]7)

$$C_{lkl'}=\int_0^\pi P_l(\cos\omega)P_k(\cos\omega)P_{l'}(\cos\omega)\sin\omega d\omega. \tag{48}$$

In order to calculate algebraically $C_{lkl'}$ we express the Legendre polynomials by means of TAS 4[3]22 and 4[3]18,

$$P_l(\cos\omega)=\bar{P}_l(\cos\omega)=[4\pi/(2l+1)]\sum_m(-1)^m\bar{\Theta}(lm)\bar{\Phi}(m)\bar{\Theta}'(l-m)\bar{\Phi}'(-m),$$
$$P_k(\cos\omega)=[4\pi/(2k+1)]\sum_q(-1)^q\Theta(kq)\Phi(q)\Theta'(k-q)\Phi'(-q),$$
$$P_{l'}(\cos\omega)=[4\pi/(2l'+1)]\sum_{m'}(-1)^{m'}\Theta(l'm')\Phi(m')\Theta'(l'-m')\Phi'(-m'),$$

and integrate their product over the spheres $(\theta\varphi)$ and $(\theta'\varphi')$; we obtain

$$8\pi^2\int_0^\pi P_l(\cos\omega)P_k(\cos\omega)P_{l'}(\cos\omega)\sin\omega d\omega=64\pi^3[(2l+1)(2k+1)(2l'+1)]^{-1}$$
$$\sum_{mqm'}\int_0^\pi\int_0^{2\pi}\bar{\Theta}(lm)\bar{\Phi}(m)\Theta(kq)\Phi(q)\Theta(l'm')\Phi(m')\sin\theta d\theta d\varphi$$
$$\cdot\int_0^\pi\int_0^{2\pi}\bar{\Theta}'(l-m)\bar{\Phi}'(-m)\Theta'(k-q)\Phi'(-q)\Theta'(l'-m')\Phi'(-m')\sin\theta' d\theta' d\varphi',$$

or, if we use successively (46), (29), (19b), and (20a),

$$(2l+1)(2l'+1)C_{lkl'}=2\sum_{mqm'}(lm|C_q^{(k)}|l'm')(l-m|C_{-q}^{(k)}|l'-m')$$
$$=2(l\|C^{(k)}\|l')^2\sum_{mqm'}V(ll'k\,;-mm'q)\,V(ll'k\,;m-m'-q)=2(-1)^{l+l'+k}(l\|C^{(k)}\|l')^2. \tag{49}$$

It follows from the comparison of (47) and (49) that

$$C_{lkl'}=2(-1)^{l+l'+k}[V(ll'k\,;000)]^2, \tag{50}$$

and owing to (22′) we obtain

$$\begin{cases} C_{lkl'}=0 & (l+l'+k\text{ odd}) \\ C_{lkl'}=\dfrac{2(l+l'-k)!(l+k-l')!(l'+k-l)!g!^2}{(l+l'+k+1)!(g-l)!^2(g-l')!^2(g-k)!^2} & (l+l'+k=2g\text{ even}), \end{cases} \tag{50′}$$

which agrees with TAS 9[6]9. The numerical values of $C_{lkl'}$ are tabulated by Shortley and Fried.[7]

It follows also from (47), (49), and (22′) that

$$(l\|C^{(k)}\|l')=(-1)^{g-l}[\tfrac{1}{2}(2l+1)(2l'+1)C_{lkl'}]^{\frac{1}{2}}, \tag{51}$$

and therefore

$$c^k(lm,l'm')=(lm|C^{(k)}_{m-m'}|l'm')=(-1)^{g+m}[\tfrac{1}{2}(2l+1)(2l'+1)C_{lkl'}]^{\frac{1}{2}}V(ll'k\,;-mm'm-m'). \tag{52}$$

We do not know to what extent this derivation is different from Gaunt's derivation, because we had no opportunity of consulting his paper;[8] in every case (52) has the same advantages in comparison to Gaunt's formula (TAS 8[6]11) as (16) in comparison to Wigner's formula.

Introducing (45) and (51) in (38) we have a direct demonstration of Eq. (12′) I, from which we obtained the coefficients of F^k and G^k for two-electron configurations in (LS) coupling.

[7] G. H. Shortley and B. Fried, Phys. Rev. **54**, 739 (1938), Table III.
[8] J. A. Gaunt, Phil. Trans. Roy. Soc. **A228**, 195 (1929).

In order to obtain from (45) and (38) the matrix elements of the electrostatic interaction in (jj) coupling, it suffices to calculate the elements $(\frac{1}{2}lj\|C^{(k)}\|\frac{1}{2}l'j')$; it follows from (44b) and (51) that

$$(\tfrac{1}{2}ll\pm\tfrac{1}{2}\|C^{(k)}\|\tfrac{1}{2}l'l'\pm\tfrac{1}{2})=(-1)^{(j'+k-j)/2}\left[\frac{(j+j'-k)!(j+k-j')!(j'+k-j)!}{(j+j'+k+1)!}\right]^{\frac{1}{2}}$$
$$\times\frac{(j+j'+k+1)!!}{(j+j'-k-1)!!(j+k-j')!!(j'+k-j)!!}, \tag{53a}$$

$$(\tfrac{1}{2}ll\pm\tfrac{1}{2}\|C^{(k)}\|\tfrac{1}{2}l'l'\mp\tfrac{1}{2})=(-1)^{(j'+k-j-1)/2}\left[\frac{(j+j'-k)!(j+k-j')!(j'+k-j)!}{(j+j'+k+1)!}\right]^{\frac{1}{2}}$$
$$\times\frac{(j+j'+k)!!}{(j+j'-k)!!(j+k-j'-1)!!(j'+k-j-1)!!}, \tag{53b}$$

and then

$$f_k(l_1j_1l_2j_2J)=\frac{(k-1)!!^4(2j_1-k)!!(2j_2-k)!!}{(2j_1+k)!!(2j_2+k)!!}$$
$$\cdot\sum_w(-1)^w\binom{j_1+j_2+J+1+w}{w}\binom{j_1+j_2-J}{w}\binom{J+j_1-j_2}{k-w}\binom{J+j_2-j_1}{k-w}. \tag{54}$$

It is remarkable that (54) depends only on the j's and not on the l's of the electrons, and therefore the coefficients of F^k for the interaction between two $p_{1\frac{1}{2}}$ electrons are the same as between two $d_{1\frac{1}{2}}$ or between a $p_{1\frac{1}{2}}$ and a $d_{1\frac{1}{2}}$.

For the coefficients of the G^k the situation is somewhat different, because, although g_k does not depend explicitly on l, in the case that both the electrons have their spins parallel or antiparallel to their orbital momenta the formula is not the same as in the case that one spin is parallel to its orbital momentum and the other is antiparallel. In the first case

$$g_k(l_1l_1\pm\tfrac{1}{2}l_2l_2\pm\tfrac{1}{2}J)=(-1)^{j_1+j_2-J}\frac{(j_1+j_2-k)!!^2(k+j_1-j_2-1)!!^2(k+j_2-j_1-1)!!^2}{(j_1+j_2+k)!!^2}$$
$$\cdot\sum_w(-1)^w\binom{j_1+j_2+J+1+w}{w}\binom{j_1+j_2-J}{w}\binom{J+j_1-j_2}{k+j_1-j_2-w}\binom{J+j_2-j_1}{k+j_2-j_1-w} \tag{55a}$$

and in the second case

$$g_k(l_1l_1\pm\tfrac{1}{2}l_2l_2\mp\tfrac{1}{2}J)=(-1)^{j_1+j_2-J}\frac{(j_1+j_2-k-1)!!^2(k+j_1-j_2)!!^2(k+j_2-j_1)!!^2}{(j_1+j_2+k+1)!!^2}$$
$$\cdot\sum_w(-1)^w\binom{j_1+j_2+J+1+w}{w}\binom{j_1+j_2-J}{w}\binom{J+j_1-j_2}{k+j_1-j_2-w}\binom{J+j_2-j_1}{k+j_2-j_1-w}. \tag{55b}$$

It must also be noted that in (LS) coupling g_k is preceded by different signs, corresponding to the singlet and triplet states; but in (jj) coupling g_k is always preceded by a minus sign, since in (jj) coupling only antisymmetrical eigenfunctions are possible.

By means of these formulas the results of Inglis[9] were checked, and the following mistakes were found: the coefficient of $-G^1$ 225 for the level $p_{\frac{1}{2}}d_{1\frac{1}{2}}$ with $J=2$ is not 25, but 75; the denominators of F^2 and F^4 in the configuration dd' are not 25 and 49, but 1225 and 441.

[9] D. R. Inglis, Phys. Rev. **38**, 862 (1931), Table II.

The non-diagonal elements of the electrostatic interaction in (jj) coupling may also easily be calculated in this way.

From our results follows also that the coefficients of F^k in (jl) coupling[10] are

$$f_k(jlK)=\frac{(k-1)!!^4(2j-k)!!(2l-k-1)!!(2l+1)}{(2j+k)!!(2l+k+1)!!}$$
$$\cdot\sum_w(-1)^w\binom{j+l+K+1+w}{w}\binom{j+l-K}{w}\binom{K+j-l}{k-w}\binom{K+l-j}{k-w}. \quad (56)$$

The particular expression for $k=2$ which we gave already for the rare-gas spectra differs from (56) in the sign, owing to the fact that in the rare-gas configurations there is an almost closed shell (see §6).

§5. MANY-ELECTRON SPECTRA. GENERAL PART

In §4 we expressed the coefficients of the F^k in the interaction between two electrons as scalar products of tensors, each of which operates on a definite electron (type (34)); thus by the general methods of §3 we may calculate for every configuration that part of the energy matrix which depends on the F^k, in a schema in which each state is defined by its "genealogical characterizations" (TAS §2[8]).

The problem is more complex for the coefficients of the G^k, since the g_k are not scalar products of tensors of the type (34); in the particular cases considered in §§5 and 6 of I we gave to g_k the form of a polynomial in λ, but in more general cases it appears convenient to develop g_k in a sum of scalar products of tensors of the type (34).[11] It follows from (6) I and (45) that

$$g_k(l_1l_2L)=(-1)^{l_1+l_2-L}(l_1l_2LM|(\mathbf{C}_1^{(k)}\cdot\mathbf{C}_2^{(k)})|l_2l_1LM), \quad (57)$$

and owing to (38), (31), and (43) we obtain

$$g_k(l_1l_2L)=(l_1\|C^{(k)}\|l_2)^2\sum_r(-1)^{L+k+r}(2r+1)W(l_1l_2l_1l_2;Lr)W(l_1l_1l_2l_2;rk);$$

if we define the tensor $\mathbf{u}^{(r)}$ by

$$(l\|u^{(r)}\|l')=\delta(l,l')$$

and take into account (38) and the fact that l_1+l_2+k is even, we may also write

$$g_k(l_1l_2L)=(l_1\|C^{(k)}\|l_2)^2\sum(-1)^r(2r+1)W(l_1l_1l_2l_2;rk)(l_1l_2LM|(\mathbf{u}_1^{(r)}\cdot\mathbf{u}_2^{(r)})|l_1l_2LM). \quad (59)$$

Following Dirac's vector model we can also substitute the operator (37) I for the double sign which precedes g_k and assume as coefficient of G^k in the exchange interaction between two electrons the expression

$$-[\tfrac{1}{2}+2(\mathbf{s}_1\cdot\mathbf{s}_2)](l_1\|C^{(k)}\|l_2)^2\sum_r(-1)^r(2r+1)W(l_1l_1l_2l_2;rk)(\mathbf{u}_1^{(r)}\cdot\mathbf{u}_2^{(r)}). \quad (60)$$

It will also be convenient to consider the quantities $(\mathbf{s}_1\cdot\mathbf{s}_2)(\mathbf{u}_1\cdot\mathbf{u}_2)$ as scalar products of "double tensors";[12] a double tensor of the degree (κ, k) is defined as a quantity which behaves as an irreducible tensor of the degree κ with respect to $\mathbf{S}$ and as an irreducible tensor of the degree k with respect to $\mathbf{L}$. The algebra of these double tensors is a trivial extension of the tensor algebra developed in §3; it must be noted only that such a double tensor does not satisfy the commutation rule (23) with respect to $\mathbf{J}$, because with respect to $\mathbf{J}$ it is reducible and may be decomposed in a sum of irreducible tensors, the degrees of which lie between $|k-\kappa|$ and $k+\kappa$. From this point of view the scalar product $(\mathbf{l}\cdot\mathbf{s})$ is the scalar part of the decomposition of the double vector $\mathbf{ls}$.

[10] G. Racah, Phys. Rev. **61**, 537 (1942).
[11] These two different possibilities correspond to the developments of a function in series of powers or of Legendre polynomials.
[12] Reference 3, p. 295.

If x electrons of a configuration are equivalent, it has no sense to speak of the tensor (or double tensor) $\mathbf{t}_L^{(\kappa k)}$ which operates on the electron i (TAS §I[8]), but we must be content to consider tensors of the type

$$\mathbf{T}^{(\kappa k)} = \sum_1^x{}_i \mathbf{t}_i^{(\kappa k)}, \tag{61}$$

which operate on the whole group of equivalent electrons; it is easily seen that every symmetrical operator may be built up with such tensors. The matrix elements of a tensor (61) must be calculated in the scheme of the allowed states of the group: for $x \geqslant 3$ this calculation is not very simple, as a general method of vector coupling for equivalent electrons is not yet known; however, it is possible at first to couple the vectors and then to antisymmetrize the obtained states, but in this paper we shall not deal with such cases.

§6. CONFIGURATIONS CONTAINING ALMOST CLOSED SHELLS

Let us consider a shell "$\mathfrak{S}$" which is complete except for ϵ missing electrons; if the number of places in the shell is m, this configuration "$\mathfrak{R}$" will contain $m-\epsilon$ electrons. We shall in this paragraph determine a simple relation between the matrix of a tensor of the type (61) which operates on $\mathfrak{R}$ and the matrix of the corresponding tensor for the simpler group "$\mathfrak{Q}$" of ϵ equivalent electrons.

Let us denote by $\Phi_{\mathfrak{Q}}(aSLM_SM_L)$ the eigenfunctions of the allowed states of $\mathfrak{Q}$ and by $\Phi_{\mathfrak{R}}(bSLM_SM_L)$ those of $\mathfrak{R}$, the parameters a and b being introduced in order to distinguish the different multiplets of the same type which may occur in the given configurations. We consider now a fictive configuration $\mathfrak{Q}+\mathfrak{R}$ in which the exclusion principle does not hold between the electrons of $\mathfrak{Q}$ and those of $\mathfrak{R}$: a complete set of eigenfunctions of such configuration is given by the functions

$$\Phi_{\mathfrak{Q}}(aS'L'M'_SM'_L)\Phi_{\mathfrak{R}}(bS''L''M''_SM''_L)$$

or by the functions

$$\Psi(abS'S''L'L''SLM_SM_L) = \sum_{M'_SM''_SM'_LM''_L} \Phi_{\mathfrak{Q}}(aS'L'M'_SM'_L)\Phi_{\mathfrak{R}}(bS''L''M''_SM''_L) \times (S'S''M'_SM''_S\|S'S''SM_S)(L'L''M'_LM''_L\|L'L''LM_L). \tag{62}$$

If the exclusion principle holds also between the two groups of electrons, only one state will be allowed, a particular ^1S state which we shall denote by $^1S^*$; its eigenfunction will be

$$\Psi(^1S^*) = \sum_{abSL} q(abSL)\Psi(abSSLL0000). \tag{63}$$

In order to establish a correlation between the states of $\mathfrak{Q}$ and those of $\mathfrak{R}$ and between the phases of their eigenfunctions, we consider, for S and L given, the Hermitian matrix

$$A_{ac} = \sum_b \bar{q}(ab)\bar{q}(cb) \tag{64}$$

and the unitary transformation $u_{c\gamma}$ which diagonalizes it: in view of the special form of (64) it will be

$$\sum_{ac} \bar{u}_{a\alpha}u_{c\gamma}A_{ac} = Q^2(\alpha)\delta(\alpha\gamma), \tag{65}$$

where the $Q(\alpha)$ are real numbers, which we may assume are not negative. If we put for each value of β for which $Q(\beta)$ does not vanish

$$v_{b\beta} = \sum_c \bar{u}_{c\beta}q(cb)/Q(\beta) \quad (Q(\beta)\neq 0), \tag{66}$$

it follows from (64) and (65) that

$$\sum_b \bar{v}_{b\beta}v_{b\alpha} = \delta(\alpha\beta). \tag{67}$$

If $Q(\beta)$ vanishes for some values of β, we complete the matrix $v_{b\beta}$ so that it be unitary: owing to (64) and (65) it will be anyway

$$Q(\beta)v_{b\beta}=\sum_c \bar{u}_{c\beta}q(cb). \tag{66'}$$

We change now the schemes of the states of $\mathfrak{L}$ and $\mathfrak{R}$, putting

$$\begin{aligned}\Phi_{\mathfrak{L}}(\alpha SLM_SM_L)&=\sum_a \Phi_{\mathfrak{L}}(aSLM_SM_L)u_{a\alpha}(SL),\\ \Phi_{\mathfrak{R}}(\alpha SLM_SM_L)&=\sum_b \Phi_{\mathfrak{R}}(bSLM_SM_L)v_{b\alpha}(SL)\end{aligned} \tag{68}$$

and shall consider two terms of $\mathfrak{L}$ and $\mathfrak{R}$ as correlated, if they have the same values of α, S, and L. It follows from (62) that

$$\Psi(\alpha'\alpha''S'S''L'L''SLM_SM_L)=\sum_{ab}\Psi(abS'S''L'L''SLM_SM_L)u_{a\alpha'}(S'L')v_{b\alpha''}(S''L''), \tag{68'}$$

and from the unitarity of $u_{a\alpha}$ and $v_{b\beta}$ that

$$\Psi(abS'S''L'L''SLM_SM_L)=\sum_{\alpha'\alpha''}\bar{u}_{a\alpha'}(S'L')\bar{v}_{b\alpha''}(S''L'')\Psi(\alpha'\alpha''S'S''L'L''SLM_SM_L)\,; \tag{68''}$$

introducing this result in (63) and owing to (66') we obtain

$$\Psi(^1S^*)=\sum_{\alpha SL}Q(\alpha SL)\Psi(\alpha\alpha SSLL0000). \tag{63'}$$

Since $\Psi(^1S^*)$ is the only antisymmetrical eigenfunction of the configuration $\mathfrak{L}+\mathfrak{R}$, the matrix elements connecting $^1S^*$ with every state (68') will vanish for every symmetrical operator, unless $S=L=0$. If $\mathbf{T}^{(\kappa k)}_{\mathfrak{L}}$ and $\mathbf{T}^{(\kappa k)}_{\mathfrak{R}}$ are two tensors which operate on the groups $\mathfrak{L}$ and $\mathfrak{R}$ according to (61), $\mathbf{T}^{(\kappa k)}_{\mathfrak{L}}+\mathbf{T}^{(\kappa k)}_{\mathfrak{R}}$ is symmetrical in all the electrons, and then

$$(\alpha'\alpha''S'S''L'L''SL\|T^{(\kappa k)}_{\mathfrak{L}}\|{}^1S^*)+(\alpha'\alpha''S'S''L'L''SL\|T^{(\kappa k)}_{\mathfrak{R}}\|{}^1S^*) \tag{69}$$

vanishes, unless $S=L=0$. Owing to the triangular conditions, each term vanishes alone unless $S=\kappa$ and $L=\kappa$; we shall therefore consider only the remaining equations

$$(\alpha'\alpha''S'S''L'L''\kappa k\|T^{(\kappa k)}_{\mathfrak{L}}\|{}^1S^*)+(\alpha'\alpha''S'S''L'L''\kappa k\|T^{(\kappa k)}_{\mathfrak{R}}\|{}^1S^*)=0 \tag{70}$$

which hold for every double tensor, excepting the double scalars.

Owing to (63') and to the fact that $\mathbf{T}^{(\kappa k)}_{\mathfrak{L}}$ is diagonal with respect to $\alpha''S''L''$ and $\mathbf{T}^{(\kappa k)}_{\mathfrak{R}}$ with respect to $\alpha'S'L'$, we get

$$\begin{aligned}&(\alpha'\alpha''S'S''L'L''\kappa k\|T^{(\kappa k)}_{\mathfrak{L}}\|\alpha''\alpha''S''S''L''L''00)Q(\alpha''S''L'')\\ &\qquad+(\alpha'\alpha''S'S''L'L''\kappa k\|T^{(\kappa k)}_{\mathfrak{R}}\|\alpha'\alpha'S'S'L'L'00)Q(\alpha'S'L')=0,\end{aligned}$$

and introducing (44) and (36') this becomes

$$\begin{aligned}&(\alpha'S'L'\|T^{(\kappa k)}_{\mathfrak{L}}\|\alpha''S''L'')Q(\alpha''S''L'')/[(2S''+1)(2L''+1)]^{\frac{1}{2}}+(-1)^{S'+L'-S''-L''+\kappa+k}\\ &\qquad\times(\alpha''S''L''\|T^{(\kappa k)}_{\mathfrak{R}}\|\alpha'S'L')Q(\alpha'S'L')/[(2S'+1)(2L'+1)]^{\frac{1}{2}}=0.\end{aligned} \tag{71a}$$

Also, since $\mathbf{T}^{(\kappa k)\dagger}_{\mathfrak{L}}+\mathbf{T}^{(\kappa k)\dagger}_{\mathfrak{R}}$ is a symmetrical operator, and since the $Q(\alpha SL)$ are real, it follows from (71a) that

$$\begin{aligned}&\langle(\alpha''S''L''\|T^{(\kappa k)\dagger}_{\mathfrak{L}}\|\alpha'S'L')\rangle Q(\alpha'S'L')/[(2S'+1)(2L'+1)]^{\frac{1}{2}}+(-1)^{S''+L''-S'-L'+\kappa+k}\\ &\qquad\times\langle(\alpha'S'L'\|T^{(\kappa k)\dagger}_{\mathfrak{R}}\|\alpha''S''L'')\rangle Q(\alpha''S''L'')/[(2S''+1)(2L''+1)]^{\frac{1}{2}}=0,\end{aligned}$$

and owing to (31′) we get

$$(\alpha' S'L' \| T^{\mathfrak{L}(\kappa k)} \| \alpha'' S''L'') Q(\alpha' S'L') / [(2S'+1)(2L'+1)]^{\frac{1}{2}} + (-1)^{S'+L'-S''-L''+\kappa+k} \times (\alpha'' S''L'' \| T^{\mathfrak{R}(\kappa k)} \| \alpha' S'L') Q(\alpha'' S''L'') / [(2S''+1)(2L''+1)]^{\frac{1}{2}} = 0. \quad (71b)$$

It follows from the homogeneous equation system (71) that the matrix elements connecting two terms $\alpha' S'L'$ and $\alpha'' S''L''$ vanish for every tensor (61) operating on $\mathfrak{L}$ or on $\mathfrak{R}$, unless

$$\frac{Q(\alpha' S'L')}{[(2S'+1)(2L'+1)]^{\frac{1}{2}}} = \frac{Q(\alpha'' S''L'')}{[(2S''+1)(2L''+1)]^{\frac{1}{2}}}; \quad (72)$$

since every symmetrical operator may be expressed as a function of tensors (61), and since there exists always at least one symmetrical operator connecting two allowed terms, it follows that (72) must hold for every couple of allowed terms, or that

$$Q(\alpha SL) = C[(2S+1)(2L+1)]^{\frac{1}{2}}.$$

Since $(2S+1)(2L+1)$ is the number of states of the term αSL, it follows from the normalization of $\Psi(^1S^*)$ that $1/C^2$ equals the number of states of the configuration $\mathfrak{L}$, or that

$$C = \binom{m}{\epsilon}^{-\frac{1}{2}}. \quad (73)$$

It follows from (65) and (72′) that the matrix (64) is a multiple of the unit matrix: the unitary matrix $u_{c\gamma}$ is then entirely arbitrary and to every αSL scheme of $\mathfrak{L}$ a scheme of $\mathfrak{R}$ may be correlated.

From (71) and (72) we have also

$$(\alpha' S'L' \| T^{\mathfrak{L}(\kappa k)} \| \alpha'' S''L'') = -(-1)^{S'+L'-S''-L''+\kappa+k} (\alpha'' S''L'' \| T^{\mathfrak{R}(\kappa k)} \| \alpha' S'L'),$$

and owing to (31′)

$$(\alpha'' S''L'' \| T^{\mathfrak{R}(\kappa k)} \| \alpha' S'L') = -(-1)^{\kappa+k} \langle (\alpha'' S''L'' \| T^{\mathfrak{L}(\kappa k)\dagger} \| \alpha' S'L') \rangle, \quad (74)$$

which is the requested relation between the matrices of $T^{\mathfrak{R}(\kappa k)}$ and $T^{\mathfrak{L}(\kappa k)}$.

This demonstration, however, does not hold for scalars. In this case $(lm \| \mathbf{t}^{(00)} \| lm')$ is a multiple of the unit matrix; if its value is a, the matrix of $\mathbf{T}^{\mathfrak{L}(00)}$ has the value ϵa and the matrix of $\mathbf{T}^{\mathfrak{R}(00)}$ has the value $ma - \epsilon a$; we may, therefore, say that apart from a constant diagonal term (74) holds also for scalars, and if only differences of energies are considered we may use (74) even in this case.

The coefficients of F^k for the terms of a configuration l^x are, apart from a constant term, the squares of the tensor $\sum_i C_i^{(k)}$; the relative electrostatic energies of correlated terms are then the same.

Since the expression for the coefficients of F^k contains only tensors with $\kappa = 0$ and k even, we obtain immediately the known rule that the coefficients of F^k in the interaction between the group $l^{m-\epsilon}$ and an electron l' are the negatives of those for l^ϵ and l'.

For the coefficients of G^k the situation is more complex, since in (60) there are tensors of even and of odd degrees. For two-electron-like configurations $l^{m-1}l'$ the result is, however, very simple, since it follows from (60), (74), and (58) that the coefficient of G^k is

$$[\tfrac{1}{2} - 2(\dot{\mathbf{s}} \cdot \mathbf{s}')] (l \| C^{(k)} \| l')^2 (-1)^{L+k} \sum_r (2r+1) W(ll'll'; Lr) W(lll'l'; rk),$$

and reduces, owing to (40), (42), and (51), to

$$\frac{1 - 4(s \cdot s')}{4} \cdot \frac{(2l+1)(2l'+1)}{(2k+1)} C_{ll'k} \delta(L, k); \quad (75)$$

this formula agrees with the result of Shortley and Fried,[7] since the first coefficient vanishes for triplets and equals unity for singlets.

Some interesting results may be obtained for the configurations with $\epsilon=m/2$, which may be considered as "self-corresponding." Since the electrostatic energies of two corresponding terms are the same, it follows that in (LS) coupling each term is self-corresponding;[13] it is therefore

$$\Phi_{\mathfrak{L}}(\alpha SLM_SM_L)=c\Phi_{\mathfrak{R}}(\alpha SLM_SM_L)$$

with $|c|=1$, and since with our choice of phases all transformation coefficients are real,

$$\Phi_{\mathfrak{L}}(\alpha SLM_SM_L)=\pm\Phi_{\mathfrak{R}}(\alpha SLM_SM_L). \tag{76}$$

According to these two possibilities the terms of a self-corresponding configuration split in two classes, and a remarkable selection rule follows from (74): the elements of $\mathbf{T}^{(\kappa k)}$ connecting two terms of the same class vanish if $k+\kappa$ is even, the elements connecting two terms of different classes vanish if $k+\kappa$ is odd. A particular case of it is the vanishing of the diagonal elements of the double vector $\sum_i \mathbf{s}_i\mathbf{l}_i$, which causes the vanishing of the spin-orbit interaction constants for all terms of $l^{m/2}$.

This splitting in two classes is also the cause of the unexpected number of rational roots found by Laporte[14] in the electrostatic-energy matrix of d^5.

§7. THE CONFIGURATIONS d^n

d^2

The formulas for this configuration are well known (TAS p. 202); we wish only to point out that putting

$$A=F_0-49F_4=F^0-F^4/9,\quad B=F_2-5F_4=(9F^2-5F^4)/441,\quad C=35F_4=5F^4/63, \tag{77}$$

they get the simpler form

$$^1S=A+14B+7C,\quad ^3P=A+7B,\quad ^1D=A-3B+2C,\quad ^3F=A-8B,\quad ^1G=A+4B+2C. \tag{78}$$

d^3

Condon and Shortley calculated the formulas for this configuration, but they could not separate the energies of the two ^2D terms; this separation was performed by Ufford and Shortley by calculating the eigenfunctions of these terms. We shall calculate in detail this configuration with the tensor method, since the same method will be used without greater complication in the cases d^4, d^5, and f^3.

The term energies of d^3 are the eigenvalues of that part of

$$3F^0+[(\mathbf{C}_1^{(2)}\cdot\mathbf{C}_2^{(2)})+(\mathbf{C}_1^{(2)}\cdot\mathbf{C}_3^{(2)})+(\mathbf{C}_2^{(2)}\cdot\mathbf{C}_3^{(2)})]F^2 +[(\mathbf{C}_1^{(4)}\cdot\mathbf{C}_2^{(4)})+(\mathbf{C}_1^{(4)}\cdot\mathbf{C}_3^{(4)})+(\mathbf{C}_2^{(4)}\cdot\mathbf{C}_3^{(4)})]F^4 \tag{79}$$

which operates in the space of the antisymmetrical states with $l_1=l_2=l_3=2$. Since this operator does not affect the spins, we shall calculate its matrix in a m_SL scheme, and it will be sufficient to consider the elements corresponding to $ms_1=ms_2=\frac{1}{2}$ and $ms_3=-\frac{1}{2}$; in this scheme only the two first electrons are to be considered as equivalent, and we can thus avoid the difficulties arising from the coupling of three equivalent electrons.

It follows from (51) that

$$(2\|C^{(2)}\|2)=-(10/7)^{\frac{1}{2}},\quad (2\|C^{(4)}\|2)=(10/7)^{\frac{1}{2}}, \tag{80}$$

[13] This holds only in (LS) coupling: it is, for instance, evident that in (jj) coupling of the three levels with $J=\frac{3}{2}$ in the p^3 configuration, only the level $p_{\frac{1}{2}}{}^2p_{\frac{3}{2}}$ is self-corresponding.

[14] O. Laporte, Phys. Rev. **61**, 302 (1942).

and hence and from (44) that

$$(22L\|C_1^{(2)}+C_2^{(2)}\|22L')=\begin{array}{c|cc} & P & F \\ P & (6/5)^{\frac{1}{2}} & -(48/35)^{\frac{1}{2}} \\ F & -(48/35)^{\frac{1}{2}} & -(12/35)^{\frac{1}{2}} \end{array}$$

$$(22L\|C_1^{(4)}+C_2^{(4)}\|22L')=\begin{array}{c|cc} & P & F \\ P & 0 & -(4/7)^{\frac{1}{2}} \\ F & -(4/7)^{\frac{1}{2}} & -(22/7)^{\frac{1}{2}} \end{array}. \tag{81}$$

From (38) we obtain now easily the interaction matrix between the d^2 group and the third d electron:

$$W(d^2,d)=2F_0+\begin{Vmatrix} (-1)^L\frac{7\Lambda}{30}\binom{7}{3-L} & \frac{2\Lambda}{15}\left[\binom{6+L}{2}\binom{5-L}{2}\right]^{\frac{1}{2}} \\ \frac{2\Lambda}{15}\left[\binom{6+L}{2}\binom{5-L}{2}\right]^{\frac{1}{2}} & \frac{\Lambda^2-35\Lambda+210}{30} \end{Vmatrix} F_2$$

$$+(-1)^L\begin{Vmatrix} 0 & \left[\binom{9}{5-L}\binom{9}{3-L}\right]^{\frac{1}{2}} \\ \left[\binom{9}{5-L}\binom{9}{3-L}\right]^{\frac{1}{2}} & \frac{\Lambda}{10}\binom{11}{5-L} \end{Vmatrix} F_4, \tag{82}$$

where

$$\Lambda=L(L+1). \tag{83}$$

It suffices now to add to (82) the diagonal matrix of the internal energy of d^2, and to diagonalize this sum for each possible value of L; with this method we cannot specify to which value of S each eigenvalue belongs, but the quartet terms may be recognized, according to (23) I, as those for which the coefficient of C vanishes. The results are

$$\begin{aligned} &{}^2P=3A-6B+3C, && {}^4F=3A-15B, \\ &{}^4P=3A, && {}^2G=3A-11B+3C, \\ &{}^2D=3A+5B+5C\pm(193B^2+8BC+4C^2)^{\frac{1}{2}}, && {}^2H=3A-6B+3C, \\ &{}^2F=3A+9B+3C, \end{aligned} \tag{84}$$

and agree with those of the above-mentioned authors (TAS pp. 206 and 233).

d^4

This configuration was calculated by Ostrofsky,[15] but Laporte and Platt[16] found some mistakes in his results.

If we assume $ms_1=ms_2=\frac{1}{2}$ and $ms_3=ms_4=-\frac{1}{2}$, the scheme will be an L_1L_2L one, where $\mathbf{L}_1=\mathbf{l}_1+\mathbf{l}_2$ and $\mathbf{L}_2=\mathbf{l}_3+\mathbf{l}_4$; the interaction matrix $W(d^2,d^2)$ between the two d^2 groups is of the fourth degree and was calculated in the same way as for d^3. Adding to it the diagonal matrix of the internal energies of the two d^2 groups, we obtained the complete energy matrix, the eigenvalues of which are the requested energies of the configuration d^4; the singlet and the triplet terms were distinguished by the

[15] M. Ostrofsky, Phys. Rev. **46**, 604 (1934).
[16] O. Laporte and J. R. Platt, Phys. Rev. **62**, 305 (1942).

irrationality of the results in the cases of two expected terms of the same kind. The results are

$$\begin{aligned}
&^1S=6A+10B+10C\pm 2(193B^2+8BC+4C^2)^{\frac{1}{2}},\\
&^3P=6A-5B+(11/2)C\pm\tfrac{1}{2}(912B^2-24BC+9C^2)^{\frac{1}{2}},\\
&^1D=6A+9B+(15/2)C\pm\tfrac{3}{2}(144B^2+8BC+C^2)^{\frac{1}{2}},\\
&^3D=6A-5B+4C,\\
&^5D=6A-21B,\\
&^1F=6A+6C,\\
&^3F=6A-5B+(11/2)C\pm\tfrac{3}{2}(68B^2+4BC+C^2)^{\frac{1}{2}},\\
&^1G=6A-5B+(15/2)C\pm\tfrac{1}{2}(708B^2-12BC+9C^2)^{\frac{1}{2}},\\
&^3G=6A-12B+4C,\\
&^3H=6A-17B+4C,\\
&^1I=6A-15B+6C,
\end{aligned}\tag{85}$$

and agree with those of Laporte and Platt, with the exception of a misprint for the term ^1F, which must be $6F_0-84F_4$.

d^5

Catalan and Antunes[17] and also Bowman[18] calculated the formulas for this configuration, but they could not separate the energies of the terms of the same kind.

Assuming $ms_1=ms_2=ms_3=\frac{1}{2}$ and $ms_4=ms_5=-\frac{1}{2}$, we need at first the elements of $(222L\|C_1^{(k)}+C_2^{(k)}+C_3^{(k)}\|222L')$ for the antisymmetrical states; but if we consider only electrons with $m_S=\frac{1}{2}$, d^3 is the almost closed shell corresponding to d^2, and according to (74) the needed matrix elements are the same as (81) with inverted signs; it follows that the interaction between the d^3 and the d^2 group is

$$W(d^3, d^2)=10F^0-W(d^2, d^2)\tag{86}$$

and we can proceed as for d^4. It must, however, be noted that the irrationality criterion is not sufficient in this case for the distinction between quartets and doublets, since almost all the eigenvalues are rational; this distinction may be based on the property that the relative positions of the quartets and of the sextet are exactly opposed to those of the terms of d^2 with the same L; this property follows immediately from the possibility of calculating these terms in a scheme in which $ms_1=ms_2=ms_3=ms_4=\frac{1}{2}$ and $ms_5=-\frac{1}{2}$. The results are

$$\begin{aligned}
&^2S=10A-3B+8C, && ^2F'=10A-25B+10C,\\
&^6S=10A-35B, && ^4F=10A-13B+7C,\\
&^2P=10A+20B+10C, && ^2G=10A-13B+8C,\\
&^4P=10A-28B+7C, && ^2G'=10A+3B+10C,\\
&^2D=10A-3B+11C\pm 3(57B^2+2BC+C^2)^{\frac{1}{2}}, && ^4G=10A-25B+5C,\\
&^2D'=10A-4B+10C, && ^2H=10A-22B+10C,\\
&^4D=10A-18B+5C, && ^2I=10A-24B+8C,\\
&^2F=10A-9B+8C,
\end{aligned}\tag{87}$$

and agree with the recent results of Laporte.[14]

[17] M. A. Catalan and M. T. Antunes, Zeits. f. Physik **102**, 432 (1936).
[18] D. S. Bowman, Phys. Rev. **59**, 386 (1941).

The Coefficients of C

It is pointed out by Laporte and Platt[16] that if B vanishes all the energies of the d^n terms are rational and show high degree degeneracies; this fact may be explained by general considerations similar to those of §3 of I.

It follows from (20)I and (77) that if B vanishes the interaction between two electrons is

$$W_{ij}=A+\frac{\lambda_{ij}^4+5\lambda_{ij}^3-15\lambda_{ij}^2-75\lambda_{ij}}{18}C; \tag{88}$$

owing to the relation

$$(\mathbf{s}_i\cdot\mathbf{s}_j)=-\frac{\lambda_{ij}^4+6\lambda_{ij}^3-13\lambda_{ij}^2-90\lambda_{ij}-18}{72}, \tag{89}$$

which corresponds for equivalent d electrons to Van Vleck's relation for p electrons,[19] we may also write

$$W_{ij}=A+[\tfrac{1}{2}-2(\mathbf{s}_i\cdot\mathbf{s}_j)+q_{ij}]C, \tag{88'}$$

where

$$q_{ij}=\frac{(\lambda_{ij}-4)\lambda_{ij}(\lambda_{ij}+3)(\lambda_{ij}+5)}{36} \tag{90}$$

is an operator which has the eigenvalue 0 in all cases, except if the resultant of the two electrons is a ^1S state. Owing to the relation

$$S(S+1)=\tfrac{3}{4}n+2\sum_{i<j}(\mathbf{s}_i\cdot\mathbf{s}_j), \tag{91}$$

we find that

$$W=\sum_{i<j}W_{ij}=\frac{n(n-1)}{2}A+\left[\frac{n(n+2)}{4}-S(S+1)+Q\right]C, \tag{92}$$

where

$$Q=\sum_{i<j}q_{ij}. \tag{93}$$

If in the configuration d^n a term occurs which does not occur in d^{n-2}, it is impossible that in this state two electrons are connected so as to have a ^1S resultant, and therefore Q vanishes in all such terms.

For the terms which occur also in d^{n-2} the calculation of Q may be made as follows. Each m_sm_l state of d^{n-2} gives rise in d^n to a "family" of states in which the first $n-2$ electrons have the quantum numbers of the "parent" state and the last two electrons have the quantum numbers m^+ and $-m^-$. The number of states of each family equals five minus the number of possibilities forbidden by the exclusion principle: if in the parent state there are no other couples of electrons of the type m'^+ and $-m'^-$ (and this is always the case when the values of M_S and M_L under consideration are not allowed for d^{n-4}), each electron of the parent state excludes a possibility, and the residual number is then $7-n$.

Since the matrix elements of q_{ij} are

$$(m_im_j|q_{ij}|m_i'm_j')=(-1)^{m_i-m_i'}\delta(m_i,-m_j)\delta(m_i',-m_j'), \tag{94}$$

and the exchange term compensates the direct term for electrons of like spins, the only non-vanishing q_{ij} is q_{n-1n} and the only non-vanishing elements of q_{n-1n} are those connecting states of the same family, the values of these elements being $(-1)^{m-m'}$. The eigenvalues of these submatrices, owing to this particular expression of their elements, are all 0 except one, which equals the trace of the submatrix, i.e., $7-n$. We can then say that each term of d^{n-2} gives rise in d^n to a term with $Q=7-n$, and that the other eigenvalues of Q vanish also in d^n.

[19] J. H. Van Vleck, Phys. Rev. **45**, 412 (1934), Eq. (33).

If more than a couple of the type m^+ and $-m^-$ may be simultaneously present in a $m_s m_l$ state, the calculation is more complex, but the result is almost the same: each term which occurs in d^{n-2} has in d^n its Q value increased by $7-n$; each further term has $Q=0$.

Since $F_2 \geqslant 9F_4$ (TAS p. 177) and it is therefore impossible that B could vanish, we omitted in §3 of I this application; but the recent paper of Laporte and Platt induced us to put here these considerations. The high degree degeneracies remarked by these authors for this hypothetical case and the relation between their Table II and an old table of Hund[20] are really based on the simple form of (92) and on the properties of the operator Q.

We take this opportunity for pointing out that Eq. (6) of Laporte and Platt is right only for certain m, since its exact form is

$$\sum_k \frac{2k+1}{2} \frac{c^k(lmlm')c^k(lm_1lm'_1)}{c^k(l0l0)} = \delta(mm_1)\delta(m'm'_1)+(-1)^{m-m_1}\delta(m,-m'_1)\delta(m_1,-m')\frac{2l+1}{4}; \quad (95)$$

its demonstration follows almost immediately from (52), (20b), and (19a).

The ratios between the distances of the ^1S terms in f^2 and g^2 from the other singlets and the distances between these singlets and the triplets are also incorrect by a factor 2.

§8. THE CONFIGURATION f^3

For the configurations f^n it is also convenient to introduce new parameters; if we put

$$A=F_0-21F_4-468F_6, \quad B=(5F_2+6F_4-91F_6)/5, \quad C=7(F_4-6F_6)/5, \quad D=462F_6, \quad (96)$$

the formulas for f^2 assume the simpler form

$$\begin{aligned} &^1S=A+60B+105C+9D, \quad &&^1G=A-30B+110C+2D,\\ &^3P=A+45B, &&^3H=A-25B,\\ &^1D=A+19B-72C+2D, &&^1I=A+25B+2D.\\ &^3F=A-10B, \end{aligned} \quad (97)$$

The calculation for f^3 was made exactly in the same way as for d^3, and gave the following results:

$$\begin{aligned} &^4S=3A-30B,\\ &^2P=3A-25B+35C+3D,\\ &^2D=3A-7B+(57/2)C+3D\pm\tfrac{1}{2}(2176B^2-18096BC+74529C^2)^{\frac{1}{2}},\\ &^4D=3A+25B,\\ &^2F=3A+55B+(75/2)C+6D\pm\tfrac{1}{2}[9700B^2-180B(45C+2D)+9(45C+2D)^2]^{\frac{1}{2}},\\ &^4F=3A-30B,\\ &^2G=3A+7B+(113/2)C+3D\pm\tfrac{1}{2}(12676B^2-31676BC+36169C^2)^{\frac{1}{2}},\\ &^4G=3A-10B,\\ &^2H=3A-23B+(63/2)C+3D\pm\tfrac{1}{2}(5056B^2-18816BC+29169C^2)^{\frac{1}{2}},\\ &^2I=3A-5B+45C+3D,\\ &^4I=3A-65B,\\ &^2K=3A-40B+80C+3D,\\ &^2L=3A+3D. \end{aligned} \quad (98)$$

[20] F. Hund, Zeits. f. Physik **33**, 345 (1925), Table IV.

§9. THE CONFIGURATIONS d^2p AND d^3p

The energy matrix of the configuration d^2p will be calculated in a scheme in which each term is characterized by a definite state of the core d^2. In this scheme the interaction between the two d electrons is diagonal and has the values given by (78); the interaction between each d electron and the p electron follows from (60) and is

$$W(d,p)=F_0+10(21)^{\frac{1}{2}}(\mathbf{u}_d^{(2)}\cdot\mathbf{u}_p^{(2)})F_2-[\tfrac{1}{2}+2(\mathbf{s}_d\cdot\mathbf{s}_p)]\{[2+9\sqrt{5}(\mathbf{u}_d^{(1)}\cdot\mathbf{u}_p^{(1)}) +5(21)^{\frac{1}{2}}(\mathbf{u}_d^{(2)}\cdot\mathbf{u}_p^{(2)})]G_1+[7-21\sqrt{5}(\mathbf{u}_d^{(1)}\cdot\mathbf{u}_p^{(1)})+5(21)^{\frac{1}{2}}(\mathbf{u}_d^{(2)}\cdot\mathbf{u}_p^{(2)})]G_3\}, \quad (99)$$

where[21]

$$F_0=F^0(nd,n'p),\quad F_2=F^2(nd,n'p)/35,\quad G_1=G^1(nd,n'p)/15,\quad G_3=3G^3(nd,n'p)/245. \quad (100)$$

In order to obtain the matrix of

$$W(d^2,p)=W(d_1,p)+W(d_2,p), \quad (101)$$

we calculate at first, by means of (44), the matrices of the tensors

$$\mathbf{U}^{(k)}=\mathbf{u}_1^{(k)}+\mathbf{u}_2^{(k)} \quad (102a)$$

and of the double tensors

$$\mathbf{V}^{(1k)}=\mathbf{s}_1\mathbf{u}_1^{(k)}+\mathbf{s}_2\mathbf{u}_2^{(k)} \quad (102b)$$

for two equivalent d electrons; the results are

$(SL\|U^{(1)}\|S'L')$

	^1S	^3P	^1D	^3F	^1G
^1S	0	0	0	0	0
^3P	0	$(1/5)^{\frac{1}{2}}$	0	0	0
^1D	0	0	1	0	0
^3F	0	0	0	$(14/5)^{\frac{1}{2}}$	0
^1G	0	0	0	0	$(6)^{\frac{1}{2}}$

(103a)

$(SL\|U^{(2)}\|S'L')$

	^1S	^3P	^1D	^3F	^1G
^1S	0	0	$(4/5)^{\frac{1}{2}}$	0	0
^3P	0	$-(21/25)^{\frac{1}{2}}$	0	$(24/25)^{\frac{1}{2}}$	0
^1D	$(4/5)^{\frac{1}{2}}$	0	$-3/7$	0	$(144/245)^{\frac{1}{2}}$
^3F	0	$(24/25)^{\frac{1}{2}}$	0	$(6/25)^{\frac{1}{2}}$	0
^1G	0	0	$(144/245)^{\frac{1}{2}}$	0	$(198/49)^{\frac{1}{2}}$

(103b)

$(SL\|V^{(11)}\|S'L')$

	^1S	^3P	^1D	^3F	^1G
^1S	0	$(2/5)^{\frac{1}{2}}$	0	0	0
^3P	$(2/5)^{\frac{1}{2}}$	$(1/5)^{\frac{1}{2}}$	$-(7/10)^{\frac{1}{2}}$	0	0
^1D	0	$-(7/10)^{\frac{1}{2}}$	0	$(4/5)^{\frac{1}{2}}$	0
F^3	0	0	$(4/5)^{\frac{1}{2}}$	$(14/5)^{\frac{1}{2}}$	$-(3/5)^{\frac{1}{2}}$
^1G	0	0	0	$-(3/5)^{\frac{1}{2}}$	0

(103c)

[21] This definition of G_3 differs by a factor 3 from that of TAS, but agrees with (50) I.

$$(SL\|V^{(12)}\|S'L')=\begin{array}{c|ccccc} & {}^1S & {}^3P & {}^1D & {}^3F & {}^1G \\ \hline {}^1S & 0 & 0 & 0 & 0 & 0 \\ {}^3P & 0 & -(21/25)^{\frac{1}{2}} & -(3/10)^{\frac{1}{2}} & (24/25)^{\frac{1}{2}} & 0 \\ {}^1D & 0 & -(3/10)^{\frac{1}{2}} & 0 & (32/35)^{\frac{1}{2}} & 0 \\ {}^3F & 0 & (24/25)^{\frac{1}{2}} & (32/35)^{\frac{1}{2}} & (6/25)^{\frac{1}{2}} & -(9/7)^{\frac{1}{2}} \\ {}^1G & 0 & 0 & 0 & -(9/7)^{\frac{1}{2}} & 0 \end{array} \tag{103d}$$

The matrix of (101) follows from (99), (103), and (38); adding to it the energy of the core we obtain the following results for the terms of d^2p [22]

$$\begin{aligned} {}^2S&=A+7B-14F_2-3G_1+7G_3 \\ {}^4S&=A+7B-14F_2+6G_1-14G_3 \\ {}^4P&=A+7B+7F_2-6G_1-21G_3 \\ {}^4F&=A-8B-3F_2-G_1-16G_3 \\ {}^4G&=A-8B+F_2-9G_1-4G_3 \\ {}^2H&=A+4B+2C+4F_2-6G_1-G_3 \end{aligned}$$

$${}^4D=\begin{Vmatrix} A+7B-(7F_2+24G_1+49G_3)/5 & (12F_2-6G_1-6G_3)(14/25)^{\frac{1}{2}} \\ (12F_2-6G_1-6G_3)(14/25)^{\frac{1}{2}} & A-8B+(12F_2+4G_1-146G_3)/5 \end{Vmatrix}$$

$${}^2G=\begin{Vmatrix} A-8B+F_2+(9/2)G_1+2G_3 & (-\tfrac{3}{2}G_1+G_3)(15)^{\frac{1}{2}} \\ (-\tfrac{3}{2}G_1+G_3)(15)^{\frac{1}{2}} & A+4B+2C-11F_2+\tfrac{3}{2}G_1-6G_3 \end{Vmatrix}$$

$${}^2P=\begin{Vmatrix} A+14B+7C-2G_1-7G_3 & (-3G_1+7G_3)(3)^{\frac{1}{2}} & (4F_2-G_1-G_3)(7)^{\frac{1}{2}} \\ (-3G_1+7G_3)(3)^{\frac{1}{2}} & A+7B+7F_2+3G_1+(21/2)G_3 & (5/2)G_3(21)^{\frac{1}{2}} \\ (4F_2-G_1-G_3)(7)^{\frac{1}{2}} & (5/2)G_3(21)^{\frac{1}{2}} & A-3B+2C-3F_2+G_1-(23/2)G_3 \end{Vmatrix}$$

$${}^2D=\begin{Vmatrix} A+7B+(-7F_2+12G_1+(49/2)G_3)/5 & (-6G_1+9G_3)(21/20)^{\frac{1}{2}} & (12F_2+3G_1+3G_3)(14/25)^{\frac{1}{2}} \\ (-6G_1+9G_3)(21/20)^{\frac{1}{2}} & A-3B+2C+3F_2-2G_1-(19/2)G_3 & (G_1+11G_3)(6/5)^{\frac{1}{2}} \\ (12F_2+3G_1+3G)(14/25)^{\frac{1}{2}} & (G_1+11G_3)(6/5)^{\frac{1}{2}} & A-8B+(12F_2-2G_1+73G_3)/5 \end{Vmatrix}$$

$${}^2F=\begin{Vmatrix} A-3B+2C-(6F_2+23G_1+23G_3)/7 & (-10G_1+10G_3)(3/7)^{\frac{1}{2}} & (24F_2-6G_1-6G_3)(3/49)^{\frac{1}{2}} \\ (-10G_1+10G_3)(3/7)^{\frac{1}{2}} & A-8B-3F_2+\tfrac{1}{2}G_1+8G_3 & (9G_1+54G_3)/(28)^{\frac{1}{2}} \\ (24F_2-6G_1-6G_3)(3/49)^{\frac{1}{2}} & (9G_1+54G_3)/(28)^{\frac{1}{2}} & A+4B+2C+(55F_2-\tfrac{3}{2}G_1-124G_3)/7 \end{Vmatrix}$$

For calculating the terms of d^8p it suffices to take into account the fact that the constant matrix and the matrices of $\mathbf{U}^{(2)}$ and $\mathbf{V}^{(11)}$ change their signs at passing from the core d^2 to d^8, according to (74). The results are:

$$\begin{aligned} {}^2S&={}^4S=A+7B+14F_2 \\ {}^4P&=A+7B-7F_2 \\ {}^4F&=A-8B+3F_2 \\ {}^4G&=A-8B-F_2 \\ {}^2H&=A+4B+2C-4F_2+15G_3 \end{aligned}$$

[22] The parameters have the meaning given in (77) and (100), with the exception of A which contains also $2F^0(nd, n'p)$.

TABLE I. The configuration $3d^24p$ of Ti II.

Term	Obs.	Calc. A	Calc. B
$(^3F)\ ^4G$	29936	29748	29823
$(^3F)\ ^4F$	31108	31028	31125
$(^3F)\ ^2F$	31369	31375	31471
$(^3F)\ ^2D$	31918	32132	32251
$(^3F)\ ^4D$	32690	32813	32890
$(^3F)\ ^2G$	34657	33951	34109
$(^3P)\ ^2S$	37431	37623	37628
$(^1D)\ ^2D$	39380	40461	40000
$(^1D)\ ^2P$	39627	40035	39496
$(^1D)\ ^2F$	40011	39983	39507
$(^3P)\ ^4S$	40027	40233	40237
$(^3P)\ ^4D$	40612	40518	40441
$(^3P)\ ^4P$	42127	42213	42100
$(^1G)\ ^2G$	43763	43259	43675
$(^3P)\ ^2D$	44907	44807	44737
$(^3P)\ ^2P$	45524	45672	45673
$(^1G)\ ^2H$	45802	44822	45184
$(^1G)\ ^2F$	47535	47751	48078
$(^1S)\ ^2P$	=	64692	(64465)
Parameters:			
B		669	=
C		2563	=
ϵ		=	0.9484
F_2		290	288
G_1		332	337
G_3		18	20.2

TABLE II. The configuration $3d^84p$ of Ni II.

Term	Obs.	Calc.
$(^3F)\ ^4D$	52588	52581
$(^3F)\ ^4G$	53883	53707
$(^3F)\ ^4F$	55394	55163
$(^3F)\ ^2G$	55775	55735
$(^3F)\ ^2F$	57685	57492
$(^3F)\ ^2D$	57933	57892
$(^3P)\ ^4P$	66649	66853
$(^1D)\ ^2F$	67943	68729
$(^1D)\ ^2D$	68442	68929
$(^1D)\ ^2P$	68636	69013
$(^3P)\ ^4D$	70716	70527
$(^3P)\ ^2D$	72011	72159
$(^3P)\ ^2P$	73256	73245
$(^3P)\ ^2S$	74282	74497
$(^3P)\ ^4S$	74299	74497
$(^1G)\ ^2H$	75460.	74713
$(^1G)\ ^2F$	75904	75494
$(^1G)\ ^2G$	79878	79505
$(^1S)\ ^2P$	=	109339
Parameters:		
B		1022
C		4509
F_2		364
G_1		303
G_3		54.4

$$^4D=\begin{Vmatrix} A+7B+7F_2/5 & -12F_2(14/25)^{\frac{1}{2}} \\ -12F_2(14/25)^{\frac{1}{2}} & A-8B-12F_2/5 \end{Vmatrix}$$

$$^2G=\begin{Vmatrix} A-8B-F_2+75G_3/2 & -5G_3(15/4)^{\frac{1}{2}} \\ -5G_3(15/4)^{\frac{1}{2}} & A+4B+2C+11F_2+5G_3/2 \end{Vmatrix}$$

$$^2P=\begin{Vmatrix} A+14B+7C+2G_1+7G_3 & (3G_1-7G_3)(3)^{\frac{1}{2}} & (-4F_2+G_1+G_3)(7)^{\frac{1}{2}} \\ (3G_1-7G_3)(3)^{\frac{1}{2}} & A+7B-7F_2+(27/2)G_1+21G_3 & (3G_1-2G_3)(21/4)^{\frac{1}{2}} \\ (-4F_2+G_1+G_3)(7)^{\frac{1}{2}} & (3G_1-2G_3)(21/4)^{\frac{1}{2}} & A-3B+2C+3F_2+(7/2)G_1+G_3 \end{Vmatrix}$$

$$^2D=\begin{Vmatrix} A+7B+(7F_2+(27/2)G_1+126G_3)/5 & (3G_1-12G_3)(21/20)^{\frac{1}{2}} & (-12F_2+9G_1+9G_3)(14/25)^{\frac{1}{2}} \\ (3G_1-12G_3)(21/20)^{\frac{1}{2}} & A-3B+2C-3F_2+(7/2)G_1+6G_3 & (7G_1-3G_3)(6/5)^{\frac{1}{2}} \\ (-12F_2+9G_1+9G_3)(14/25)^{\frac{1}{2}} & (7G_1-3G_3)(6/5)^{\frac{1}{2}} & A-8B+(-12F_2+84G_1+9G_3)/5 \end{Vmatrix}$$

$$^2F=\begin{Vmatrix} A-3B+2C+(6F_2+2G_1+72G_3)/7 & (2G_1-18G_3)(3/7)^{\frac{1}{2}} & (-24F_2+6G_1+6G_3)(3/49)^{\frac{1}{2}} \\ (2G_1-18G_3)(3/7)^{\frac{1}{2}} & A-8B+3F_2+6G_1+(27/2)G_3 & (18G_1-(9/2)G_3)/(7)^{\frac{1}{2}} \\ (-24F_2+6G_1+6G_3)(3/49)^{\frac{1}{2}} & (18G_1-(9/2)G_3)/(7)^{\frac{1}{2}} & A+4B+2C+(-55F_2+54G_1+\tfrac{3}{2}G_3)/7 \end{Vmatrix}$$

We fitted the experimental values[23] of Ti II and Ni II to the theoretical formulas by least squares, and obtained the results given in Table I (column A) and Table II. The mean deviations are ± 430 for Ti II and ± 347 for Ni II, and confirm the known fact that the agreement is better for the elements on the right side of the periodic table.

It must also be observed that these deviations show a certain regularity: in almost all the cases the differences between observed and calculated values are positive for the terms grounded on the

[23] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932).

^3F and ^1G terms of the core, and negative for those grounded on ^3P and ^1D. Since the configurations d^2, d^2s, d^8, d^8s of the whole iron group show the same regularities in the deviations,[24] the main part of these deviations may be attributed to second-order effects in the coupling of the core electrons.

It seems therefore reasonable to substitute in the formulas of d^2p and d^8p for the part depending on the energy of the core (terms with B and C) the experimental values of the corresponding ions d^2 and d^8; these values must, however, be multiplied with a convenient reduction factor ϵ, since with increasing ionization all coupling parameters increase slightly.

The result of fitting the terms of Ti II to such semi-theoretical formulas by least squares is shown in Table I, column B; the mean deviation reduces to ± 332, although the number of free parameters is also reduced (ϵ instead of B and C).

For writing down the matrix of the ^2P terms we needed also the value of the term $3d^2\ ^1S$ of Ti III: since this is still unknown, we calculated it from the other $3d^2$ terms by least squares; this approximated value suffices for calculating the perturbation of $(^1S)\ ^2P$ of Ti II on the other ^2P terms, but cannot be of use for predicting with the same approximation the position of $(^1S)\ ^2P$ himself.

We could not apply this method of calculation to Ni II, since the terms of Ni III are still unknown, as far as known to us.

§10. THE INTEGRALS G^k

It is noted in TAS (p. 177) that F^k is essentially positive and a decreasing function of k, and it is stated as an empirical fact that also G^k shares the same properties, although they do not follow from its definition. Since this fact was sometimes questioned,[25] it seemed worth while to us to seek for a mathematical demonstration: we found that the first property may be proved, but only $G^k/(2k+1)$ is necessarily a decreasing function of k.

According to its definition, G^k has the form

$$G^k = \int_0^\infty \int_0^\infty (r_<^k / r_>^{k+1}) f(r_1) f(r_2) dr_1 dr_2, \tag{104}$$

where $r_<$ is the lesser and $r_>$ the greater of r_1 and r_2; we may also write

$$G^k = \int_0^\infty f(x)\, \varphi(x) dx \tag{105}$$

with

$$\varphi(x) = x^{-k-1} \int_0^x y^k f(y) dy + x^k \int_x^\infty y^{-k-1} f(y) dy. \tag{106}$$

It follows from (106) that

$$f(x) = -x^{k+1}[x^{-2k}(x^{k+1}\varphi)']'/(2k+1)\,; \tag{106'}$$

introducing this expression in (105) and integrating by parts we get

$$G^k = \int_0^\infty x^{-2k}[(x^{k+1}\varphi)']^2 dx/(2k+1) \geqslant 0. \tag{107}$$

In the same way, putting

$$G^k/(2k+1) - G^{k+1}/(2k+3) = \int_0^\infty f(x)\psi(x) dx \tag{108}$$

[24] TAS, Figs. 3[7] and 4[7]; G. Racah, Phys. Rev. **61**, 538 (1942), Table I.
[25] TAS, p. 366.

with

$$\psi(x)=\left[x^{-k-1}\int_0^x y^k f(y)dy+x^k\int_x^\infty y^{-k-1}f(y)dy\right]/(2k+1)$$
$$+\left[x^{-k-2}\int_0^x y^{k+1}f(y)dy+x^{k+1}\int_x^\infty y^{-k-2}f(y)dy\right]/(2k+3), \quad (109)$$

we have

$$f(x)=x^{k+2}[x^{-2k}(x^{k+2}\psi)'']''/(2k+2), \quad (109')$$

and from (108) we get with a double integration by parts

$$G^k/(2k+1)-G^{k+1}/(2k+3)=\int_0^\infty x^{-2k}[(x^{k+2}\psi)'']^2dx/(2k+2)\geqslant 0. \quad (110)$$

It is also possible to find particular functions $f(x)$ for which the ratio G^{k+1}/G^k tends to the theoretical limit $(2k+3)/(2k+1)$; an example is given by

$$f(x)=\delta(x-a)-\delta(x-a-b) \quad (111)$$

with $b\ll a$.

APPENDIX A

From the definition (17) we have

$$v(abc\,;000)=\frac{a!b!c!}{a+b-c}\Sigma_z(-1)^{c+z}\frac{(a+b-c-z)+z}{z!(a+b-c-z)!(a-z)!(b-z)!(c-a+z)!(c-b+z)!}$$
$$=\frac{a!b!c!}{a+b-c}\Sigma_z(-1)^{c+z}\{[z!(a+b-c-z-1)!(a-z)!(b-z)!(c-a+z)!(c-b+z)!]^{-1}$$
$$+[(z-1)!(a+b-c-z)!(a-z)!(b-z)!(c-a+z)!(c-b+z)!]^{-1}\},$$

and changing the summation parameter in the second term of the brackets,

$$v(abc\,;000)=\frac{a!b!c!}{a+b-c}\Sigma_z(-1)^{c+z}\{[z!(a+b-c-z-1)!(a-z)!(b-z)!(c-a+z)!(c-b+z)!]^{-1}$$
$$-[z!(a+b-c-z-1)!(a-z-1)!(b-z-1)!(c-a+z+1)!(c-b+z+1)!]^{-1}\}$$
$$=\frac{a!b!(c+1)!}{a+b-c}\Sigma_z(-1)^{c+z+1}\frac{a+b-c-2z-1}{z!(a+b-c-z-1)!(a-z)!(b-z)!(c-a+z+1)!(c-b+z+1)!};$$

owing to the identity

$$a(a+b-c-2z-1)=(a-z)(a+b-c-z-1)-z(c-b+z+1),$$

we have also

$$v(abc\,;000)=\frac{(a-1)!b!(c+1)!}{a+b-c}\Sigma_z(-1)^{c+z+1}\{[z!(a+b-c-z-2)!(a-z-1)!(b-z)!(c-a+z+1)!(c-b+z+1)!]^{-1}$$
$$-[(z-1)!(a+b-c-z-1)!(a-z)!(b-z)!(c-a+z+1)!(c-b+z)!]^{-1}\},$$

and changing again the summation parameter in the second term of the brackets,

$$v(abc\,;000)=\frac{(a-1)!b!(c+1)!}{a+b-c}\Sigma_z(-1)^{c+z+1}\{[z!(a+b-c-z-2)!(a-z-1)!(b-z)!(c-a+z+1)!(c-b+z+1)!]^{-1}$$
$$+[z!(a+b-c-z-2)!(a-z-1)!(b-z-1)!(c-a+z+2)!(c-b+z+1)!]^{-1}\}$$
$$=\frac{b+c-a+2}{a+b-c}\Sigma_z(-1)^{c+z+1}\frac{(a-1)!b!(c+1)!}{z!(a+b-c-z-2)!(a-z-1)!(b-z)!(c-a+z+2)!(c-b+z+1)!}$$
$$=[(g-a+1)/(g-c)]v(a-1bc+1\,;000).$$

From this recursion formula we have

$$v(abc\,;000)=(g-a+x)!(g-c-x)!v(a-xbc+x\,;000)/[(g-a)!(g-c)!],$$

and for $x=g-c$,

$$v(abc\,;000)=b!v(g-bbg\,;000)/[(g-a)!(g-c)!];$$

since

$$v(g-bbg\,;000)=(-1)^g g!/[b!(g-b)!],$$

we obtain at last (22).

APPENDIX B

Using repeatedly Eqs. (52), and (55′) of I, and also the relation

$$\Sigma_s \frac{(a+s)!(b-s)!}{(c+s)!(d-s)!}=\frac{(a+b+1)!(a-c)!(b-d)!}{(c+d)!(a+b-c-d+1)!}, \tag{112}$$

which follows from (51) I for x and y negative, we obtain from the definition (17):

$$\sum_{\alpha\beta\gamma\delta\varphi}(-1)^{f+\varphi}v(abe;\alpha\beta-e)v(acf;-\alpha\gamma\varphi)v(bdf;-\beta\delta-\varphi)v(cde;\gamma\delta-e)$$

$$=\sum_{\alpha\gamma}(-1)^{f+\alpha-\gamma}v(abe;\alpha e-\alpha-e)v(acf;-\alpha\gamma\ \alpha-\gamma)v(bdf;\alpha-e\ e-\gamma\ \gamma-\alpha)v(cde;\gamma e-\gamma-e)$$

$$=\sum_{\alpha\gamma tu}\frac{(-1)^{a-c-f+t+u}2e!(a+\alpha)!(b+e-\alpha)!(c+\gamma)!(d+e-\gamma)!(f+\alpha-\gamma)!(f-\alpha+\gamma)!}{(e+a-b)!(e+b-a)!(e+c-d)!(e+d-c)!t!(a+c-f-t)!u!(b+d-f-u)!(a+\alpha-t)!(f-a-\gamma+t)!}$$
$$\cdot(d+e-\gamma-u)!(f-d+\alpha-e+u)!(c+\gamma-t)!(f-c-\alpha+t)!(b+e-\alpha-u)!(f-b+\gamma-e+u)!$$

$$=\sum_{\alpha\gamma tuvw}\frac{(-1)^{a-c-f+t+u}2e!(a+\alpha)!(b+e-\alpha)!(c+\gamma)!(d+e-y)!}{(e+a-b)!(e+b-a)!(e+c-d)!(e+d-c)!t!(a+c-f-t)!u!(b+d-f-u)!}$$
$$\cdot(f-a+c+t-v)!(c+d+e-u-v)!(a-c-d-e+\alpha-t+u+v)!(v-c-\gamma)!$$
$$\cdot(v-t-w)!(f-b-c-e+u+v-w)!(b+e-\alpha+t-u-v+w)!(c+\gamma-v+w)!$$

$$=\sum_{tuvw}\frac{(-1)^{a-c-f+t+u}2e!(a+b+e+1)!(c+d+e+1)!(c+d+e-v)!(v-w)!(u+v-t-w)!(c+d+e+t-u-v)!}{(e+a-b)!(e+b-a)!(e+c-d)!(e+d-c)!w!(a+b-c-d+w)!(c+d+e+1-w)!^2(f-b-c-e+u+v-w)!}$$
$$\cdot u!(v-t-w)!(a+c-f-t)!(f-a+c+t-v)!t!(c+d+e-u-v)!(b+d-f-u)!$$

$$=\sum_{tuvwxz}\frac{(-1)^{a-c-f+t+u}2e!(a+b+e+1)!(c+d+e+1)!(c+d+e-v)!(v-w)!(f-a-c+u+v-w)!(c+e+f-b+t-v)!}{(e+a-b)!(e+b-a)!(e+c-d)!(e+d-c)!w!(a+b-c-d+w)!(c+d+e+1-w)!^2}$$
$$\cdot(f-b-c-e+u+v-w)!(u-x)!(a+c-f-t-x)!(f-a-c+v-w+x)!x!$$
$$\cdot(f-a+c+t-v)!(t-z+x)!(b+d-f-u-z+x)!(c+e+f-b-v+z-x)!(z-x)!$$

$$=\sum_{vwxz}\frac{(-1)^{2e+f+d-b+z}2e!(a+b+e+1)!(c+d+e+1)!(c+d+e-v)!(v-w)!}{(e+c-d)!(e+d-c)!w!(a+b-c-d+w)!(c+d+e+1-w)!^2(2c-v-x)!(d-c-e+v-w+x-z)!}$$
$$\cdot x!(z-x)!(a+c-f-z)!(b+d-f-z)!(e+f-a-d+z)!(e+f-b-c+z)!$$

$$=\sum_{wx}\frac{(-1)^{2e+f+d-b+z}2e!(a+b+e+1)!(c+d+e+1)!(d+e-c+x)!(c+e-d+z-x)!}{(e+c-d)!(e+d-c)!w!(a+b-c-d+w)!(c+d+e+1-w)!(c+d-e-w-z)!(2e+z+1)!}$$
$$\cdot x!(z-x)!(a+c-f-z)!(b+d-f-z)!(e+f-a-d+z)!(e+f-b-c+z)!$$

$$=\frac{(-1)^{2e+f+d-b}}{2e+1}\Sigma_z\frac{(-1)^z(a+b+c+d+1-z)!}{(a+b-e-z)!(c+d-e-z)!z!(a+c-f-z)!(b+d-f-z)!(e+f-a-d+z)!(e+f-b-c+z)!}.$$

ERRATA OF PART I

Last line of the summary: read p^n for p''; element $(^1D|E|^3P)$ of the ^2P matrix on p. 195: read $(\frac{1}{2}G_0+2G_2)\sqrt{5}$ for $(-G_0+2G_2)\sqrt{5}$; second line of §6: read G^{l+1} for G^{l+2}.