

Multiplet Splitting and Intensities of Intercombination Lines Part I

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Kramers' symbolic representation method for the treatment of those properties of free atoms which can be derived on the basis of irreducible representations of rotations in R_3 is outlined. Wave functions and operators are represented by functions of spinor quantities (ξ, η) whose properties are known from the theory of invariants. Integrations yielding matrix elements are only symbolic and the results, being determined by the rotation invariance properties, contain therefore undetermined constant factors of the nature of radial integrals. The method is particularly adapted to the problem of multiplets (interaction between two or more "vectors"—e.g., orbital angular momenta, spins—treated as a perturbation). The method is applied to configurations involving two valence electrons of which one is in an s state. Such a configuration gives rise to a singlet and a triplet with the l value of the second electron. The deviations from the normal l to $l+1$ interval ratio in the triplet are due to a repulsion between the singlet level and the center triplet level, their j values being the same. The mixing up of the wave functions of these two levels gives rise to singlet-triplet intercombinations. The constants which represent the interaction energies (1) interchange, (2) spin-orbit, (3) spin of one electron—orbit of the other (assuming that other types of interaction may be neglected) are found in terms of the three intervals of the multiplet. Corrections to the Kronig-Hönl intensity formulas are found in terms of the intervals of the two multiplets between which the transitions occur. These formulas then give the relative intensities of combination and intercombination lines. The sum rules for intensity hold for the complete multiplet and not for the singlet and triplet separately. Part II will contain application of the theory to observed spectra.

IN HIS book, *Quantenmechanik und Gruppentheorie*, Weyl has shown that many of the properties of free atoms can be derived on the basis of irreducible representations of the rotations in three dimensional space. Kramers¹ has obtained a very elegant formulation of Weyl's methods through the use of symbolic representations of wave functions and operators with properties well known from the theory of invariants. We propose here to outline this method and to show its application to a problem in complex spectra.

THE SYMBOLIC METHOD

1.

Let ξ and η be the components of a *spinor* or *half-vector*, i.e., a two-dimensional complex vector. The transformations of the monomials $\xi^{l+m}\eta^{l-m}$ ($m = -l, -l+1, \dots, l$), when ξ and η suffer a unitary transformation, constitute an irreducible representation of degree $2l+1$ ($l = 1/2, 1, 3/2, \dots$) of the space rotation group. Except the identity, there are no other irreducible

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¹ H. A. Kramers, Proc. Amst. Acad. **33**, 953 (1930) and **34**, 965 (1931).

representations. Then a series of $2\tau+1$ quantities G_f , which transform into each other in an irreducible way under space-rotation, may be gathered up in the one formula

$$\sum_f \binom{2\tau}{\tau-f} a^{\tau-f} (-b)^{f} G^f = (a\eta - b\xi)^{2\tau}, \quad (1)$$

where a and b are the components of an arbitrary constant spinor. The G_f can always be so chosen that they transform like $\xi^{\tau+f}\eta^{\tau-f}$. $(a\eta - b\xi)$ is invariant.

2.

In the study of multiplets, a free atom may be treated as if it consisted of two or more *vector-frames* (Vektorgerüste), to each of which belongs a quantum number of the total angular momentum and whose mutual orientation has, in first approximation, no influence on the energy of the stationary states. In the complete energy expression there appear small interaction terms which depend, in a not purely additive fashion, on the elements (Bestimmungsstücke) of a pair of vectors and which denote an energetic coupling of these vectors.² As a consequence of this coupling every *state*, defined by the quantum numbers of the vectors, splits up into a multiplet.

Consider the coupling of just two vectors. In analogy with the notation for Russell-Saunders coupling but without assuming anything about the physical nature of the vectors, we may designate their quantum numbers of angular momentum by l and s .

The interaction terms in the complete energy expression may be written down in the form

$$\Omega = \sum_n a_n \lambda_n \sigma_n. \quad (2)$$

Here λ_n and σ_n are functions, respectively, only of the elements of the l -frame and only of the elements of the s -frame in such fashion that λ_n and σ_n are not invariant under an arbitrary space-rotation but transform according to some linear law. The coefficients a_n may contain any combination of rotation-invariant functions of the elements of either frame. In practice, Ω is usually given immediately in this form or else, when the l -frame and the s -frame are associated with different particles, Ω contains terms involving $1/r_{12}$. The expansion

$$\frac{1}{r_{12}} = \frac{1}{r_b} \sum_m \left(\frac{r_a}{r_b}\right)^m P_m\left(\frac{(\mathbf{r}_1 \cdot \mathbf{r}_2)}{r_1 r_2}\right), \quad (3)$$

where r_a and r_b are, respectively, the smaller and the larger of the distances r_1 and r_2 (the distances of the two particles from the center of gravity), brings these terms into the required form.

In an arbitrarily rotated coordinate system K' a selected λ_n , call it $\lambda^{(1)}$, assumes the form

$$\lambda^{(1)} = \sum_{p=1}^q \gamma_p^{(1)} \lambda'^{(p)},$$

² There may also be energy terms involving more than two vectors. To avoid complication, we shall not discuss these for the present. They are treated by an extension of the method.

where $\lambda^{(1)}$ is the same quantity with respect to K' as $\lambda^{(1)}$ with respect to the original coordinate system K . Thus there are $g-1$ other l -frame functions $\lambda^{(p)}$ ($p=2, \dots, g$) associated with $\lambda^{(1)}$ and these quantities transform in a way which gives a representation of the space-rotation group of degree g . If this representation is irreducible we shall say, for brevity: $\lambda^{(1)}$ transforms irreducibly. If it is not, one can always reduce the transformation with the result that each $\lambda^{(p)}$ is expressed by the finite sum $\sum_f \lambda_f^{(p)}$ where the $\lambda_f^{(p)}$ transform irreducibly. Thus it is always possible to express Ω in the form (2) in such a way that every λ_n and also every σ_n transforms irreducibly.

Since we are dealing with a free atomic system, the series (2) is rotation-invariant and therefore can be divided up into parts such that the λ and σ in each part transform irreducibly with the same degree g .³ Thus we may write

$$\Omega = \sum_{g=1}^{\infty} T_g, \tag{4}$$

$$T_g = \sum a \lambda_{(g)} \sigma_{(g)}, \tag{5}$$

where the summation indices have been omitted in the last sum.

In the quantum theory, the elements which determine an atomic system are uniquely defined according to their significance; the elements of the electron spin (its angular momentum components) as well as the ordinary coordinates and momenta have this property. That we consider them as operators makes no difference. But, for even values of g , the transforming quantities are only defined up to a factor ± 1 . Actually, in the series (4), only odd values of g occur and, if we set $g = 2\tau + 1$ and $T_g = \Omega_\tau$, (4) assumes the form

$$\Omega = \sum_{\tau=0}^{\infty} \Omega_\tau. \tag{6}$$

We are now ready to consider the symbolic representation of the energy operators. We have already remarked that $2\tau + 1$ quantities which transform irreducibly under space-rotation may be represented by $\xi^{\tau+f} \eta^{\tau-f}$. If we represent the $\lambda_{(g)}$ by $x_1^{\tau+f_1} y_1^{\tau-f_1}$ and the $\sigma_{(g)}$ by $x_2^{\tau+f_2} y_2^{\tau-f_2}$, then Ω_τ must contain these quantities in the form

$$\omega_\tau = (x_2 y_1 - y_2 x_1)^{2\tau}. \tag{7}$$

For Ω_τ is invariant under rotation and the only simultaneous invariant that can be formed of two spinors is $(x_2 y_1 - y_2 x_1)^n$, where n is a positive integer. In general, Ω_τ may be a sum of expressions like (7).⁴

3.

Let us now consider the symbolic representation of the wave functions. Each state of a multiplet is uniquely defined by the quantum number j of the

³ It is well known that $\sum a \lambda_{(g)} \lambda_{(g')}$ is never invariant for $g \neq g'$.

⁴ In case of an energy term involving three vector-frames, we shall have symbolic terms of the type

$$(x_2 y_1 - y_2 x_1)^\alpha (x_3 y_1 - y_3 x_1)^\beta (x_3 y_2 - y_3 x_2)^\gamma,$$

where α , β , and γ must be all even or all odd integers.

resultant angular momentum, where

$$|l - s| \leq j \leq l + s.$$

Wave functions satisfying the unperturbed (i.e., interaction terms neglected) wave equation may be composed of products of two functions, one of coordinates associated only with the l -frame and one of coordinates associated only with the s -frame. There are $2l+1$ functions of the first type which transform irreducibly under space-rotation and may be represented symbolically by $\xi_1^{l+m_1} \eta_1^{l-m_1}$ and $2s+1$ functions of the second type, which may be represented by $\xi_2^{s+m_2} \eta_2^{s-m_2}$. For the state with quantum number j of the multiplet there must be $2j+1$ functions which transform irreducibly under rotation and are composed linearly of terms $\xi_1^{l+m_1} \eta_1^{l-m_1} \xi_2^{s+m_2} \eta_2^{s-m_2}$. We introduce a constant spinor (a, b) and form the invariants

$$P = (\xi_2 \eta_1 - \eta_2 \xi_1); Q = (a \eta_1 - b \xi_1); R = (a \eta_2 - b \xi_2). \quad (8)$$

Then the state with quantum number j is represented by the invariant

$$\psi_{lsj} = P^\alpha Q^\beta R^\gamma, \quad (9)$$

where

$$\alpha + \beta = 2l; \alpha + \gamma = 2s; \beta + \gamma = 2j. \quad (10)$$

The $2j+1$ functions, which would be required for the study of the Zeeman effect, are the coefficients in ψ_{lsj} of $a^{j-m'} b^{j+m'}$ ($m' = -j, -j+1, \dots, j$).⁵

4.

We now proceed to show that every term of (6) makes a contribution to the energetic splitting of the multiplet which is, up to a numerical constant C_τ which does not depend on j , a completely determined function of l, s, j , and τ .

According to the principles of the quantum mechanics, the energy splitting E_τ , due to the interaction term (7), is given by

$$E_\tau \int \psi_{lsj}^* \psi_{lsj} = \int \psi_{lsj}^* \omega_\tau \psi_{lsj}, \quad (11)$$

where \int means integration and summation over all space and spin coordinates. Both integrals are invariant under rotation and every term must contain (a, b) and (a^*, b^*) each to the power $2j$. The only invariant of (a, b) and (a^*, b^*) is $(a^*a + b^*b)$ to some integral power. Therefore, these quantities appear in both integrals only in the form of a factor $(a^*a + b^*b)^{2j}$ and E_τ does not depend on (a, b) .

⁵ In case there were more than two vector frames composing our atomic system, we should form our wave functions of products of all the invariants $(\xi_i \eta_k - \eta_i \xi_k)$ and $(a \eta_k - b \xi_k)$ in such a way that in every term the sum of the powers of ξ_i and η_i is $2l_i$ and the sum of the powers of a and b is $2j$. In general, it will be possible to do this in a number of linearly independent ways, say f , which means that there will be f states of the multiplet with the same j value. To find the *stabilized* linear combinations of these f functions is a perturbation problem involving the solution of an f order secular determinant.

In (11), ω_τ is an operator which works on ψ_{lsj} . ω_τ is built up by multiplication and addition of operators which involve only the coordinates of the l -frame or only those of the s -frame. Accordingly, when we have written out all the terms in (11), every term may be put in the form

$$CI_1I_2$$

where I_1 and I_2 involve, respectively, the coordinates of the l -frame and of the s -frame and are integrals of the type:

$$I_1 = \int \xi_1^{*l+m_1'} \eta_1^{*l-m_1'} x_1^{\tau+\mu_1} y_1^{\tau-\mu_1} \xi_1^{l+m_1} \eta_1^{l-m_1}, \quad (12a)$$

$$I_2 = \int \xi_2^{*s+m_2'} \eta_2^{*s-m_2'} x_2^{\tau+\mu_2} y_2^{\tau-\mu_2} \xi_2^{s+m_2} \eta_2^{s-m_2}. \quad (12b)$$

The j value appears only in the factor C which contains, in a known manner, the expansion coefficients of the various factors in (11). We will show that, on account of the irreducibility of the transformations which the factors in I_1 and in I_2 suffer under space-rotation, both integrals are completely determined in their dependence on the various m 's. There remains over only a common constant C_τ , in principle undeterminable by the symbolic method, which depends in general on l, s, τ , and the particular atomic system with which we have to do and which is of the nature of a radial integral.

All integrals of the type (12a) are obtained by comparing coefficients of like powers of the components of the constant spinors on the two sides of

$$\begin{aligned} & \int (a^* \eta_1^* - b^* \xi_1^*)^{2l} (A y_1 - B x_1)^{2\tau} (a \eta_1 - b \xi_1)^{2l} \\ & = \text{const} (a^* a + b^* b)^{2l-\tau} (a^* A + b^* B)^\tau (a B - b A)^\tau. \end{aligned} \quad (13)$$

The evaluation of this integral follows directly from the invariance under rotation of all the factors in the integrand and of the domain of integration. The result must be built up of the three invariants of (a^*, b^*) , (a, b) and (A, B) and these quantities appear to the proper powers only in the form given in (13).

5.

Having seen that the results of the integrations in (11) are determined by the transformation properties of the factors and therefore do not depend on the special form of the operators which occur in ω_τ , we may simplify the integration in (11) by choosing special expressions for the operators $x_k^{\tau+\mu} y_k^{\tau-\mu}$ which transform in the same way. We have only to take care that in so doing we do not make the integral vanish identically.

Replacing $x_k^{\tau+\mu} y_k^{\tau-\mu}$ by operators acting on functions of the symbols ξ_k and η_k , we shall obtain, in place of (12a) and (12b), integrals of the type

$$\int \xi_k^{*\rho'+\nu'} \eta_k^{*\rho'-\nu'} \xi_k^{\rho+\nu} \eta_k^{\rho-\nu}. \quad (14)$$

All integrals of this type are found by comparing coefficients on the two sides of

$$\int (a^*\eta^* - b^*\xi^*)^{2\rho'} (a\eta - b\xi)^{2\rho} = \text{const.} (a^*a + b^*b)^{2\rho} \delta_{\rho'\rho}, \quad (15)$$

where the results of integration are again determined immediately by the invariance. We find for (14) the result

$$\text{const.} \left(\frac{2\rho}{\rho + \nu} \right)^{-1} \delta_{\rho'\rho\nu}. \quad (16)$$

Thus we find that our choice of operators to replace $x_k^{\tau+\mu}$, $y_k^{\tau-\mu}$ is limited to such as make $\psi_{l s_j}^* \omega_\tau \psi_{l s_j}$ homogeneous in (ξ_k^*, η_k^*) to the same degree as in (ξ_k, η_k) . The most satisfactory operators fulfilling this requirement are obtained from the formula

$$(A y_k - B x_k)^{2\tau} = (A \eta_k - B \xi_k)^\tau \left(A \frac{\partial}{\partial \xi_k} + B \frac{\partial}{\partial \eta_k} \right)^\tau. \quad (17)$$

Both sides are rotation-invariant and the $x_k^{\tau+\mu}$, $y_k^{\tau-\mu}$ are uniquely defined by comparison of terms with the same powers of A and B . We may remark that the order of the factors on the right hand side of (17) is arbitrary since we have the same thing still after exchanging them. (17) is the special case $\rho=0$ of the more general formula

$$(A y_k - B x_k)^{2\tau} = (A \eta_k - B \xi_k)^{\tau+\rho} \left(A \frac{\partial}{\partial \xi_k} + B \frac{\partial}{\partial \eta_k} \right)^{\tau-\rho}. \quad (18)$$

THE CONFIGURATION: TWO ELECTRONS, ONE IN AN s -STATE

6.

We shall now see how this symbolic method works as applied to spectra involving two valence electrons, of which one is in an s -state.⁶

The two electrons have angular momentum quantum numbers respectively l for the orbit, $1/2$ for the spin and 0 for the orbit, $1/2$ for the spin. The $2l+1$ wave functions of the orbital coordinates of the first particle, which transform irreducibly under rotation, may be represented symbolically by the $2l+1$ monomials $\xi^{l+m} \eta^{l-m}$. Likewise we have two monomials S_+ and S_- (the two components of a *spinor*; hence the name) to represent the spin functions of the first particle and two monomials \bar{S}_+ and \bar{S}_- to represent the spin functions of the second. From the spinors (ξ, η) , (S_+, S_-) , (\bar{S}_+, \bar{S}_-) , and (a, b) we form the six invariants:

$$(a\eta - b\xi), (aS_- - bS_+), (a\bar{S}_- - b\bar{S}_+), (S_+\eta - S_-\xi), (\bar{S}_+\eta - \bar{S}_-\xi), (S_+\bar{S}_- - S_-\bar{S}_+).$$

⁶ Houston (Phys. Rev. **33**, 297 (1929)) has treated this case, using the explicit wave functions and energy operators. The present treatment takes account of the interaction of the spin of each electron with the orbit of the other, which Houston did not consider. As we shall see in Part II, this interaction is not negligible.

These must be multiplied together to form polynomials homogeneous in (ξ, η) to the power $2l$, in (S_+, S_-) and in (\bar{S}_+, \bar{S}_-) to the power one, and in (a, b) to the power $2j$.

We find (as we should expect from the vector model) that the only possible values of j are $l+1, l, l-1$. The symbolic functions for $j=l+1$ and $j=l-1$ are uniquely determined but there are three functions for $j=l$, of which two are independent. Thus our multiplet will consist of four levels (a triplet and a singlet in case of pure Russell-Saunders coupling). We form the symbolic functions:

$$\begin{aligned}
 j = l + 1 \quad I &= A \{ (a\eta - b\xi)^{2l} (S_+ b - S_- a) (\bar{S}_+ b - \bar{S}_- a) \} \\
 j = l \quad \left\{ \begin{aligned}
 II_\alpha &= A \{ (a\eta - b\xi)^{2l-1} (\bar{S}_+ \eta - \bar{S}_- \xi) (S_+ b - S_- a) \} \\
 II_\beta &= A \{ (a\eta - b\xi)^{2l-1} (S_+ \eta - S_- \xi) (\bar{S}_+ b - \bar{S}_- a) \} \\
 II_\gamma &= A \{ (a\eta - b\xi)^{2l} (S_+ \bar{S}_- - S_- \bar{S}_+) \}
 \end{aligned} \right. \quad (19) \\
 j = l - 1 \quad III &= A \{ (a\eta - b\xi)^{2l-2} (S_+ \eta - S_- \xi) (\bar{S}_+ \eta - \bar{S}_- \xi) \}.
 \end{aligned}$$

The symbol A in front of a bracket means to subtract from the expression in the bracket the same expression with (S_+, S_-) and (\bar{S}_+, \bar{S}_-) interchanged and (ξ, η) replaced by $(\bar{\xi}, \bar{\eta})$. Expressions in $(\bar{\xi}, \bar{\eta})$ refer to functions of the coordinates of the second particle. Thus our wave functions are made to satisfy the Pauli principle requirement of antisymmetry.

7.

Of all the terms in the interaction energy of two electrons,⁷ we shall neglect, to begin with, all except Ω_1 , the electrostatic interaction,⁸ e^2/r_{12} ; Ω_2 , the leading terms,

$$\frac{Ze^2}{2m_0c^2} \left\{ \frac{([\mathbf{r}_1, \mathbf{v}_1] \cdot \mathbf{s}_1)}{r_1^3} + \frac{([\mathbf{r}_2, \mathbf{v}_2] \cdot \mathbf{s}_2)}{r_2^3} \right\},$$

in the interaction of the spin of each electron with its own orbital motion; Ω_3 , the leading terms,

$$\frac{e^2}{m_0c^2} \left\{ \frac{([\mathbf{r}_1, \mathbf{v}_1] \cdot \mathbf{s}_2)}{r_1^3} + \frac{([\mathbf{r}_2, \mathbf{v}_2] \cdot \mathbf{s}_1)}{r_2^3} \right\},$$

in the interaction of each spin with the orbit of the other electron. In Ω_2 and Ω_3 we have neglected all terms but the first in the expansion (3) of $1/r_{12}^3$.

To find the symbolic representation of Ω_1 , we must use the expansion (3). Ω_1 then assumes the form $\sum_n a_n (\mathbf{r}_1 \cdot \mathbf{r}_2)^n$, where the a_n are functions of the invariants, r_1 and r_2 . Then the symbolic representation is

$$\sum_n a_n (x\bar{y} - y\bar{x})^{2n}. \quad (20)$$

⁷ See, for example, Heisenberg, Zeits. f. Physik **39**, 499 (1926).

⁸ Of course, the term e^2/r_{12} does not properly constitute a small perturbation, since it is of considerable importance in fixing what one should like to consider as the *unperturbed* orbit. However, the true perturbation may be considered to be the difference between some well-chosen *central field* Hamiltonian and the true Hamiltonian in which e^2/r_{12} appears. The symbolic representation of this perturbation is the same as that of e^2/r_{12} .

In the matrix integrals which we wish to calculate, the factors coming from the wave functions will give us either (ξ^*, η^*) and (ξ, η) [or $(\bar{\xi}^*, \bar{\eta}^*)$ and $(\bar{\xi}, \bar{\eta})$] to the same power $2l$ or (ξ^*, η^*) and $(\bar{\xi}, \bar{\eta})$ [or $(\bar{\xi}^*, \bar{\eta}^*)$ and (ξ, η)] to the same power $2l$. Consequently, only the terms $n=0$ and $n=l$ in (20) will yield integrals different from zero. The term from $n=l$ is the so-called resonance term. Thus, for our purpose, the operator may be represented by⁹

$$\Omega_1 = A_0 + \frac{C_1}{(2l)!} \left\{ \left(\xi \frac{\partial}{\partial \bar{\xi}} + \eta \frac{\partial}{\partial \bar{\eta}} \right)^{2l} + \left(\bar{\xi} \frac{\partial}{\partial \xi} + \bar{\eta} \frac{\partial}{\partial \eta} \right)^{2l} \right\}. \quad (21)$$

The operator Ω_2 is in the form to be represented symbolically by

$$C_2 \{ (Xy - Yx)^2 + (\bar{X}\bar{y} - \bar{Y}\bar{x})^2 \}$$

where (x, y) is associated with the orbital coordinates and (X, Y) with the spin coordinates. We find the representation of Ω_2 in terms of the spinors which occur in the wave functions by a double use of (17):

$$\left\{ \begin{array}{l} (Xy - Yx)^2 = (X\eta - Y\xi) \left(X \frac{\partial}{\partial \xi} + Y \frac{\partial}{\partial \eta} \right) \\ x^2 = -\xi \frac{\partial}{\partial \eta}; \quad xy = \frac{1}{2} \left(\xi \frac{\partial}{\partial \xi} - \eta \frac{\partial}{\partial \eta} \right); \quad y^2 = \eta \frac{\partial}{\partial \xi} \end{array} \right.$$

$$\left\{ \begin{array}{l} (Xy - Yx)^2 = (xS_- - yS_+) \left(x \frac{\partial}{\partial S_+} + y \frac{\partial}{\partial S_-} \right) \\ X^2 = -S_+ \frac{\partial}{\partial S_-}; \quad XY = \frac{1}{2} \left(S_+ \frac{\partial}{\partial S_+} - S_- \frac{\partial}{\partial S_-} \right); \quad Y^2 = S_- \frac{\partial}{\partial S_+} \end{array} \right.$$

Substituting these expressions, we obtain

$$\Omega_2 = C_2 S \left\{ (S_+\eta - S_-\xi) \left(\frac{\partial^2}{\partial S_+ \partial \eta} - \frac{\partial^2}{\partial S_- \partial \xi} \right) - \frac{1}{2} \left(\xi \frac{\partial}{\partial \xi} + \eta \frac{\partial}{\partial \eta} \right) \left(S_+ \frac{\partial}{\partial S_+} + S_- \frac{\partial}{\partial S_-} \right) \right\} \quad (22)$$

where the symbol S in front of the bracket means to add to the expression in the bracket the same expression with barred and unbarred symbols interchanged.

The operator Ω_3 differs from Ω_2 only in the interchange of (S_+, S_-) and (\bar{S}_+, \bar{S}_-) .

$$\Omega_3 = C_3 \bar{S} \left\{ (\bar{S}_+\eta - \bar{S}_-\xi) \left(\frac{\partial^2}{\partial \bar{S}_+ \partial \eta} - \frac{\partial^2}{\partial \bar{S}_- \partial \xi} \right) - \frac{1}{2} \left(\xi \frac{\partial}{\partial \xi} + \eta \frac{\partial}{\partial \eta} \right) \left(\bar{S}_+ \frac{\partial}{\partial \bar{S}_+} + \bar{S}_- \frac{\partial}{\partial \bar{S}_-} \right) \right\}. \quad (23)$$

⁹ The term for $n=l$ comes from (18) with $\tau=l$ and $\rho=-\tau$.

Applying the operator

$$\Omega = \Omega_1 + \Omega_2 + \Omega_3 \quad (24)$$

to the wave functions (19), we find

$$\begin{aligned} \Omega I &= \{A_0 + C_1 - l(C_2 + C_3)\} I \\ \Omega II_\alpha &= \{A_0 - lC_2 + (l+1)C_3\} II_\alpha + \{C_1 + C_2\} II_\beta \\ \Omega II_\beta &= \{A_0 + (l+1)C_2 - lC_3\} II_\beta + \{C_1 + C_3\} II_\alpha \\ \Omega III &= \{A_0 + C_1 + (l+1)(C_2 + C_3)\} III . \end{aligned} \quad (25)$$

The multiplet energy levels ϵ_1 and ϵ_3 , defined by

$$\epsilon_1 \int I^* I = \int I^* \Omega I; \quad \epsilon_3 \int III^* III = \int III^* \Omega III, \quad (26)$$

are given immediately by (25) without integration:

$$\begin{aligned} \epsilon_1 &= A_0 + C_1 - l(C_2 + C_3) \\ \epsilon_3 &= A_0 + C_1 + (l+1)(C_2 + C_3). \end{aligned} \quad (27)$$

To find the other two energy levels and to find the linear combinations of II_α and II_β to represent the stabilized zero-approximation wave functions, we must solve the second order secular perturbation problem. The stabilized functions may be written in the form

$$\begin{aligned} \phi_2 &= \gamma_2 II_\alpha + \delta_2 II_\beta \\ \phi_4 &= \gamma_4 II_\alpha + \delta_4 II_\beta . \end{aligned} \quad (28)$$

Then our γ_2 , δ_2 and γ_4 , δ_4 are the two solutions of

$$\begin{aligned} \gamma(\Omega_{\alpha\alpha} - \epsilon\Delta_{\alpha\alpha}) + \delta(\Omega_{\alpha\beta} - \epsilon\Delta_{\alpha\beta}) &= 0 \\ \gamma(\Omega_{\beta\alpha} - \epsilon\Delta_{\beta\alpha}) + \delta(\Omega_{\beta\beta} - \epsilon\Delta_{\beta\beta}) &= 0 \end{aligned} \quad (29)$$

corresponding to the two roots ϵ_2 , ϵ_4 of the determinant of the coefficients in (29). Here we have defined

$$\Omega_{\alpha\beta} = \int II_\alpha^* \Omega II_\beta; \quad \Delta_{\alpha\beta} = \int II_\alpha^* II_\beta; \quad \text{etc.} \quad (30)$$

Making use of (15) and of the integration formula

$$\begin{aligned} \int (a^* \eta^* - b^* \xi^*)^{q+t} (a \xi^* + b \eta^*)^{q-t} (a \eta - b \xi)^{q+t'} (a^* \xi + b^* \eta)^{q-t'} \\ = \text{const.} \delta_{t't} \binom{2q}{q-t}^{-1} (a^* a + b^* b)^{2q}, \end{aligned} \quad (31)$$

which is obtained by replacing a by $a + fb^*$ and b by $b - fa^*$ in (15) and equating the coefficients of like powers of ff^* in the result, we proceed to carry out

the integrations (30). It is convenient to integrate first over the spin variables and then to make use of the relation

$$(a^*a + b^*b)(\xi^*\xi + \eta^*\eta) = (a^*\eta^* - b^*\xi^*)(a\eta - b\xi) + (a\xi^* + b\eta^*)(a^*\xi + b^*\eta), \quad (32)$$

which leaves us integrals of the type (31). We find

$$\begin{aligned} \Delta_{\alpha\alpha} &= \Delta_{\beta\beta} = \text{const. } (2l+1)(a^*a + b^*b)^{2l} \cdot (1/l) \\ \Delta_{\alpha\beta} &= \Delta_{\beta\alpha} = \text{const. } (a^*a + b^*b)^{2l} \cdot (1/l). \end{aligned} \quad (33)$$

The integrals $\Omega_{\alpha\alpha}$, etc. are given in terms of these by (25).

For the secular determinant, we find

$$\begin{vmatrix} C_1 + C_2 + (2l+1)\{A_0 - lC_2 + (l+1)C_3 - \epsilon\} & & & \\ & (2l+1)C_1 + (l+1)(C_2 + C_3) + A_0 - \epsilon & & \\ & & (2l+1)C_1 + (l+1)(C_2 + C_3) + A_0 - \epsilon & \\ & & & C_1 + C_3 + (2l+1)\{A_0 + (l+1)C_2 - lC_3 - \epsilon\} \end{vmatrix} = 0. \quad (34)$$

The solution is

$$\epsilon = A_0 + \left(\frac{1}{2}\right)(C_2 + C_3) \pm [l(l+1)(C_2 - C_3)^2 + [C_1 + \left(\frac{1}{2}\right)(C_2 + C_3)]^2]^{1/2}.$$

If we define the quantities ρ and θ by

$$\begin{aligned} C_1 + \left(\frac{1}{2}\right)(C_2 + C_3) &= \rho \cos 2\theta \\ [l(l+1)]^{1/2}(C_2 - C_3) &= \rho \sin 2\theta, \end{aligned} \quad (35)$$

we have, as the roots of (33),

$$\begin{aligned} \epsilon_2 &= A_0 + \left(\frac{1}{2}\right)(C_2 + C_3) + \rho \\ \epsilon_4 &= A_0 + \left(\frac{1}{2}\right)(C_2 + C_3) - \rho. \end{aligned} \quad (36)$$

The complete multiplet, given by (27) and (36), is

$$\begin{aligned} \epsilon_1 &= A_0 + C_1 - l(C_2 + C_3) \\ \epsilon_2 &= A_0 + C_1 + (C_2 + C_3) + 2\rho \sin^2 \theta \\ \epsilon_3 &= A_0 + C_1 + (l+1)(C_2 + C_3) \\ \epsilon_4 &= A_0 - C_1 - 2\rho \sin^2 \theta. \end{aligned} \quad (37)$$

We observe that, in the limit $\theta=0$, ϵ_1 , ϵ_2 , ϵ_3 form a Russell-Saunders triplet with the intervals in the ratio $l+1$ to l , while ϵ_4 appears as a singlet at a distance proportional to the resonance energy, C_1 . Using these limit values of ϵ_2 and ϵ_4 in (29) and substituting in (28), we find for the *pure triplet* and *pure singlet* linear combinations of Π_α and Π_β

$$\begin{aligned} \phi_t &= N_t(\Pi_\alpha + \Pi_\beta) \\ \phi_s &= N_s(\Pi_\alpha - \Pi_\beta) = N_s\Pi_\gamma. \end{aligned} \quad (38)$$

From (33), we find for the normalizing constants

$$N_t = \text{const. } l^{1/2}; N_s = \text{const. } (l + 1)^{1/2}. \tag{39}$$

ϕ_t , like I and III, is antisymmetric in the coordinates, symmetric in the spins; ϕ_s is symmetric in the coordinates, antisymmetric in the spins.

Now, substituting for II_α and II_β in terms of ϕ_s and ϕ_t in (28) and using the values of γ and δ obtained by putting (36) in (29), we find for our stabilized wave functions

$$\begin{aligned} \phi_2 &= -\sin \theta \phi_s + \cos \theta \phi_t \\ \phi_4 &= \cos \theta \phi_s + \sin \theta \phi_t. \end{aligned} \tag{40}$$

Here the normalizing factors have already been introduced.

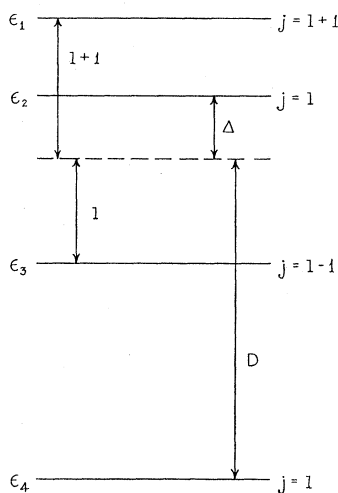


Fig. 1.

Introducing the notation $d_{12} = \epsilon_1 - \epsilon_2$, etc. and using the symbols Δ and D to represent the distances from the *normal* position of the center triplet level to ϵ_2 and ϵ_4 respectively (see Fig. 1) we find from (37)

$$\begin{aligned} \Delta &= | [(l + 1)d_{23} - ld_{12}] / (2l + 1) | \\ \Delta &= | d_{24} | - \Delta \\ \sin^2 \theta &= [(l + 1)d_{23} - ld_{12}] / [(2l + 1)d_{24}] \\ C_1 &= (\frac{1}{2})(d_{24} + d_{12} - d_{23}) \\ C_2 + C_3 &= -(d_{12} + d_{23}) / (2l + 1) \\ C_2 - C_3 &= (\Delta D / l(l + 1))^{1/2}. \end{aligned} \tag{41}$$

Since $\sin^2 \theta$ must be positive, the sign of $(l + 1)d_{23} - ld_{12}$ must be the same as the sign of d_{24} . This means that, if the singlet, ϵ_4 , lies below the triplet, the

center triplet level, ϵ_2 , must lie above its normal position and vice versa. A convenient way of stating this rule is that: *the center triplet level is repelled by the singlet level.*¹⁰

In (41), the quantities C_2 and C_3 are not completely determined since we do not know the sign of $C_2 - C_3$. They become determined when we make the physical assumption that the interaction of the spin of each electron with its own orbital motion is larger than with that of the other electron, i.e., $|C_2| > |C_3|$. This is equivalent to making the sign of $C_2 - C_3$ the same as the sign of $C_2 + C_3$. This determines also the sign in (40) of the angle, θ , which was defined by (35). The sign of $C_2 + C_3$ (and so likewise the sign of $C_2 - C_3$) is always the same. Since we can express $C_2 - C_3$ in the form

$$C_2 - C_3 = d_{24} \sin \theta \cos \theta / [l(l+1)]^{1/2},$$

we must change the sign of θ according as d_{24} is positive or negative, i.e., according as the singlet lies above or below the triplet.

8.

While ϵ_2 is regarded as a triplet level in spectral classification and ϵ_4 as a singlet, we observe in (40) that the wave functions for these states are partly singlet and partly triplet in character so that we may expect transitions between both of these levels and other singlet and triplet levels—i.e., we shall expect *forbidden* intercombinations between singlet and triplet systems as well as combinations within these systems—with relative intensities determined by θ .

The intensities of transitions between levels are proportional to the squared absolute values of the corresponding matrix elements of the polarization. Kramers has shown¹ how the symbolic method is adapted to calculating the matrix elements. The operators for the components of the polarization must have the transformation properties of the components of a space-vector. These operators may all be represented symbolically by the spinor invariant

$$\Omega = (AY - BX)^2, \quad (42)$$

where we make the association, according to the transformation properties,

$$P_x + iP_y \rightarrow X^2; \quad -P_x + iP_y \rightarrow Y^2; \quad P_z \rightarrow XY.$$

Brinkman¹¹ has shown in detail that calculation with the wave functions corresponding to Russell-Saunders multiplets leads to the well-known intensity rules as given by Kronig and by Hönl.¹² Hence, for our purpose, we may regard the matrix elements associated with the functions I, ϕ_t , III, ϕ_s as

¹⁰ We must not expect this rule to hold in case of very small displacements of the center triplet from its normal position, since this may arise from cancellation of the opposite effects of the perturbations Ω_2 and Ω_3 , in which case the effect of the other perturbation terms we have left out may not be negligible in comparison.

¹¹ Brinkman, Dissertation Utrecht 1932.

¹² Kronig, *Zeits. f. Physik* **31**, 885 (1925); **33**, 261 (1925). Hönl, *Ann. d. Physik* **79**, 273 (1926).

known. We may indicate the matrix elements for the group of transitions $l+1 \rightarrow l$ by

$$\int I\Omega\phi_l' = \Omega_{1l}, \text{ etc.} \quad (43)$$

where quantities referring to the final state are distinguished by a dash. We shall make explicit use of the fact that all matrix elements Ω_{1s} , Ω_{st} , etc., and all matrix elements for $|\Delta j| > 1$ vanish and that¹³

$$\Omega_{ss} = \frac{l+1}{[l(l+2)]^{1/2}} \Omega_{tt}. \quad (44)$$

Then we obtain, for the actual multiplet, the matrix elements

$$\begin{aligned} \int I\Omega I' &= \Omega_{11} \\ \int \phi_2\Omega I' &= \cos \theta \Omega_{t1} \\ \int III\Omega I' &= \Omega_{31} \\ \int \phi_4\Omega I' &= \sin \theta \Omega_{t1} \\ \int \phi_2\Omega\phi_2' &= \left\{ \frac{l+1}{[l(l+2)]^{1/2}} \sin \theta \sin \theta' + \cos \theta \cos \theta' \right\} \Omega_{tt} \\ \int III\Omega\phi_2' &= \cos \theta' \Omega_{3t} \\ \int \phi_4\Omega\phi_2' &= \left\{ -\frac{l+1}{[l(l+2)]^{1/2}} \cos \theta \sin \theta' + \sin \theta \cos \theta' \right\} \Omega_{tt} \\ \int \phi_2\Omega\phi_4' &= \left\{ -\frac{l+1}{[l(l+2)]^{1/2}} \sin \theta \cos \theta' + \cos \theta \sin \theta' \right\} \Omega_{tt} \\ \int III\Omega\phi_4' &= \sin \theta' \Omega_{3t} \\ \int \phi_4\Omega\phi_4' &= \left\{ \frac{l+1}{[l(l+2)]^{1/2}} \cos \theta \cos \theta' + \sin \theta \sin \theta' \right\} \Omega_{tt} \\ \int III\Omega III' &= \Omega_{33}. \end{aligned} \quad (45)$$

The sum rules for intensity hold for the complete multiplet and not for the singlet and the triplet separately.¹⁴ In applying the formulas (45), we must use the rule at the end of section 7 for determining the signs of θ and θ' .

¹³ This relation is given by carrying out the symbolic integrations. Apart from the sign, it follows from the sum rules.

¹⁴ Compare with Ornstein and Burger, *Zeits. f. Physik* **40**, 403 (1926).

9.

The formulas for the relative intensities of spectral lines, which are obtained by squaring the expressions in (45) and substituting in the Kronig-Hönl values for $|\Omega_{11}|^2$, $|\Omega_{21}|^2$, etc., hold only in a sort of first approximation, i.e., with neglect of quantities of the order of magnitude $\Delta\nu/\nu$, where $\Delta\nu$ is the interval between the frequencies of the lines compared. In many cases this ratio is not small and the ambiguity may be correspondingly large. Thus we should not attempt to compare our results with experimental intensity ratios except for groups of lines of about the same frequency. The origin of this ambiguity lies in the fact that the matrix elements calculated, while assumed to be those of the polarization, might equally well be those of, say, the second time derivative of the polarization; for this quantity has the same rotation properties. But the squared matrix elements for these two quantities differ by a factor ν^4 .

As remarked at the beginning of section 7, we have taken account only of certain selected terms in the interaction energy of two electrons as given by Heisenberg (reference 7). With the exception of the leading term in the spin-spin interaction, all of the neglected terms involve more than two vector-frames. To show how the method is applied in such cases, we treat now the leading term (i.e., we take only the first term in the expansion (3)) in the interaction

$$\frac{e^2}{m_0c^2} \left\{ \frac{([\mathbf{r}_1, \mathbf{v}_2] \cdot \mathbf{s}_1) + ([\mathbf{r}_2, \mathbf{v}_1] \cdot \mathbf{s}_2)}{r_{12}^3} \right\}. \quad (46)$$

The expression $([\mathbf{r}_1, \mathbf{v}_2] \cdot \mathbf{s}_1)$ involves the orbital motions of both particles and the spin of one of them. To obtain a symbolic representation, we associate each of the vectors with a spinor:

$$\mathbf{r}_1 \rightarrow (x, y); \quad \mathbf{v}_2 \rightarrow (X, Y); \quad \mathbf{s}_1 \rightarrow (r, s).$$

We may make the association in this way. If (a, b, c) are the components of a vector and (ξ, η) are the components of a spinor, we may set¹⁵

$$a = \frac{1}{2}(\xi^2 - \eta^2); \quad b = -\frac{i}{2}(\xi^2 + \eta^2); \quad c = -\xi\eta.$$

This gives us, as the symbolic representation of $([\mathbf{r}_2, \mathbf{v}_2] \cdot \mathbf{s}_2)$,

$$(rY - sX)(ry - sx)(Xy - Yx). \quad (47)$$

We proceed to replace each of these spinors by operators involving the spinor representing the corresponding vector-frame in the wave functions. Thus we substitute

$$\begin{aligned} &\text{for } (x, y) \quad \text{expressions involving } \xi, \eta, \partial/\partial\xi, \partial/\partial\eta; \\ &\text{for } (X, Y) \quad \text{expressions involving } \bar{\xi}, \bar{\eta}, \partial/\partial\bar{\xi}, \partial/\partial\bar{\eta}; \\ &\text{for } (r, s) \quad \text{expressions involving } S_+, S_-, \partial\bar{S}_+, \partial/\partial\bar{S}_-. \end{aligned}$$

We observe that, in general, it will not be possible to find an operator representing this interaction term whose matrix elements do not vanish identically. Only in case $l=1$ do we get integrals different from zero. The operator may be

¹⁵ ξ, η are the coordinates by stereographic projection of a point a, b, c on the zero sphere.

put into a form where it contains first derivatives with respect to S_+ and S_- and either second derivatives with respect to ξ and η and no derivatives with respect to $\bar{\xi}$ and $\bar{\eta}$ or second derivatives with respect to $\bar{\xi}$ and $\bar{\eta}$ and no derivatives with respect to ξ and η . We then obtain nonvanishing resonance integrals when $l=1$.

To get (47) into a form where we can use (18), we introduce a symbol T_f which means to pick out the coefficient of f in the expression following.

$$(ry - sx)(Xy - Yx) = \frac{1}{2}T_f\{(X + fr)y - (Y + fs)x\}^2 \\ \rightarrow \frac{1}{2}T_f\left\{(X + fr)\frac{\partial}{\partial\xi} + (Y + fs)\frac{\partial}{\partial\eta}\right\}^2 = \left(r\frac{\partial}{\partial\xi} + s\frac{\partial}{\partial\eta}\right)\left(X\frac{\partial}{\partial\xi} + Y\frac{\partial}{\partial\eta}\right).$$

Applying (18) a second time¹⁶

$$(rY - sX)\left(r\frac{\partial}{\partial\xi} + s\frac{\partial}{\partial\eta}\right) = \frac{1}{2}T_f\left\{\left(Y + f\frac{\partial}{\partial\xi}\right)r - \left(X - f\frac{\partial}{\partial\eta}\right)s\right\}^2 \\ \rightarrow \frac{1}{2}T_f\left\{\left(Y + f\frac{\partial}{\partial\xi}\right)S_+ - \left(X - f\frac{\partial}{\partial\eta}\right)S_-\right\}\left\{\left(X - f\frac{\partial}{\partial\eta}\right)\frac{\partial}{\partial S_+} + \left(Y + f\frac{\partial}{\partial\xi}\right)\frac{\partial}{\partial S_-}\right\} \\ = \frac{1}{2}\left\{(S_+Y - S_-X)\left(\frac{\partial^2}{\partial\xi\partial S_-} - \frac{\partial^2}{\partial\eta\partial S_+}\right) + \left(S_+\frac{\partial}{\partial\xi} + S_-\frac{\partial}{\partial\eta}\right)\left(X\frac{\partial}{\partial S_+} + Y\frac{\partial}{\partial S_-}\right)\right\}.$$

In the final step, we have simply $X \rightarrow \bar{\xi}$, $Y \rightarrow \bar{\eta}$. This gives us the symbolic operator for (47) in the form

$$\left\{(S_+\bar{\eta} - S_-\bar{\xi})\left(\frac{\partial^2}{\partial\xi\partial S_-} - \frac{\partial^2}{\partial\eta\partial S_+}\right) + \left(S_+\frac{\partial}{\partial\xi} + S_-\frac{\partial}{\partial\eta}\right)\left(\bar{\xi}\frac{\partial}{\partial S_+} + \bar{\eta}\frac{\partial}{\partial S_-}\right)\right\}\left(\bar{\xi}\frac{\partial}{\partial\xi} + \bar{\eta}\frac{\partial}{\partial\eta}\right).$$

The other usable form of the operator differs from this only in the interchange of $(\bar{\xi}, \bar{\eta})$ and (ξ, η) . The term $([\mathbf{r}_2, \mathbf{v}_1] \cdot \mathbf{s}_2)$ yields operators which differ from these two by a complete interchange of barred and unbarred quantities. Obtaining symmetrical operators by lumping together those operators that differ from each other by a complete interchange and putting them in a somewhat different form, we find as the operator representing the leading term in (46),

$$\omega = C_4 \cdot S \left\{ \left(\bar{\xi}\frac{\partial}{\partial\xi} + \bar{\eta}\frac{\partial}{\partial\eta} \right) \left[(S_+\bar{\eta} - S_-\bar{\xi}) \left(\frac{\partial^2}{\partial S_+\partial\eta} - \frac{\partial^2}{\partial S_-\partial\xi} \right) - \frac{1}{2} \left(\bar{\xi}\frac{\partial}{\partial\xi} + \bar{\eta}\frac{\partial}{\partial\eta} \right) \left(S_+\frac{\partial}{\partial S_+} + S_-\frac{\partial}{\partial S_-} \right) \right] \right\} \\ + C_5 \cdot S \left\{ \left(\xi\frac{\partial}{\partial\xi} + \eta\frac{\partial}{\partial\eta} \right) \left[(S_+\eta + S_-\xi) \left(\frac{\partial^2}{\partial S_+\partial\bar{\eta}} - \frac{\partial^2}{\partial S_-\partial\bar{\xi}} \right) - \frac{1}{2} \left(\xi\frac{\partial}{\partial\xi} + \eta\frac{\partial}{\partial\eta} \right) \left(S_+\frac{\partial}{\partial S_+} + S_-\frac{\partial}{\partial S_-} \right) \right] \right\}. \tag{48}$$

¹⁶ $\partial/\partial\xi$ transforms like η and $\partial/\partial\eta$ like $-\xi$.

In the special case $l=1$, we apply the operator (48) to the wave functions (19) and find

$$\begin{aligned}\omega\text{I} &= (C_4 + C_5)\text{I} \\ \omega\text{II}_\alpha &= -C_4\text{II}_\alpha + (C_4 - 2C_5)\text{II}_\beta \\ \omega\text{II}_\beta &= -C_5\text{II}_\beta + (C_5 - 2C_4)\text{II}_\alpha \\ \omega\text{III} &= (C_4 + C_5)\text{III}.\end{aligned}$$

In addition to neglecting what we believe to be the unimportant terms in the interaction energy, we have made another omission which may in some cases completely invalidate our results. We have assumed in our treatment of the interaction of two electrons as a perturbation that each electron configuration (defined by the n and l values for the two electrons) may be treated quite by itself. This treatment is valid only so long as there are not similar terms of nearly equal energy arising from different configurations.¹⁷ As we follow through a series of terms from configurations differing in the n value of one of the electrons, irregularities in the values of n^* reveal the presence of perturbing terms arising from other types of configuration. Shenstone and Russell¹⁸ have shown that perturbations of this sort are common. We cannot expect our formulas (41) for the energies of the different interaction terms as functions of the multiplet intervals to have much meaning for a configuration which is much perturbed by a neighboring one.

Part II of this paper, containing the application of the theory developed in Part I to observed spectra, will appear later. The relative energy values of the different types of interaction will be calculated for many spectra. The calculated intensities of certain multiplet lines in the spectrum of mercury will be compared with the experimental values.

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¹⁷ This was first emphasized by Condon, *Phys. Rev.* **36**, 1121 (1930).

¹⁸ Shenstone and Russell, *Phys. Rev.* **39**, 415 (1932).