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THE THEORY OF COMPLEX SPECTRA

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Abstract

Atomic multiplets are treated by wave mechanics, without using group theory. In part 1 Hund's scheme for multiplet classification is derived directly from theory. Part 2 is devoted to the computation of the energy distances between multiplets, and comparison of these distances with experiment in some typical examples. There is no treatment of the separations between the various terms of a multiplet, since that has been done elsewhere, but only between one multiplet and another. It is found that Hund's rule, that terms of large L and S values lie lowest, has no general significance; the present theory leads to the same results as the rule when it is obeyed experimentally, but many cases which were exceptions to that rule are in agreement with the theory. The method of calculation of multiplet distances is described in sufficient detail, with the necessary tables of coefficients, etc., so that further checks with experiment could easily be made.

THE theory of complex spectra is treated in this paper by the method of wave mechanics. The results of the calculation may be divided into two parts: first, the classification of the terms into multiplets; second, the energy values of these multiplets. The first part contains no new results of physical interest, for it leads precisely to Hund's[1] scheme of classification, and uses almost the identical steps that Hund uses. Its value lies in the fact that this well-known scheme is shown in an elementary way to follow directly from wave mechanics. The second part, however, is almost entirely new, and it leads to definite formulas for the intervals between the different multiplets in spectra, intervals which could previously be considered only very roughly from an empirical rule of Hund, which proves to have no general significance. These calculations, of course, give the intervals in terms of certain integrals, which we do not calculate, but merely estimate well enough to permit some comparison with experiment. The agreement is in general fairly good. A third part would be also included, dealing with the intervals within the multiplets, produced by the magnetic interaction, were

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[1] F. Hund, Linienspektren und periodisches System der Elemente, Springer.

it not that Goudsmit[2] has already answered the question by a method closely analogous to that used here.

It will be noted that the objects of the present paper resemble closely those aimed at by Heisenberg, Wigner, Hund, Heitler, Weyl, and others,[3] who employ the methods of the group theory. That method is not used at all in the present calculation,and, in contrast, no mathematics but the simplest is required, until one actually comes to the computation of the integrals. This, it is believed, is in itself sufficient justification for paralleling to some extent work already done. The simplification is achieved largely by introducing the spin at the very beginning of the calculation, rather than later. Thus we need only consider antisymmetric wave functions, which can be treated very simply as determinants, and can avoid the other symmetry characters, with which the other papers have been mostly concerned. The process of building up wave functions of the proper symmetry by using determinants is not new; it is found in Dirac's earlier papers, and has been used, for example, by Waller and Hartree.[4] The spin function, however, is introduced into the determinant in the present paper in a new and more satisfactory way. The results which we obtain, concerning the diagonal term of the energy with respect to the antisymmetric wave functions, are of the sort found by the group theory, and also by the recent method of Dirac,[5] but it seems worth while to derive them in a simple fashion.

The essentially new results of the present paper, those relating to energy, in the second part, come from the fact that we consider the whole degeneracy, that coming from orbital as well as spin angular momentum, which most of the other papers have failed to do. The present method is essentially equivalent to the others in that it gives sums of energies, rather than individual energies. When it is applied to the case in which the degeneracy with respect to orbital angular momentum is not considered, it leads, as do the others, merely to the sum of all terms of a given multiplicity; the writer is indebted to Dr. Bloch for pointing out that in that case all the results of Heitler can be easily demonstrated by the present method. But we make the observation that, by considering the whole problem with all its degeneracy, the method of energy sums can be used much more effectively, so much so that in most important cases we can get the actual energies of the individual terms. In connection with this, it should be noted that in several cases the actual perturbation problems have been solved directly, rather than by the method of energy sums, obtaining results[6] that hold even when the magnetic energy is appreciable.

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[2] S. Goudsmit, Phys. Rev. **31**, 946 (1928).

[3] W. Heisenberg, Zeits. f. Physik **41**, 239 (1927). E. Wigner, Zeits. f. Physik **40**, 492, 883, etc. (1927). F. Hund, Zeits. f. Physik **43**, 788 (1927). W. Heitler, Zeits. f. Physik **46**, 47 (1928). H. Weyl, Gruppentheorie und Quantenmechanik, Hirzel, 1928.

[4] I. Waller and D. R. Hartree, Proc. Roy. Soc. **A124**, 119 (1929). The writer is indebted to Dr. Hartree for calling his attention to this paper.

[5] P. A. M. Dirac, Proc. Roy. Soc. **A123**, 714 (1929).

[6] W. V. Houston, Phys. Rev. **33**, 297 (1929). J. A. Gaunt, Trans. Camb. Phil. Soc. (1929).

PART 1. THE CLASSIFICATION OF MULTIPLETS

1. As a preface, we remind the reader of the theory of multiplets, as developed before wave mechanics. This theory considered the interactions of the various angular momenta of the parts of an atom, and treated the various energy levels resulting from different relative orientations of these parts. In a logical development of atomic structure it would follow directly after Bohr's theory of electron orbits; for Bohr went as far as was possible on the assumption that each electron moved in a field with spherical symmetry, so that its orientation with respect to the rest of the atom was a matter of no concern. We start then, as Bohr finished, with an atom composed of a number of electrons, each characterised by a total quantum number n, and an azimuthal quantum number l, the latter determining the angular momentum, and being often regarded as a vector (normal to the plane of the orbit, in Bohr's theory, but this is of no importance). The orientation of this vector in space was arbitrary, on account of the spherical symmetry. As an additional part of the formulation, we need to consider the electronic spin of Goudsmit and Uhlenbeck: each electron has an angular momentum (with consequent magnetic moment) entirely apart from the momentum l which it acquires by its motion. This additional angular momentum, denoted by s, (which like l, is often regarded as a vector), can likewise be oriented arbitrarily in space, without reference to the direction of l. Since the values which n, l, and s can take on, and the notation, are rather significant, we observe that l can equal 0, 1, 2, $\cdots$; n can be any integer greater than or equal to $(l+1)$; and s is always equal to 1/2. The values of n and l are denoted by symbols, as $1s$, $2s$, $\cdots$; $2p$, $3p$ $\cdots$; $3d$, $4d$, $\cdots$; $4f$, $5f$ $\cdots$; referring respectively to the cases where n and l are 10, 20, $\cdots$; 21, 31, $\cdots$; 32, 42, $\cdots$; etc. Then the structure of an entire atom in a given state can be given, as far as Bohr's theory is concerned, by giving the n and l of each electron, denoted as in the example: $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^2$, meaning that there are two $(1s)$ electrons, two $(2s)$, six $(2p)$, two $(3s)$. Another state of the same atom (in this case magnesium) would be $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)$ $(3p)$; and so on. These two states would be often abbreviated $3s$ and $3p$ respectively. The spin, having always the same value, need not be mentioned at this stage.

Having described the atom to the degree of accuracy considered by Bohr, we next must consider that the angular momentum vectors really are coupled together; there are differences of energy depending on orientation, and a consequent splitting up of each energy level into a number of different ones. In the commonest case, which alone we shall consider, the coupling can be considered in several stages. First, the l's of the various electrons group themselves into a vector sum L, which takes on only integral values, 0, 1, 2, $\cdots$, as the separate l's do. Each such arrangement gives a different energy, and a different term in the spectrum. The terms with L equal respectively to 0, 1, 2, 3, $\cdots$, are called S, P, D, F, $\cdots$ terms. Second, the spins of the electrons group themselves into a vector sum S, taking on the integral or half integral values (for any case, the orientation where all s's are parallel is allowed; if it is integral, only integral S's are allowed, and if it is half integral, only half integers are allowed for S). The different values of S lead to terms of different multiplicities, as we shall see in a moment, and different energies; thus $S=0$ gives singlets, $S=1/2$ doublets, $S=2$ triplets, etc. Finally L and S are coupled together, their sum being called J, and being integral or half integral to correspond with S. Since J can vary from $|L+S|$ to $|L-S|$, there are (if $L>S$) $2S+1$ different terms so obtained. These terms are the various terms of a single multiplet, which is named singlet $(2S+1=1)$, doublet $(2S+1=2)$, etc., to agree with the number of terms. The energies involved in going from one value of L to another, or of S to another, are generally large; they are (as one sees from wave mechanics) electrostatic energies. On the other hand, the energy of orientation of L with respect to S is small, coming from magnetic interaction of the parts of the atom, so that the different levels of a multiplet (same L and S, different J) lie near enough together to be grouped together. If one neglects the magnetic interaction as a first approximation, the levels of a multiplet all have just the same energy. As to notation, we speak, for example, of $^3P_2$, meaning a triplet P term with $J=2$. And if we wish to indicate the state of the electrons which produce the multiplet terms, we write it as $(1s)^2\,(2s)^2\,(2p)^6\,(3s)\,(3p)\;{}^3P_2$, which would often be abbreviated $(3p)\;{}^3P_2$.

The process of coupling can also be described in the language of space quantization. If one has an angular momentum vector, as l, acted on by no torques, so that its direction is arbitrary, it is legitimate to choose any axis in space, and consider that the component of the vector along this direction can take up any one of a set of values, integrally spaced between the parallel and antiparallel orientations. Thus, if m_l is the component of l along this axis, m_l can equal $l, l-1, l-2, \cdots -l$. These $(2l+1)$ values are considered to denote $(2l+1)$ separate stationary states, all with the same energy. Now we follow by this method the process of coupling, beginning with the uncoupled vectors, and carrying it through to the case where the l's are coupled to give L, and the s's to give S, but the magnetic interactions are not considered. In the uncoupled case, each electron has its own m_l and m_s. As the coupling forces are introduced, torques appear which make the components of the individual l's and s's vary with time, so that the same space quantization is no longer possible. But the torques are internal; they cannot change the total angular momentum. The total sum of all the l's and the sum of all the s's, and their components along the axes, remain constant, and hence quantized: $\sum m_l$ and $\sum m_s$ are quantized even when the coupling has taken its full value. On the other hand, when the electrons are coupled, the atom consists of vectors L and S, each separately free, so that these can be space quantized, giving components M_L and M_S along the axis. We need now only identify the M_L and M_S for the coupled system with the $\sum m_l$ and $\sum m_s$ for the uncoupled one, to get the correspondence necessary to show what multiplets appear from any combination of electrons. The exact method is easily shown from an example.

For illustration, we take the coupling of two p electrons. Each has $l=1$; the first has principal quantum number n, the second n'. For each, we can have $m_l=1,\ 0,\ -1$; $m_s=1/2,\ -1/2$; that is, $2(2l+1)=6$ different sets $(m_l,\ m_s)$, each representing a stationary state. With the combined atom, there are 36 combinations of one state of the first electron with one of the second. These are partly given in Table I. Two different notations are used in this table for comparison. First we simply give the four quantum numbers $(n\ l\ m_l\ m_s)$ for each of the electrons. For the other scheme of notation, which is often convenient in practice, we take advantage of the fact that each m_s is capable of only the two values $1/2,\ -1/2$: we set up two brackets, one containing the symbols $(n\ l\ m_l)$ of each electron with $m_s=1/2$, the second containing the symbols for those with $m_s=-1/2$. Such a bracket symbol, in which the arrangement of terms within a bracket is of no significance, is equivalent to a state of the first sort. After each symbol is given the value of $\sum m_l$ and of $\sum m_s$ for that state. Finally, after some of the terms, are notes which will be explained later.

TABLE I. *Two p electrons.*

First notation	Second notation	Σm_l	Σm_s	Notes
$(n\ 1\ 1\ \tfrac{1}{2})\ (n'\ 1\ 1\ \tfrac{1}{2})$	$\{(n\ 1\ 1)\ (n'\ 1\ 1)\}\ \{\ \}$	2	1	Exc
$(n\ 1\ 0\ \tfrac{1}{2})\ (n'\ 1\ 1\ \tfrac{1}{2})$	$\{(n\ 1\ 0)\ (n'\ 1\ 1)\}\ \{\ \}$	1	1	A
$(n\ 1\ -1\ \tfrac{1}{2})\ (n'\ 1\ 1\ \tfrac{1}{2})$	$\{(n\ 1\ -1)\ (n'\ 1\ 1)\}\ \{\ \}$	0	1	
$(n\ 1\ 1\ -\tfrac{1}{2})\ (n'\ 1\ 1\ \tfrac{1}{2})$	$\{(n'\ 1\ 1)\}\ \{(n\ 1\ 1)\}$	2	0	
$(n\ 1\ 0\ -\tfrac{1}{2})\ (n'\ 1\ 1\ \tfrac{1}{2})$	$\{(n'\ 1\ 1)\}\ \{(n\ 1\ 0)\}$	1	0	
$(n\ 1\ -1\ -\tfrac{1}{2})\ (n'\ 1\ 1\ \tfrac{1}{2})$	$\{(n'\ 1\ 1)\}\ \{(n\ 1\ -1)\}$	0	0	
$(n\ 1\ 1\ \tfrac{1}{2})\ (n'\ 10\ \tfrac{1}{2})$	$\{(n\ 1\ 1)\ (n'\ 1\ 0)\}\ \{\ \}$	1	1	A
$(n\ 1\ 0\ \tfrac{1}{2})\ (n'\ 10\ \tfrac{1}{2})$	$\{(n\ 1\ 0)\ (n'\ 1\ 0)\}\ \{\ \}$	0	1	Exc
$(n\ 1\ -1\ \tfrac{1}{2})\ (n'\ 1\ 0\ \tfrac{1}{2})$	$\{(n\ 1\ -1)\ (n'\ 1\ 0)\}\ \{\ \}$	-1	1	
etc.				

The values of $\sum m_l$ and $\sum m_s$ are conveniently plotted by giving $\sum m_s$ as abscissa, $\sum m_l$ as ordinate, and putting a dot for each state. Thus in Fig. 1, a, we give a single p state; and in b, the points for the sum of the two (the numbers indicate the number of states with the same $\sum m_s$, $\sum m_l$). But now in Fig. 1, b, each point should also represent the M_L, M_S of one of the multiplets existing in the coupled atom. This can be brought about in but one way: by assuming the multiplets ${}^1S\ {}^1P\ {}^1D\ {}^3S\ {}^3P\ {}^3D$, whose separate representations are shown below (in Fig. 1, d—i), and whose patterns, if superposed, would just give Fig. 2b. Thus it must be that two p electrons produce these multiplets. But that is just what our other method gives; for two l's, each equal to unity, can add to give $L=0,\ 1,\ 2$, (S, P, D terms); while two s's, each 1/2, can give $S=0,\ 1$ (singlet, triplet). In every case, the two methods lead to the same result, just as here.

The scheme as described above will result, in an atom with many electrons, in an enormous variety of terms, comparatively few of which are realized in actual atoms. The principle limiting the number is the exclusion principle of Pauli. It cannot be stated in the language of vectors, but only in terms of the space quantization just described. It is: no two electrons can have identical sets of numbers ($n\ l\ m_l\ m_s$); further, two combinations of electrons which differ only in the interchange of the quantum numbers of two electrons are to be treated as identical. Stated in terms of the bracket method of writing the electronic combinations, this means that no two sets of quantum numbers ($n\ l\ m_l$) within a bracket can be identical; and that the order of arrangement within a bracket is immaterial. By these restrictions, the number of terms is often enormously decreased. Many points on our diagrams are removed, and just the remaining ones must be fitted into multiplets, resulting in a much smaller number. For example, in our Table I, the two electrons have the same l; hence, if they have also the same total quantum number (that is, if $n=n'$), they cannot both have the same set of m_l and m_s. Thus the two terms marked *Exc* (and many other terms not included in the table) must be excluded; and the two terms marked *A* (and many more pairs) are to be considered identical. When the terms not allowed are removed, the new pattern in place of Fig. 1b proves to be Fig. 1c; and this is the superposition of $^3P\ ^1S\ ^1D$, which then are the multiplets allowed with two equivalent p electrons (that is, two electrons, each with $l=1$, and with the same n). As a general thing, the exclusion principle is active only when there are equivalent electrons; its many properties, as in limiting the number of electrons in a closed shell, are well known and need not be elaborated.

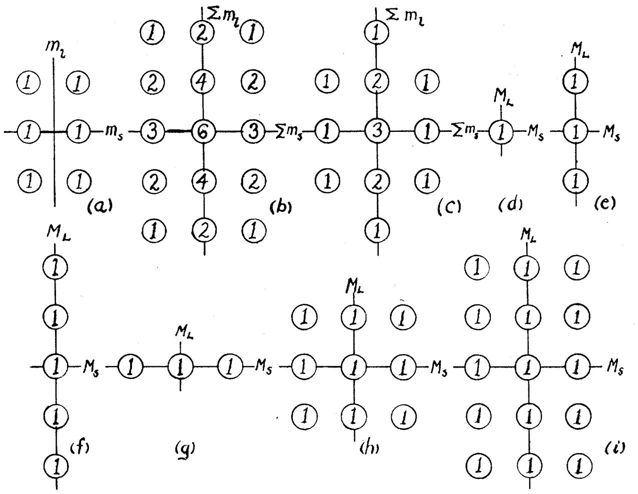

Fig. 1. (a) Single p electron; (b) Two p electrons; (c) Two equivalent p electrons; (d) ^1S (e) ^1P; (f) ^1D; (g) ^3S; (h) ^3P; (i) ^3D.

2. In quantum mechanics, we meet the problem of complex spectra as one step in the approximate solution of the wave equation for the atom. There are two fundamental principles which govern the structure of matter: quantum dynamics, and the principle of antisymmetry which shows itself

in the exclusion principle and the Fermi-Dirac statistics. The first states that only those energy levels are possible which are characteristic numbers of Schrödinger's equation for the system; the second further restricts the possible energies to those connected with characteristic functions antisymmetric in the electrons. Our whole object is to find such characteristic functions and numbers. And as before, the first step is to approximate by supposing that the separate electrons move in fields of force with spherical symmetry, so that there is no tendency for orientation of the various angular momenta. There are various ways of doing this; one scheme which gives good results is that of Hartree.[7] For simplicity in description we shall imagine that scheme modified slightly in one detail; according to it, each electron moves in a field of force slightly different from the others. We shall neglect the difference, assuming that all the electrons move in precisely the same field. And this field is to be so chosen as to give the best agreement with the correct values even without further corrections.

An electron moving in a central field of force, according to wave mechanics, is characterized by the same two quantum numbers n and l that we have previously described. The arbitrary direction of the angular momentum is, as before, most conveniently described by quantizing the component m_l in a fixed direction. Similarly the orientation of the spin is most conveniently given by specifying its component m_s in the same fixed direction. Thus each electron in an atom, in the approximation in which we can neglect the interactions of their rotations, is specified by the four quantum numbers $n\ l\ m_l\ m_s$, just as it was before. All relations of these numbers remain unchanged. But now, each electron has a wave function—a function of its coordinates (and, as we shall describe presently, of a coordinate representing its spin) depending on the numbers $n\ l\ m_l\ m_s$, which is a solution of Schrödinger's equation for a particle in a central field. We can denote the function for the ith electron by $u(n_i/x_i)$, where n_i stands for the four numbers $n_i\, l_i\, m_{li}\, m_{si}$, and x_i symbolizes the four coordinates (three of position, one of spin) of the ith electron. Now it is well known that the product of these functions, for all the electrons $(1 \cdots N)$ of the atom, gives a function which approximately satisfies Schrödinger's equation. That is, $u(n_1/x_1)u(n_2/x_2) \cdots u(n_N/x_N)$ is an approximate solution. But it is not antisymmetric in the electrons, so that it does not satisfy the exclusion principle. To build up an antisymmetric solution, we first note that we still have an approximate solution, connected with the same energy value, if we interchange any two x's, obtaining for example $u(n_1/x_2)\ u(n_2/x_1) \cdots u(n_N/x_N)$. We still have an approximation with the same energy if we make a linear combination of any such solutions. Then we can make the one possible combination which is antisymmetric, and it will both satisfy the exclusion principle, and will be an approximate solution of Schrödinger's equation. This combination is conveniently written as a determinant:

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[7] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928). See also J. C. Slater, Phys. Rev. **32**, 339 (1928) for discussion of Hartree's method and application of some of present results to it.

$$\begin{vmatrix} u(n_1/x_1) & u(n_1/x_2) & \cdots & u(n_1/x_N) \\ \cdot & \cdot & \cdots & \cdot \\ u(n_N/x_1) & u(n_N/x_2) & \cdots & u(n_N/x_N) \end{vmatrix}$$

It is obviously antisymmetric, for interchanging, say, x_1 and x_2 interchanges two columns of the determinant, which by a familiar property merely changes the sign. It can be shown that it is the only antisymmetric combination of these functions. And it leads at once to the familiar interpretation of the exclusion principle. For if two of the functions had the same quantum numbers (say $n_1 = n_2$, symbolizing equality of four quantum numbers), then the corresponding rows of the determinant would be identical (since they contain the functions $u(n_1/x_1) = u(n_2/x_1)$, $u(n_1/x_2) = u(n_2/x_2)$, etc.) and by another familiar rule, the determinant will vanish. Thus there is no solution corresponding to the case where two electrons have the same set of quantum numbers. Further, the determinant treats all electrons alike; hence we cannot count as separate two states which differ only by the interchange of the quantum numbers of two electrons. Our exclusion principle then coincides with the one previously described.

We now have, corresponding to each set of quantum numbers, or to each independent bracket expression of quantum numbers (as given in Table I), which is allowed by Pauli's principle, a single, antisymmetric function of the electrons, which is an approximate solution of Schrödinger's equation. Our next task is, beginning with this, to introduce the interaction between the various angular momenta, and to try to improve the agreement with Schrödinger's equation, without destroying the property of antisymmetry. We use essentially the method of perturbations. The fundamental result of this method is that, if we take the approximate but incorrect wave function, and compute the matrix of the real energy with respect to this, the diagonal terms of this matrix are good approximations to the actual energy values of the problem. The errors remaining are of the order of the square of the ratio of non-diagonal to diagonal terms. Since we can easily show in our case that the non-diagonal terms here are really small, this method will give a good approximation to the energy values. We are then to take the real energy operator (involving the interactions between electrons, rather than with fictitious central fields), find its matrix with respect to the wave functions already determined and take these diagonal terms as energy levels.

There is, however, one case in which our criterion for the accuracy of this approximation is not valid. This is the case where a number of terms lie close together. Then in the first place one can no longer say that the errors are as small as we have assumed; in the second place, since we are generally interested in the energy differences between the neighboring terms, we really demand a much greater accuracy than usual, to give this difference correctly. Thus this case—that of degeneracy—demands special treatment. We see that, in our case, we actually meet this difficulty, for the various wave functions with the same values of n's and l's, but different m_l's and m_s's, have very nearly the same energy, and yet the energy differences, giving the separations between multiplet levels, are just what we wish to find. Thus the problem of degeneracy is the essential part of the calculation for complex spectra. We may describe the situation this way: the non-diagonal energy terms connected with transitions between states with different n's and l's for the electrons are negligible; but those between states with the same n's and l's but different m_l's although they may be no greater numerically, are not negligible for our purpose. This situation can be described graphically. Suppose we make a scheme for the energy matrix, giving stationary states (the incorrect ones that we determine from the central field, denoted by the numbers $n_1 \cdots m_{sN}$) along the two sides of a square array, and putting in the matrix components. Then if we arrange together all terms with one set of n's and l's, then those with another set, and so on, we see that the matrix components in the double shaded regions

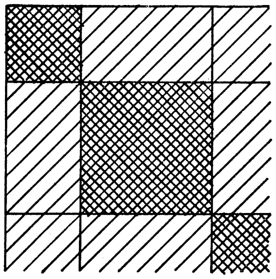

FIG. 2

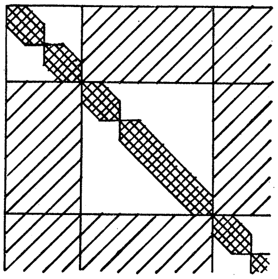

FIG. 3

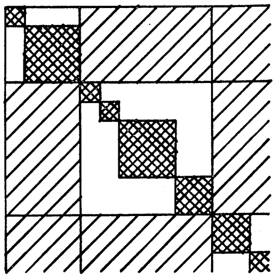

FIG. 4

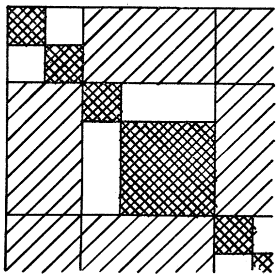

FIG. 5

Figs. 2–5. Figures 2, 3, 4 represent the energy matrix schematically. In Fig. 2, it is with respect to the unperturbed wave functions. The terms in the double shaded squares represent transitions between two states with the same electron quantum numbers. These terms are all significant; those outside the squares are negligible. In Fig. 3 we have made the linear combinations to the perturbed wave functions, reducing each square to a diagonal matrix. Fig. 4 is with respect to unperturbed wave functions, as is Fig. 2; but we take account of the fact that there are no components between states of different $\sum m_l$, $\sum m_s$. In Fig. 4, energy levels are arranged according to the values of $\sum m_l$, $\sum m_s$. Fig. 5 (see Note 3) represents the matrix of angular momentum, in the final perturbed wave functions. Each square represents a separate multiplet. In Figs. 3 and 5 the terms are arranged according to multiplets.

of Fig. 2 are all important (even the non-diagonal ones); but those in the singly shaded regions are negligible. The method of treatment is now this: we take a particular square of the matrix, as A, coming from transitions between different states with the same n's and l's. And, by linear combinations of the wave functions connected with these states, we reduce the matrix to a diagonal one. This can always be done for a finite matrix. Then we do the same thing with each such double-shaded square. The result after that is then a matrix of the form shown in Fig. 3. Here the only important non-diagonal terms have disappeared; so that we can take the diagonal terms as the approximate energy values of the real problem, with assurance that the errors are not large. We observe that, after this is done, there will still be just as many wave functions connected with each set of values of the n's and l's as before.

In our problem of complex spectra, there is a feature which greatly simplifies the calculation. For we shall prove[8] that the energy has no matrix components connected with transitions in which $\sum m_l$ or $\sum m_s$ change (if we neglect the magnetic energy, as we are doing for the present). To show the effect of this graphically, we can arrange the terms, first according to the n's and l's, as we have done; but under each such classification, we can arrange according to $\sum m_l$ and $\sum m_s$. Then the original energy matrix really has the simplified form shown in Fig. 4. And the process of removing the important non-diagonal terms reduces to separate linear combinations between the functions of each set having a given set of n's, l's, $\sum m_l$, and $\sum m_s$. Generally the number of functions actually present in one of these groups is very small; thus the problem by this method becomes very simple, and can be readily carried out. As a result of it, we see that the number of states with a given set of n's and l's, and a given $\sum m_l$ and $\sum m_s$, remains unchanged as we apply the interaction between angular momenta. And this is the essential point required in the classification of the terms.

3. The essential features of the perturbation theory as applied to complex atoms have been described; and we can now make connections with Hund's scheme for classifying the terms. Each unperturbed wave function can be described by its set of $(n\ l\ m_l\ m_s)$ for each electron (Pauli's principle being actually satisfied by our condition of antisymmetry). Then, just as before, we can make a table of all the possible terms with any set of n's and l's; we can find $\sum m_l$ and $\sum m_s$ for each of the terms; and we can make a diagram, as before, plotting $\sum m_l$ against $\sum m_s$, obtaining just the sort of point diagram that was shown in Fig. 1, b or c. The small square arrays of matrix components, in Fig. 4, are just the components between different terms represented by coincident points in Fig. 1, b and c. The components between terms lying at different points on the $\sum m_l$—$\sum m_s$ diagram are zero. Now we have just proved that, even when the interactions are considered, we still have the same diagram representing the number of states with each set of $\sum m_l$ and $\sum m_s$. To verify Hund's method completely, we need only show that we can correctly break up this diagram into a number of separate

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[8] See Note 1 for the proof.

ones, as Fig. 1, d—i, each representing a separate multiplet. Obviously we can separate the diagram into rectangular arrays of points (that is, sets of wave functions with particular values of $\sum m_l$ and $\sum m_s$), but there are other conditions that must be satisfied to make these wave functions really represent a multiplet.

In looking for the conditions that a set of wave functions must satisfy to represent a multiplet, we first observe that, so long as we neglect magnetic energies, they must all have the same energy value. Now after we have made our linear combinations, we shall have perfectly definite wave functions, each with a perfectly definite energy value (the diagonal terms in Fig. 3). Without proof, it is not obvious that we can pick out sets of functions, with different $\sum m_l$ and $\sum m_s$, but all with the same energy. Even if we can (and we shall prove that it is possible),[9] the set of functions must satisfy further conditions. Somehow we must work in the fact that they all represent the same vector L, and the same S, but with different orientations in space. Now the wave functions corresponding to an angular momentum vector with different orientations have perfectly definite relations, which are expressed by computing the matrix components of the angular momentum. If, then, our group of terms of the same energy really is to represent a multiplet, the matrix of angular momentum must also have the required form. But we shall prove that this also is the case.[9] Thus, with these proofs given, we see that we have a perfect right to separate the wave functions into a group of multiplets, as Hund does. Since the method of doing this is unique, the result must give precisely the same classification of multiplets that Hund finds. And since at present we wish only classification, we need not actually make the linear combinations, and get the diagonal matrix of H, at all.

It remains to be proved that the terms, after making the proper linear combinations, really can be divided up into groups of terms, having the following properties: every wave function of the group has the same energy value; and the angular momentum matrix has just the same values that it would if the wave functions referred to the vectors L and S with their various orientations in space. The details of the proof are given in the notes[9]; but we can state the essential features. First we show, by fundamental methods, that the total angular momentum matrix can have components only between states of the same energy. Since we can show that the angular momentum matrix is not diagonal, this proves that there must be at least several states of each energy, in order that the angular momentum can have components between them. This breaks up the terms associated with a given set of n's and l's into sets each of the same energy. Next we show that each of these sets is just the sort we need for a multiplet. We do this by detailed consideration of the angular momentum matrix; the essential point being that the entire matrix can be determined uniquely from certain commutation relations between the x, y, z components of the angular momentum vector, and that these relations are just the same for the whole atom as for a single angular momentum vector, so that we must have just the same matrix. We then

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[9] See Note 2.

have the complete proof that the wave functions of the atom really break up into sets each having all the properties of a multiplet; the M_L—M_S diagram of such a multiplet is just as we assumed in the first section; and the result is that the method of finding what multiplets arise from any configuration of electrons, is precisely the method of Hund.

PART 2. DETERMINATION OF THE ENERGIES

1. To find the energy values of the multiplets, the natural procedure is to solve the various problems of linear combination encountered above, find the correct wave functions, and compute the diagonal terms of the energy with respect to them. But we can find a simpler way, a way that even here will allow us to omit the actual calculation of the wave functions altogether. This is done by the use of the principle that the sum of a number of energy values is in some cases not changed by applying a perturbation, even if the individual values are. The principle is this: given a set of wave functions $u_1 \cdots u_i$; make a set of orthogonal linear combinations of them, $u_1' \cdots u_i'$. Consider the diagonal terms of a matrix, as the energy matrix, referred to the original wave functions: say $E_1 \cdots E_i$. Consider also the diagonal terms of the matrix of the same function, referred to the new wave functions, as $E_1' \cdots E_i'$. Then $E_1 + \cdots + E_i = E_1' + \cdots + E_i'$. In our case, we can use this as follows. We consider a set of terms, all with the same n's, l's, $\sum m_l$, $\sum m_s$ (that is, the terms connected with a small square in Fig. 4, or with coincident points in Fig. 2b and c). Before making our linear combinations, we can easily calculate the diagonal terms of the energy. We can add these terms for all the wave functions. Then the sum is equal to the sum of the corresponding energy values after making the linear combinations; that is, it is the sum of certain energy values that we wish to calculate. By proper use of this method, we can generally get the energies of all the multiplets.

To make the process clear, we shall illustrate by the case of two equivalent p electrons, shown in Fig. 2c. We compute the energy of the function $\sum m_s = 0, \sum m_l = 2$; that is, the energy of the configuration $\{(n11)\}\ \{(n11)\}$. But there is only one function connected with this point in the diagram. Hence the sum degenerates to one term. The process of making linear combinations is not necessary here; the corresponding square matrix array in Fig. 4 has but one row and column. Thus the energy we have found is also the energy of the term after interaction is considered; and comparison with (f) shows that it is the energy of the ^1D multiplet. Similarly the point $\sum m_s = 1$, $\sum m_l = 1$, gives the energy of ^3P. Again, $\sum m_s = 1, \sum m_l = 0$ or ± 1, and $\sum m_s = -1\ \sum m_l = 1,\ 0,\ -1$, should all give the energy of P; and in consequence of certain identities between the energy matrix components, these actually do give the same result as before. Also, the point $\sum m_s = 0$, $\sum m_l = 1$, has two wave functions, for the states $\{(n\ 1\ 0)\}\ \{(n1\ 1)\}$ and $\{(n1\ 1)\}\ \{(n1\ 0)\}$. We calculate the energies of these terms, and add. And the result should, and does, come out to be the sum of the ^1D and ^3P energies. Finally, the point $\sum m_l = 0, \sum m_s = 0$ has three wave functions. We add their energies, and the result should be the sum of the energies of

^1D, ^3P, and ^1S. Since the first two of these energies are known, we need only subtract them from the sum to get the energy of ^1S. Thus the energies of all the multiplets are computed, without finding any perturbed wave functions at all. It is readily seen that extension of the same scheme will give complete information in all cases except where there is more than one multiplet of the same kind; for example, if a given configuration of electrons contains two ^2D multiplets, the method will give only the sum of the two terms. To get the individual terms, we must carry through the more elaborate scheme of taking linear combinations. But such cases are not found among the more important terms, so that in practical use the limitation is not important.

For actual use, the essential step is to find the energy values referred to the original wave functions; then it is simply a matter of adding and subtracting to get the energies of the multiplets. This is merely a problem of integration; for we know the original wave functions (they are the determinants mentioned above), and we can easily find the matrix components of energy with respect to them. The process is somewhat complicated, however, in many cases, and a careful arrangement of the arithmetic simplifies it greatly. To work out the actual method properly, we shall have to go more into detail than we have about the whole problem. This calculation will be made in sections 2 and 3; finally we give a number of examples of calculation of energy in section 4.

2. Our problem in the present section is this: to compute the diagonal term of the energy with respect to one of the approximate wave functions, written as a determinant, which we discussed earlier. If H represents the energy operator, and

$$u = \begin{vmatrix} u(n_1/x_1) & \cdots & u(n_1/x_N) \\ \cdot & \cdots & \cdot \\ u(n_N/x_1) & \cdots & u(n_N/x_N) \end{vmatrix}$$

is the wave function, we then have as the desired diagonal term

$$\frac{\int u^* H u dv}{\int u^* u dv}.$$

The functions u are determinants; that is, sums of the $N!$ terms formed from the product $u(n_1/x_1) \cdots u(n_N/x_N)$ by carrying out all permutations of the coordinates $x_1 \cdots x_N$, even permutations having the coefficient $+1$, odd ones the coefficient -1. The product u^*u is then a double sum, and each of the integrals would be likewise; except that, in consequence of orthogonality relations, they really reduce to single sums, of which all the terms are identical.

We consider first the energy integral. The energy operator H consists, as we shall see, of three parts: first, a constant, which we need consider no further; second, a sum of terms each depending on the coordinates of a single electron, and all the same in form, which we can write $H(x_1)+\cdots+H(x_N)$; third, a sum of terms (the Coulomb repulsions) each depending on the coordinates of two electrons, which we can write explicitly as Σ(all pairs) e^2/r, where r is the distance between the two. The whole integral then consists of a constant, and two triple sums, two of the summations being over the permutations found in u and u^*, the third over the terms in the energy operator. Consider a single term out of this triple sum, of the sort connected with the coordinates of just one electron. Then, if the permutations involved in u and u^* are different, at least two x's must have different quantum numbers in the product; for example, we may have

$$u^*(n'/x_k)u^*(n''/x_l)u(n'''/x_k)u(n''''/x_l),$$

where n' is different from n''', and n'' different from n''''. When we multiply this by a function of one electron, and integrate, there will always be at least one product (as $u^*(n'/x_k)u(n'''/x_k)$), which by orthogonality will integrate to zero. Thus the only terms which are not zero are those where we have the same permutation in u and in u^*; the double sum over permutations reduces to a single one. We are left, then, with

$$\Sigma(\text{permutations of } x_1\cdots x_N)\int u^*(n_1/x_1)\cdots u^*(n_N/x_N)$$
$$(H(x_1)+\cdots+H(x_N))u(n_1/x_1)\cdots u(n_N/x_N)dx_1\cdots dx_N.$$

A single integral from this sum, by normalization, immediately reduces to

$$\left[\int u^*(n_1/x_1)H(x_1)u(n_1/x_1)dx_1+\cdots+\int u^*(n_N/x_N)H(x_N)u(n_N/x_N)dx_N\right].$$

If we let these terms be $I(n_1),\cdots I(n_N)$, we see that the whole is simply the sum of the I's, counted $N!$ times; so that this part of the energy integral is $N!(I(n_1)+\cdots+I(n_N))$, where it will be observed that the sum of terms $H(x_i)$, each depending on the coordinates of one electron, has been changed into a sum of terms each depending on a single set of quantum numbers.

Next we take the terms e^2/r_{kl} in the energy. As before, we take a typical term of the triple summation. If it happens that the same permutation occurs both in u and u^*, then the integral will reduce to

$$\int u^*(n/x_k)u^*(n'/x_l)e^2/r_{kl}u(n/x_k)u(n'/x_l)dx_kdx_l,$$

which we will call $J(n;n')$. Each permutation will yield, from terms of this kind, the summation over all pairs x_kx_l; this reduces to the summation of J's over all pairs $n\ n'$; and the $N!$ permutations finally give, from terms of this sort, $N!\sum$(pairs of n's) $J(n;n')$. Next, it may be that the permutation in u^* differs from that in u by the interchange of two electron coordinates.

If in addition the term e^2/r_{kl} happens to refer to the particular coordinates x_kx_l which have been interchanged, we have an integral which reduces to

$$\int u^*(n/x_l)u^*(n'/x_k)e^2/r_{kl}u(n/x_k)u(n'/x_l)dx_kdx_l,$$

which we call $K(n;n')$. Such terms all occur with negative sign; for, since the permutation in u^* differs by one interchange from that in u, one of the terms is always an even, the other an odd, permutation, resulting in a coefficient -1 in the double sum. Then by a similar argument to that above, these terms yield a contribution $-N!\sum$(pairs of n's) $K(n;n')$ to the energy integral. Finally, if the term of u^* differs from that of u by more than a single interchange, there will always be at least one coordinate whose wave functions will integrate to zero on account of orthogonality, so that no other terms exist.

Finally we need the normalization integral $\int u^*u\,dv$. Formally, we can find this as we did the first part of the energy integral, replacing $H(x_1)+\ldots+H(x_N)$ by unity. This results in replacing $\sum I(n)$ by unity; so that the integral is just $N!$. Thus division by the normalization factor simply removes the factor $N!$ which occurs in each term of the energy integral. We have then, for the diagonal term of the energy which we desire, constant$+\sum(n\text{'s})I(n)+\sum$(pairs of n's) $J(n;n')-\sum$(pairs of n's)$K(n;n')$.

3. Now we must consider the exact form of the wave function, to compute I,J and K. In connection with this, we must answer the question which no doubt will be felt at this point, as to the part which the spin plays in the calculations. We begin by considering the individual functions $u(n_i/x_i)$. Each such function is a solution of Schrödinger's equation for an electron in a central field. Let the potential of such a field be $U(xyz)$. Then Schrödinger's equation is

$$H_1u=\left(-\frac{h^2}{8\pi^2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+U\right)u=\epsilon u.$$

Here u is a function of x, y, z, and certain coordinates representing the spin, depending parametrically on n, l, m_l, and m_s; ϵ is a function of the quantum numbers alone. To describe the spin, we proceed as Pauli[10] does: we use as a coordinate the component of the spin along our fixed axis, m_s (which thus appears both as quantum number and as coordinate). Thus we could write our equation

$$H_1u(n\,l\,m_l\,m_s/x\,y\,z\,m_s)=\epsilon(n\,l\,m_l\,m_s)u(n\,l\,m_l\,m_s/x\,y\,z\,m_s).$$

Since H_1 is independent of the spin coordinate m_s, (neglecting magnetic interactions), we can separate variables, writing u as a product of a function of xyz, and a function of m_s:

$$u(n\,l\,m_l\,m_s/x\,y\,z\,m_s)=u(n\,l\,m_l/x\,y\,z)u(m_s/m_s).$$

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[10] W. Pauli Jr., Zeits. f. Physik **43,** 601 (1927).

The function $u(m_s/m_s)$ is to be interpreted as follows: m_s (the quantum number) can have two possible values, $\pm\frac{1}{2}$, and we have a different wave function for each quantum number. For example, we may have $u(\frac{1}{2}/m_s)$. But now assuming that the quantum number is $\frac{1}{2}$, we know that the wave function is different from zero only if the spin points along the positive axis, so that m_s (the coordinate) is $\frac{1}{2}$; for $m_s = -\frac{1}{2}$, there is no wave function. Thus $u\ (\frac{1}{2}/\frac{1}{2}) = 1$, $u(\frac{1}{2}/-\frac{1}{2}) = 0$. We can then write $u(\frac{1}{2}/m_s) = \delta\ (\frac{1}{2}/m_s)$. Similarly $u(-\frac{1}{2}/m_s) = \delta(-\frac{1}{2}/m_s)$; and we can write the whole symbolically as $u(m_s/m_s) = \delta(m_s/m_s)$. We now have

$$u(n\ l\ m_l\ m_s/x\ y\ z\ m_s) = u(n\ l\ m_l/x\ y\ z)\delta(m_s/m_s).$$

And for the first factor, the equation is

$$H_1 u(n\ l\ m_l/x\ y\ z) = \epsilon(n\ l)u(n\ l\ m_l/x\ y\ z),$$

where, since the energy does not depend on m_l or m_s, we have left out those quantum numbers in describing ϵ.

The solution of the central field problem is well known. We separate variables in spherical coordinates $r\ \theta\ \phi$. Then we have

$$u(n\ l\ m_l/x\ y\ z) = R(n\ l/r)\Theta(l\ m_l/\theta)\,\Phi(m_l/\phi)$$

where

$$\Theta(l\ m_l/\theta) = \left[\frac{(2l+1)(l-|m_l|)!}{(l+|m_l|)!}\right]^{1/2} P_l^{|m_l|}(\cos\theta)$$

where

$$P_l^{|m_l|}(\cos\theta) = \frac{1}{2^l l!}\sin^{|m_l|}\theta\frac{d^{|m_l|+l}(-\sin^2\theta)^l}{d(\cos\theta)^{|m_l|+l}}$$

and

$$\Phi(m_l/\phi) = e^{im_l\phi}/(2\pi)^{1/2}.$$

Thus we have

$$u(n\ l\ m_l\ m_s/x\ y\ z\ m_s) = R(n\ l/r)\Theta(l\ m_l/\theta)\,\Phi(m_l/\phi)\delta(m_s/m_s).$$

To proceed further, we must investigate the value of H operating on the product of u's. By definition,

$$H = -\frac{h^2}{8\pi^2 m}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)+V,$$

where V is the potential energy, given by

$$V = \sum_{i=1}^{N}\left(-\frac{Ze^2}{r_i}\right)+\sum_{1}^{N}(i>j)\frac{e^2}{r_{ij}},$$

where r_i is the distance of the ith electron from the nucleus, r_{ij} the distance between the ith and jth electrons. Thus we have

$$Hu(n_1/x_1)\cdots u(n_N/x_N)=-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2 u(n_1/x_1)}{\partial x_1^2}+\frac{\partial^2 u(n_1/x_1)}{\partial y_1^2}+\frac{\partial^2 u(n_1/x_1)}{\partial z_1^2}\right)u(n_2/x_2)\cdots u(n_N/x_N)\cdots+Vu(n_1/x_1)\cdots u(n_N/x_N).$$

But by our assumptions,

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2 u(n_1/x_1)}{\partial x_1^2}+\frac{\partial^2 u(n_1/x_1)}{\partial y_1^2}+\frac{\partial^2 u(n_1/x_1)}{\partial z_1^2}\right)=(\epsilon(n_1)-U(x_1))u(n_1/x_1),$$

etc. Thus we are left with

$$Hu(n_1/x_1)\cdots u(n_N/x_N)=\left[\sum_{i=1}^{N}(\epsilon(n_i)-U(x_i))+V\right]u(n_1/x_1)\cdots u(n_N/x_N).$$

This is of the form used above: Constant $+\sum H(x)+\sum e^2/r$, where constant $=\sum(n)\epsilon(n)$, and $H(x)=-U(x)-Ze^2/r$.

We are now ready to compute the integrals I, J, and K. We must first note that by integrating over the coordinates of one electron, we really mean integrating over the $dx\,dy\,dz$, and summing over the spins:

$$\int dv\equiv\sum_{-1/2}^{1/2}(m_s)\int dxdydz.$$

Thus, for example, we have the normalization and orthogonality of the individual wave functions:

$$\begin{aligned}&\int u^*(n'/x)u(n''/x)\\&\equiv\sum_{-1/2}^{1/2}(m_s)\delta(m_s'/m_s)\delta(m_s''/m_s)\\&\qquad\int u^*(n'l'm_l'/xyz)u(n''l''m_l''/xyz)dxdydz\\&=\delta(m_s'/m_s'')\delta(n'l'm_l'/n''l''m_l'').\end{aligned}$$

This orthogonality is all that is needed in the proofs of the preceding paragraphs.

For the integral I, we have

$$I(nlm_lm_s)=\sum_{-1/2}^{1/2}(m_s)\delta(m_s/m_s)\delta(m_s/m_s)\int u^*(nlm_l/xyz)H(xyz)u(nlm_l/xyz)dxdydz.$$

The summation over m_s merely reduces to the factor unity, independent of m_s. When we insert the value of $H(xyz)$, we note that the result is also independent of m_l; for H is a function of r only, the functions of angles integrate to unity, and we are left with

$$I(nlm_lm_s)=I(nl)=-\int R^2(nl/r)(U(r)+Ze^2/r)4\pi r^2dr.$$

Next we are to find J and K. For J, we have

$$\begin{aligned}J(nlm_lm_s\,;\,n'l'm_l'm_s')\\ =\sum_{-1/2}^{1/2}(m_s)_k\sum_{-1/2}^{1/2}(m_s)_l\ \delta(m_s/(m_s)_k)\delta(m_s'/(m_s)_l)\delta(m_s/(m_s)_k)\delta(m_s'/(m_s)_l)\\ \int u^*(nlm_l/x_ky_kz_k)u^*(n'l'm_l'/x_ly_lz_l)e^2/r_{kl}u(nlm_l/x_ky_kz_k)u(n'l'm_l'/x_ly_lz_l)\\ dx_kdy_kdz_kdx_ldy_ldz_l.\end{aligned}$$

The summation again reduces to unity, independent of m_s and m_s'. Then our quantity reduces to the integral, which we can write

$$J(nlm_lm_s;n'l'm_l'm_s')=J(nlm_l;n'l'm_l').$$

Similarly we have

$$\begin{aligned}K(nlm_lm_s;n'l'm_l'm_s')\\ =\sum_{-1/2}^{1/2}(m_s)_k\sum_{-1/2}^{1/2}(m_s)_l\ \delta(m_s/(m_s)_l)\delta(m_s'/(m_s)_k)\delta(m_s/(m_s)_k)\delta(m_s'/(m_s)_l)\\ \int u^*(nlm_l/x_ly_lz_l)u^*(n'l'm_l'/x_ky_kz_k)e^2/r_{kl}u(nlm_l/x_ky_kz_k)u(n'l'm_l'/x_ly_lz_l)\\ dx_kdy_kdz_kdx_ldy_ldz_l.\end{aligned}$$

The summation reduces to $\delta(m_s/m_s')$; so that we are left with

$$K(nlm_lm_s;n'l'm_l'm_s')=\delta(m_s/m_s')K(nlm_l;n'l'm_l'),$$

where the integral is symbolized by the last K. We thus observe that these exchange integrals only exist for electrons with spins parallel to each other.

We are now to compute

$$J(nlm_l;n'l'm_l')$$

and

$$K(nlm_l;n'l'm_l')$$

We recall the expression for u previously given. Also we use the familiar expansion

$$\frac{1}{r(xx')}=\sum(k,m)\frac{(k-|m|)!}{(k+|m|)!}\ \frac{r(a)^k}{r(b)^{k+1}}P_k^{|m|}(\cos\theta)P_k^{|m|}(\cos\theta')\exp\,(im(\phi-\phi'))$$

where $r(xx')$ is the distance between (xyz) and $(x'y'z')$, and where $r(a)$ is the smaller, $r(b)$ the greater, of r and r'. Forming the expression for J, we have integrals of the form $\int_0^{2\pi}\exp(im\phi)d\phi$ which vanish unless $m=0$.

The double sum over k and m thus reduces to a single one over k, m being always zero. Then we easily have

$$J(nlm_l;n'l'm_l')=\sum(k)a^k(lm_l;l'm_l')F^k(nl;n'l')$$

where

$$a^k(lm_l;l'm_l')=\frac{(2l+1)(l-|m_l|)!}{(l+|m_l|)!}\,\frac{(2l'+1)(l'-|m_l'|)!}{(l'+|m_l'|)!}$$
$$\int_0^\pi[P_l^{|m_l|}(\cos\theta)]^2P_k^0(\cos\theta)\frac{\sin\theta}{2}d\theta$$
$$\int_0^\pi[P_{l'}^{|m'_l|}(\cos\theta')]^2P_k^0(\cos\theta')\frac{\sin\theta'}{2}d\theta'$$

and

$$F^k(nl;n'l')=e^2(4\pi)^2\int_0^\infty\int_0^\infty R^2(nl/r)R^2(n'l'/r')\frac{r(a)^k}{r(b)^{k+1}}r^2r'^2drdr'.$$

One notes that the a's can be computed once for all, in terms of the spherical harmonics; the special properties of the atom in question appear only in the integrals F.

In a similar way we form K. Here the integrals over ϕ are of the form $\int_0^{2\pi}\exp\, i(m_l-m_l'+m)\phi\, d\phi$, vanishing unless $|m|=|m_l-m_l'|$. Thus we have

$$K(nlm_l;n'l'm_l')=\sum(k)b^k(lm_l;l'm_l')G^k(nl;n'l'),$$

where

$$b^k(lm_l;l'm_l')=\frac{(k-|m_l-m_l'|)!}{(k+|m_l-m_l'|)!}\,\frac{(2l+1)(l-|m_l|)!}{(l+|m_l|)!}\,\frac{(2l'+1)(l'-|m_l'|)!}{(l'+|m_l'|)!}$$
$$\left[\int_0^\pi P_l^{|m_l|}(\cos\theta)P_l'^{\,|m_l'|}(\cos\theta)P_k^{|m_l-m_l'|}(\cos\theta)\frac{\sin\theta}{2}d\theta\right]^2$$

and

$$G^k(nl;\,n'l')=e^2(4\pi)^2\int_0^\infty\int_0^\infty R(nl/r)R(n'l'/r)R(nl/r')R(n'l'/r')\frac{r(a)^k}{r(b)^{k+1}}r^2r'^2drdr'.$$

Using the values of the associated spherical harmonics one can compute the various a's and b's; although the writer has not succeeded in setting up closed formulas for them, since this would involve the integrals of products of three spherical harmonics, an unfamiliar form.[11] We give a table, including all the coefficients involved with s, p, d electrons (that is, $l, l'\leq 2$).

We have now obtained the diagonal term of energy which we desired: in section 2 we have found it in terms of certain integrals I, J, K, and in section 3 we have evaluated those integrals. Before passing to the examples, we should note one fact: that in finding the energy differences between multiplets, one needs only the integrals J and K, which do not depend

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[11] See, however, J. A. Gaunt, l. c. Whether one has formulas or not, the table of values is certainly most convenient for computation.

Table of $a^k(lm_l; l'm_l')$.
(Note: in cases with two ± signs, the two can be combined in any of the four possible ways).

Electrons	l	m_l	l'	m_l'	$k=0$	2	4
ss	0	0	0	0	1	0	0
sp	0	0	1	±1	1	0	0
	0	0	1	0	1	0	0
pp	1	±1	1	±1	1	1/25	0
	1	±1	1	0	1	−2/25	0
	1	0	1	0	1	4/25	0
sd	0	0	2	±2	1	0	0
	0	0	2	±1	1	0	0
	0	0	2	0	1	0	0
pd	1	±1	2	±2	1	2/35	0
	1	±1	2	±1	1	−1/35	0
	1	±1	2	0	1	−2/35	0
	1	0	2	±2	1	−4/35	0
	1	0	2	±1	1	2/35	0
	1	0	2	0	1	4/35	0
dd	2	±2	2	±2	1	4/49	1/441
	2	±2	2	±1	1	−2/49	− 4/441
	2	±2	2	0	1	−4/49	6/441
	2	±1	2	±1	1	1/49	16/441
	2	±1	2	0	1	2/49	−24/441
	2	0	2	0	1	4/49	36/441

Table of $b^k(lm_l; l'm_l')$
(Note: in cases where there are two ± signs, the two upper, or the two lower, signs must be taken together).

Electrons	l	m_l	l'	m_l'	$k=0$	1	2	3	4
ss	0	0	0	0	1	0	0	0	0
sp	0	0	1	±1	0	1/3	0	0	0
	0	0	1	0	0	1/3	0	0	0
pp	1	±1	1	±1	1	0	1/25	0	0
	1	±1	1	0	0	0	3/25	0	0
	1	±1	1	∓1	0	0	6/25	0	0
	1	0	1	0	1	0	4/25	0	0
sd	0	0	2	±2	0	0	1/5	0	0
	0	0	2	±1	0	0	1/5	0	0
	0	0	2	0	0	0	1/5	0	0
pd	1	±1	2	±2	0	2/5	0	3/245	0
	1	±1	2	±1	0	1/5	0	9/245	0
	1	±1	2	0	0	1/15	0	18/245	0
	1	±1	2	∓1	0	0	0	30/245	0
	1	±1	2	∓2	0	0	0	45 ~~9~~/245	0
	1	0	2	±2	0	0	0	15/245	0
	1	0	2	±1	0	1/5	0	24/245	0
	1	0	2	0	0	4/15	0	27/245	0
dd	2	±2	2	±2	1	0	4/49	0	1/441
	2	±2	2	±1	0	0	6/49	0	5/441
	2	±2	2	0	0	0	4/49	0	15/441
	2	±2	2	∓1	0	0	0	0	35/441
	2	±2	2	∓2	0	0	0	0	70/441
	2	±1	2	±1	1	0	1/49	0	16/441
	2	±1	2	0	0	0	1/49	0	30/441
	2	±1	2	∓1	0	0	6/49	0	40/441
	2	0	2	0	1	0	4/49	0	36/441

explicitly on the central field U at all. The integral I is needed only in finding the center of gravity of a multiplet system. The reasón is that I depends only on n and l, and so is the same for all the various degenerate states with which we start our perturbation problem.

4 *Examples. One electron outside closed shells.* We need take but one case: a $3p$ electron outside completed K and L shells. Thus the scheme of electrons is $(1s)^2(2s)^2(2p)^6 3p$. We must now consider the various antisymmetric wave functions which are possible. By the method of symbolization mentioned above, in which we group in separate brackets the quantum numbers of electrons with parallel and antiparallel spins, we see that there are six wave functions, which we give below, together with the values of $\sum m_l$ and $\sum m_s$:

		Σm_l	Σm_s
$\{(100)(200)(211)(210)(21-1)(311)\}$	$\{(100)(200)(211)(210)(21-1)\}$	1	$\frac{1}{2}$
$\{(100)(200)(211)(210)(21-1)(310)\}$	$\{(100)(200)(211)(210)(21-1)\}$	0	$\frac{1}{2}$
$\{(100)(200)(211)(210)(21-1)(31-1)\}$	$\{(100)(200)(211)(210)(21-1)\}$	-1	$\frac{1}{2}$
$\{(100)(200)(211)(210)(21-1)\}$	$\{(100)(200)(211)(210)(21-1)(311)\}$	1	$-\frac{1}{2}$
$\{(100)(200)(211)(210)(21-1)\}$	$\{(100)(200)(211)(210)(21-1)(310)\}$	0	$-\frac{1}{2}$
$\{(100)(200)(211)(210)(21-1)\}$	$\{(100)(200)(211)(210)(21-1)(31-1)\}$	-1	$-\frac{1}{2}$

We note that the arrangement of $\sum m_l, \sum m_s$, is just that for a single multiplet ^2P. There are no cases in which more than one term has a given value of $\sum m_l, \sum m_s$; thus there is no need of applying the sum rule at all. The diagonal terms of the energy, computed with respect to these six wave functions, should give directly the energies of the six terms of the multiplet. But now we come back to our general principle; these six terms must have the same energy. We must actually compute the energies by our rules, and see that they are the same in each of the six functions. As has been mentioned before, we need only use the J and K terms. These terms, we recall, were $\sum(\text{pairs})J - \sum(\text{pairs with par. spins})K$. Now in these sums, many terms are the same for each of the six wave functions; all the terms, in fact, relating to pairs of electrons both in the closed shells. These terms can exert no influence on the multiplet separations, or anything of that sort. Thus we can leave them out, for our present purpose, as we left out the terms depending on the integrals I. The only terms we need retain are those in which our $3p$ electron is a member of the pairs. Thus for the first wave function we must compute the following:

$$
\begin{aligned}
&2J(311;100)+2J(311;200)+2J(311;211)+2J(311;210)+2J(311;21-1)\\
&\qquad -K(311;100)-K(311;200)-K(311;211)-K(311;210)-K(311;21-1).
\end{aligned}
$$

For the second and third, we substitute respectively 310, 31-1 in place of 311; the fourth, fifth, and sixth evidently give the same three results already given. Let us now group these terms according to the shells that the $3p$'s interact with:

$$
\begin{aligned}
&1s: 2J(311;100)-K(311;100)\\
&2s: 2J(311;200)-K(311;200)\\
&2p: 2J(311;211)+2J(311;210)+2J(311;21-1)-K(311;211)\\
&\qquad\qquad -K(311;210)-K(311;21-1).
\end{aligned}
$$

For the interaction with $1s$, we have

$$\begin{aligned}
2J(311;100) &= 2\sum(k)a^k(11;00)F^k(31;10) = 2F^0(31;10)\\
-K(311;100) &= -\sum(k)b^k(11;00)G^k(31;10) = -\tfrac{1}{3}G^1(31;10).
\end{aligned}$$

Before going further, let us find the corresponding terms in the interaction of a 310 electron with the $1s$ shell:

$$\begin{aligned}
2J(310;100) &= 2\sum(k)a^k(10;00)F^k(31;10) = 2F^0(31;10)\\
-K(310;100) &= -\sum(k)b^k(10;00)G^k(31;10) = -\tfrac{1}{3}G^1(31;10).
\end{aligned}$$

That is, the interaction integrals of an outer p electron with an s shell are the same whether the p electron has $m_l=1$ or 0 (or -1, as one immediately verifies). We shall show the same result to hold for the interaction with the $2p$ shell: for the (311) electron, the terms are

$$\begin{aligned}
&2J(311;211)+2J(311;210)+2J(311;21-1)-K(311;211)\\
&\quad -K(311;210)-K(311;21-1)\\
&\quad = 2\sum(k)a^k(11;11)F^k(31;21)+2\sum(k)a^k(11;10)F^k(31;21)\\
&\qquad +2\sum(k)a^k(11;1-1)F^k(31;21)-\sum(k)b^k(11;11)G^k(31;21)\\
&\qquad -\sum(k)b^k(11;10)G^k(31;21)-\sum(k)b^k(11;1-1)G^k(31;21)\\
&\quad = 2\sum(k)(a^k(11;11)+a^k(11;10)+a^k(11;1-1)F^k(31;21)\\
&\qquad -\sum(k)(b^k(11;11)+b^k(11;10)+b^k(11;1-1))G^k(31;21)\\
&\quad = 6F^0(31;21)-G^0(31;21)-\tfrac{2}{5}G^2(31;21).
\end{aligned}$$

Similarly for the (310) electron interacting with the $2p$ shell, we have

$$\begin{aligned}
&2\sum(k)(a^k(10;11)+a^k(10;10)+a^k(10;1-1)F^k(31;21)\\
&\quad -\sum(k)(b^k(10;11)+b^k(10;10)+b^k(10;1-1))G^k(31;21)\\
&\qquad = 6F^0(31;21)-G^0(31;21)-\tfrac{2}{5}G^2(31;21).
\end{aligned}$$

This agrees with the former value, showing that the interaction of either a 311 or a 310 (or, by a simple extension, a 31–1) electron with a completed p shell, give the same result, independent of m_l. Putting all these results together, all six levels of the ^2P multiplet give the same energy, by direct computation. Of course, this is merely a check of our general theorem that all the levels of any multiplet must have the same energy. The special properties of the a's and b's which lead to this result could be proved by use of that theorem.

Any configuration outside closed shells. We have just seen that the interaction energy of a single electron with a closed shell is independent of the m_l of the outer electron. We have proved this by direct computation for a p electron interacting with s or p shells, but we could extend the result to the general case, from our general theorem that all the terms of any multiplet have the same energy. But this has an important bearing on our general problem. For in any case an atom consists of a certain number of electrons outside closed shells, and the central closed shells. In the various unperturbed wave functions which we are to use, the outer electrons have different m_l's. In the energies of the terms, we are to compute all J's and K's connected with pairs of electrons in the atom. We have already seen that all pairs, both of which are in closed shells, will give identical contributions to each of the unperturbed terms. But now we can go further: all sets of pairs, in which one is an outer electron, the other one of the electrons of a closed shell, will, when summed over the electrons of the closed shell, give the same result for each unperturbed state. That is, as far as multiplet separations are concerned, closed shells exert no influence at all; they affect only the position of the whole set of multiplet terms. It is well known that the classification of the terms is independent of the existence of closed shells; this proves that the energy relations also depend only on the outer electrons.[12] For the rest of our examples, then, we shall consider only those electrons which are outside closed shells.

Two electrons outside closed shells, one in s state (helium, alkaline earths). Suppose we have the scheme (ns), $(n'p)$, for example. There are, in this case, the unperturbed wave functions symbolized by

	Σm_l	Σm_s
$\{(n\,0\,0)(n'\,1\,1)\}\ \{\quad\}$	1	1
$\{(n\,0\,0)(n'\,1\,0)\}\ \{\quad\}$	0	1
$\{(n\,0\,0)(n'\,1\,-1)\}\ \{\quad\}$	-1	1
$\{(n\,0\,0)\}\ \{(n'\,1\,1)\}$	1	0
$\{(n\,0\,0)\}\ \{(n'\,1\,0)\}$	0	0
$\{(n\,0\,0)\}\ \{(n'\,1\,-1)\}$	-1	0
$\{(n'\,1\,1)\}\ \{(n\,0\,0)\}$	1	0
$\{(n'\,1\,0)\}\ \{(n\,0\,0)\}$	0	0
$\{(n'\,1\,-1)\}\ \{(n\,0\,0)\{$	-1	0
$\{\quad\}\ \{(n\,0\,0)(n'\,1\,1)\}$	1	-1
$\{\quad\}\ \{(n\,0\,0)(n'\,1\,0)\}$	0	-1
$\{\quad\}\ \{(n\,0\,0)(n'\,1\,-1)\}$	-1	-1

By our general scheme of classification, we have a ^1P and ^3P term. The terms with $\sum m_l$, $\sum m_s$ equal respectively to (1 1), (0 1), (−1 1), (1 −1), (0 −1), (−1 −1), belong to the ^3P state. On the other hand, the remaining terms, as (1 0), are each degenerate. The sum of the energies of two such terms equals the sum of the ^1P and ^3P energy. Thus for example we have

$$^3P\colon \{(n\,0\,0)(n'\,1\,1)\}$$

$$^3P+{}^1P\colon \{(n\,0\,0)\}\{(n'\,1\,1)\}+\{(n'\,1\,1)\}\{(n\,0\,0)\}=2\{(n\,0\,0)\}\{(n'\,1\,1)\}.$$

That is, for the energies, we have

$$^3P\colon J(n\,0\,0;n'\,1\,1)-K(n\,0\,0;n'1\,1)$$

$$^3P+{}^1P=2J(n\,0\,0;n'\,1\,1).$$

Therefore $^1P=J(n\ 0\ 0;\ n'\ 1\ 1)+K(n\ 0\ 0;\ n'\ 1\ 1)$
The singlet and triplet are thus given by a definite value $\pm K(n\ 0\ 0;n'\ 1\ 1)$. This checks with Heisenberg's[13] calculation of this case; our integral K is readily seen to be the same exchange integral which he computes.

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[12] See W. Heitler, Zeits. f. Physik **46,** 70 (1928).

[13] W. Heisenberg, Zeits. f. Physik **39,** 499 (1926).

Shell of equivalent p electrons. (Elements C, N, O, F, etc.) p^2. This is the case shown in Fig. 1c. There are 15 wave functions, of which we give those with $\sum m_l \geq 0, \sum m_s \geq 0$; for simplicity we omit the total quantum number from our descriptions, so that (1 0), for example, stands for (n 1 0). Then, correlating the $\sum m_l$, $\sum m_s$ with the multiplets represented (from the figure), we have

Multiplet	M_l	M_s	Wave function
^1D	2	0	$\{(1\ 1)\}\quad\{(1\ 1)\}$
$^1D+{}^3P$	1	0	$\{(1\ 0)\}\quad\{(1\ 1)\}$
	1	0	$\{(1\ 1)\}\quad\{(1\ 0)\}$
$^1D+{}^3P+{}^1S$	0	0	$\{(1\ 1)\}\quad\{(1\ -1)\}$
	0	0	$\{(1\ 0)\}\quad\{(1\ 0)\}$
	0	0	$\{(1\ -1)\}\{(1\ 1)\}$
^3P	1	1	$\{(1\ 1)\ \ (1\ 0)\}\quad\{\quad\}$
^3P	0	1	$\{(1\ 1)\,(1\ -1)\}\quad\{\quad\}$

Now we have for the energies

$$^1D{:}\,J(n\,1\,1;n\,1\,1)=F^0(n\,1;\,n\,1)+\frac{1}{25}F^2(n\,1;n\,1)$$

$$^3P{:}\,J(n\,1\,1;n\,1\,0)-K(n\,1\,1;n\,1\,0)=F^0(n\,1;n\,1)-\frac{2}{25}F^2(n\,1;n\,1)-\frac{3}{25}G^2(n\,1;n\,1)$$

We note that, for equivalent electrons, the F's and G's of the same indices are equal. Hence

$$^3P=F^0(n\,1;n\,1)-\frac{5}{25}F^2(n\,1;n\,1).$$

We can check the same value from the other ^3P term ($\Sigma m_l=0$, $\Sigma m_s=1$) and from the two terms giving $^1D+{}^3P$. Finally we have

$$^1D+{}^3P+{}^1S{:}\,J(n\,1\,1;n\,1\,-1)+J(n\,1\,0;n\,1\,0)+J(n\,1\,-1;n\,1\,1)$$
$$=3F^0(n\,1;n\,1)+\frac{6}{25}F^2(n\,1;n\,1).$$

Therefore $^1S=F^0(n\,1;n\,1)+\dfrac{10}{25}F^2(n\,1;n\,1)$.

We note that the term $F^0(n\ 1;\ n\ 1)$ is common to all the levels; thus we can leave it out, as we have all the terms which do not affect the separation. We note from its definition that $F^2(n\ 1;\ n\ 1)$ is positive. Thus we see that of the three multiplets, the ^3P lies lowest, ^1D next, ^1S highest, in accordance with Hund's rule that the terms of largest L and S lie lowest. The separations are in a simple ratio: $^3P-{}^1D=6/25\ F^2(n\ 1;\ n\ 1)$, and $^1D-{}^1S=9/25\ F^2(n\ 1;\ n\ 1)$ so that the ratio is 2 to 3.

We should find an example in the lowest levels of C, $(1s)^2\ (2s)^2\ (2p)^2$; these levels, however, have not been observed, as far as the writer knows. For Si $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^2$, however, the term values are[14] $^3P=65{,}615$,

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[14] McLennan and Shaver, Roy. Soc. Canada **18**, 1, (1924). A. Fowler, Proc. Roy. Soc. **A123**, 422 (1929).

$^1D=59{,}466$, $^1S=50{,}370$, giving $^3P-{}^1D=6149$, $^1D-{}^1S=9096$, the first giving $F^2(3\ 1;\ 3\ 1)=25{,}602$, the second $F^2(3\ 1;\ 3\ 1)=25{,}267$, in good agreement.

p^3. The method is so similar to that used for p^2 that the calculations need not be given in detail. The multiplets are ^4S ^2D ^2P, the ^4S lying lowest and ^2P highest, again in agreement with Hund's rule. The separations are given by $^4S-{}^2D=9/25\ F^2(n\ 1;\ n\ 1)$ $^2D-{}^2P=6/25\ F^2(n\ 1;\ n\ 1)$. An example is found in the normal N spectrum, $(1s)^2$ $(2s)^2$ $(2p)^3$, observed by Compton and Boyce.[15] They find $^4S=117{,}345$, $^2D=98{,}143$, $^2P=88{,}537$,giving $^4S-{}^2D=19{,}200$, $^2D-{}^2P=9{,}600$. From the first, $F^2(2\ 1;\ 2\ 1)=53{,}400$, and from the second, it is 40,000; a somewhat poorer agreement than before, probably on account of the tighter binding of the electrons.

p^4. Here the relations prove to be as in p^2 as regards energy, as well as in the arrangement of terms: $^3P-{}^1D=6/25\ F^2(n\ 1;\ n\ 1)$ $^1D-{}^1S=9/25\ F^2(n\ 1;\ n\ 1)$. An example is normal O, $(1s)^2$ $(2s)^2$ $(2p)^4$. Here it is estimated[16] that, counting terms up from ^3P as zero, $^1D=25{,}500$, and $^1S=65{,}000$, giving $^3P-{}^1D=25{,}500$, $^1D-{}^1S=39{,}500$. From the first, $F^2(2\ 1;\ 2\ 1)=106{,}000$, and from the second 109,700, a very good agreement. It is interesting to note the increase in the integral from N to O on account of the tighter binding.

p^5 and p^6 yield each only one multiplet, so that they need not be considered.

Shell of equivalent d electrons (Iron group) d^2. The multiplets are ^3F ^3P ^1G ^1D ^1S. When we work out the separations, however, it appears that they are not arranged in this order; the singlet terms are anomalous, disobeying Hund's rule, in that the ^1D lies lower than ^1G. Except for this, however, the arrangement is as we should expect, ^3F lying below ^3P, and being the lowest term of the combination. The separations are given by

$$\begin{aligned}
{}^3F-{}^3P&=(135/441)\ F^2(n\ 2;\ n\ 2)-(75/441)\ F^4(n\ 2;\ n\ 2)\\
{}^3F-{}^1G&=(108/441)\ F^2(n\ 2;\ n\ 2)+(10/441)\ F^4(n\ 2;\ n\ 2)\\
{}^3F-{}^1D&=(45/441)\ F^2(n\ 2;\ n\ 2)+(45/441)\ F^4(n\ 2;\ n\ 2)\\
{}^3F-{}^1S&=(198/441)\ F^2(n\ 2;\ n\ 2)+(135/441)\ F^4(n\ 2;\ n\ 2)
\end{aligned}$$

The separations now depend on the two parameters $F^2(n\ 2;\ n\ 2)$ and $F^4(n\ 2;\ n\ 2)$, which bear no fixed relation to each other. Nevertheless we can estimate their relative magnitude. For by definition F^k is the integral of a certain function of r_1 and r_2, multiplied by $r_a{}^k/r_b{}^{k+1}$ where r_b is the greater, r_a the less, of r_1 and r_2. Thus increasing k necessarily decreases the integrand, and hence the function F: $F^4(n\ 2;\ n\ 2)<F^2(n2\ ;\ n\ 2)$. Rough calculation indicates that the decrease is about to a half. If then we provisionally take F^4 to be half of F^2, we have the separations in the ratio

$$\begin{aligned}
&{}^3F-{}^3P{:}\,135-37=\ 98 &\qquad &{}^3F-{}^1D{:}\ 45+22=\ 67\\
&{}^3F-{}^1G{:}\,108+\ 5=113 &\qquad &{}^3F-{}^1S{:}\,198+67=265.
\end{aligned}$$

The order of terms is thus expected to be ^3F ^1D ^3P ^1G ^1S.

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[15] K. T. Compton and J. C. Boyce, Phys. Rev. **33,** 145 (1929).

[16] McLennan, McLeod, and Ruedy, Phil. Mag. Sept., 1928, p. 558. These values are estimated from the energy level diagram in that paper.

Experimentally we find an example in the normal spectrum of Ti,[17] $(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^6\,(4s)^2\,(3d)^2$. Here the order of terms is in fact just what our calculation predicts, the exception to Hund's rule being found experimentally. The observed separations are approximately

$$^3F-{}^3P=\ 8500 \qquad {}^3F-{}^1D=\ 7200$$

$$^3F-{}^1G=12100 \qquad {}^3F-{}^1S=15100.$$

If we assume that F^4 is really half of F^2, these give $F^2(n\ 2;\ n\ 2)$ equal respectively to 38,000, 47,000, 41,000, 72,000, in fair agreement except for the last one. This last results from the ^1S, which is not nearly so far above the rest of the terms as the theory would indicate—probably because the second order corrections for this term would be large, and would have the effect of depressing it. The agreement with observations can be somewhat, but not much, improved by taking a slightly different ratio of F^4 to F^2.

$d^3..d^8$. We shall give only the lowest terms for the rest of the d shell. The terms of highest multiplicity prove to lie in general lower than the others, as the rule would predict. Of these, we have for d^3: $^4F\ {}^4P$; d^4, ^5D; d^5, ^6S; d^6, ^5D; d^7, $^4F\,{}^4P$; d^8, $^3F\,{}^3P$. Evidently the only cases where there are significant separations in the multiplets of highest multiplicity are the $d^2\ d^3\ d^7\ d^8$ F–P separations. When one calculates, one discovers the fact that all these are given by the same formula, $(135/441)F^2(n\ 2;\ n\ 2)-(75/441)F^4(n\ 2;\ n\ 2)$. This permits an interesting comparison with experiment: we can compare the observed separations for Ti (d^2), V(d^3), Co(d^7) and Ni (d^8). We should expect these to increase regularly with the number of d electrons. Experimentally this separation is about 8000 for Ti, 9500 for V, 14000 for Co, 15000 for Ni, indicating a fairly uniform increase of about 1000 to 1500 for the addition of one d electron.

Non-equivalent p's: Two *p's*: pp'. The multiplets are $^3D\ {}^3P\ {}^3S\ {}^1D\ {}^1P\ {}^1S$. The triplets are particularly interesting, and we give their separations. If the principal quantum numbers of the electrons are n and n', they are

$$^3D-{}^3P=-6/25F^2(n\ 1;\ n'\ 1)+2G^0(n\ 1;\ n'\ 1)-4/25G^2(n\ 1;\ n'\ 1)$$

$$^3D-{}^3S=9/25F^2(n\ 1;\ n'\ 1)-9/25G^2(n\ 1;\ n'\ 1).$$

The significant feature of these results is that they depend in such a complicated way on several integrals. That is, in a case like this— and it is the simplest set of multiplets that can be built up from non-equivalent electrons—we must not look for simple numerical relations between the separations, or even for a definite, fixed order for the terms. We may rather expect that, as we go from one element to another, the relative order of terms can change.

We find an example in N^+ $(1s)^2\,(2s)^2\,2p\,3p$.[18] Here the experimental separations are approximately $^3D-{}^3P=4000$ $^3D-{}^3S=2300$, disobeying Hund's rule, in that ^3S lies below ^3P. We can make from these figures a rough estimate of the integrals F and G. We note that G differs from F in having

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[17] H. N. Russell, Astroph. Jour. **66,** 283 (1927).

[18] A. Fowler, Proc. Roy. Soc. **A107,** 31 (1925).

the product $R(n/x_1)\ R(n'/x_1)$ in its integrand instead of $R^2(n/x_1)$. The first is less than the second—very much less if the orbits n and n' are of decidedly different size, for then either $R(n/x_1)$ or $R(n'/x_1)$ will be small through most of the range of x_1. Thus each G integral is small compared to the corresponding F. It is reasonable to suppose that G^0 is of the same order of magnitude as F^2. Further, G^2 will be smaller than G^0, by analogy with what we have already seen, and as a rough assumption we may take $G^2=\frac{1}{2}\ G^0$. Thus we have the two equations

$$4000=-(6/25)F^2+(48/25)G^0$$
$$2300=(9/25)F^2-(9/50)G^0,$$

giving $F^2(2\,1;3\,1)=7900$, $G^0(2\,1;3\,1)=3070$, $G^2(2\,1;3\,1)=1535$. These values are reasonable, but provide no definite check for the equations.

Five equivalent p's, one other p: p^5p'. Again we have $^3D\,^3P\,^3S\ ^1D\ ^1P\ ^1S$, by combination of the p' with the ^2P of p^5. But now it proves that the triplet separations are quite different, and have a much simpler formula. We have

$$^3D-{}^3P=(6/25)F^2(n\,1;n'\,1)$$
$$^3D-{}^3S=-(9/25)F^2(n\,1;n'\,1)$$

depending on only one parameter (the others all cancel out, seemingly, although perhaps not really, by chance). Thus we can predict definitely the order of terms: ^3S lies lowest, then ^3D, finally ^3P, in direct contradiction to Hund's rule. We find an example, however, in Ne $(1s)^2\ (2s)^2\ (2p)^5\ 3p$, Paschen's p terms,[19] and it definitely verifies the contradiction. Experimentally, Paschen's $2p_{10}$, which is the ^3S, lies well below any others. On account of the wide multiplet separations it is impossible to show any good check of the ratio 2:3 for the $^3D-{}^3P$ and $^3D-{}^3S$ separations. If one takes centers of gravity of Paschen's terms, one finds

$$^3D-{}^3P=570 \qquad {}^3D-{}^3S=-2023$$

the first giving $F^2(2\ 1;\ 3\ 1)=2370$, the second 5620. The correct figure is probably between these. It is interesting to note the agreement as to order of magnitude of this with the same one, 7900, for N^+.

NOTES

1. We wish to prove that the energy has no matrix components (taken with reference to the incorrect, approximate wave functions) connected with transitions in which $\sum m_l$ or $\sum m_s$ changes. The essential part of the proof is the demonstration that the energy operator H commutes with the operators connected with $\sum m_l$ or $\sum m_s$. For $\sum m_s$ the proof is obvious: $\sum m_s$ is a quantity depending only on the spins, H only on the coordinates, and operators depending on entirely independent quantities always commute. For $\sum m_l$, the essential point is that $\sum m_l$ is the operator connected with an infinitesimal rotation of space about the z axis, and on account of the fact that H is in-

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[19] F. Paschen, Ann. d. Physik **60**, 405 (1920).

dependent of orientation, such a rotation does not affect it, and so commutes with it. To be more specific, one can write the three components of angular momentum of an electron in operator form, using the operators for linear momentum. Put in spherical coordinates, the z component of angular momentum is represented by the operator $(h/2\pi i)\partial/\partial\phi$. Operating on a single electron wave function with the factor $e^{im_l\phi}$, this operator reduces to the multiplication by $m_l h/2\pi$, so that it has a diagonal matrix, and m_l measures the z component of angular momentum, in units $h/2\pi$. Then the operator connected with $\sum m_l$ is $-i\sum\partial/\partial\phi$, where the sum is over the ϕ's of the various electrons in the many-electron wave function; this operator is in the many electron problem again a diagonal matrix. This holds, we note, even with the incorrect, unperturbed wave functions. Except for the factor $-i$, this operator simply represents the change in the function it operates on, if all φ's are increased by the same amount; that is, if the whole electronic system is rotated rigidly. Then we have

$$\left(-i\sum\frac{\partial}{\partial\phi}\right)Hu=-i\sum\frac{\partial H}{\partial\phi}u-iH\sum\frac{\partial}{\partial\phi}u.$$

But on account of its spherical symmetry, $\Sigma\partial H/\partial\phi=0$. Hence

$$\left(-i\sum\frac{\partial}{\partial\phi}\right)Hu=H\left(-i\sum\frac{\partial}{\partial\phi}\right)u,\quad\text{or}$$

$$\left(\sum m_l\right)H-H\left(\sum m_l\right)=0,$$

showing that the operator $\sum m_l$ commutes with H.

Knowing that both $\sum m_l$ and $\sum m_s$ commute with H, and that both have diagonal matrices, the rest of the proof is simple. We merely write down the commutation laws in matrix form:

$$\sum(n'')\ \sum m_l(n'/n'')H(n''/n''')-H(n'/n'')\ \sum m_l(n''/n''')=0.$$

On account of the diagonal relation, this amounts to

$$\left(\sum m_l(n'/n')-\sum m_l(n'''/n''')\right)H(n'/n''')=0.$$

This cannot be satisfied unless either $\sum m_l(n'/n')=\sum m_l(n'''/n''')$ or unless $H(n'/n''')=0$; that is, H has matrix components different from zero only if $\sum m_l$ has the same values in initial and final states. The same proof holds for $\sum m_s$.

2. *Theorems regarding angular momentum.* It is assumed that we have wave functions which, although not exact, are the good approximations used in this paper; that is, linear combinations have been made so that the energy matrix has components different from zero only between states of decidedly different energy; it is diagonal as far as the states are concerned which come from one set of electron quantum numbers. We wish to show first that matrix components of angular momentum have non-negligible components only between states of the same energy (or diagonal term of the energy matrix). Suppose we let the operators connected with the three com-

ponents of orbital angular momentum be M_L^x, M_L^y, M_L^z, where M_L^z is the quantity usually denoted by M_L, and is equal to $\sum m_l$. Similarly for spin we have M_S^x, M_S^y, M_S^z. Now we have seen that M_L^z and M_S^z commute with H; and, since there is nothing peculiar about the z axis, we can equally well show that M_L^x, M_L^y, M_S^x, M_S^y commute with H. Thus for example $M_S^x H - H M_S^x = 0$, or in matrix form

$$\sum(n'') M_S^x(n'/n'') H(n''/n''') - H(n'/n'') M_S^x(n''/n''') = 0.$$

We can write this, for non-diagonal terms,

$$\begin{aligned} &M_S^x(n'/n''')\left[H(n'''/n''') - H(n'/n')\right] \\ &\qquad = -\sum(n'' \neq n', n''')\left[M_S^x(n'/n'') H(n''/n''') - H(n'/n'') M_S^x(n''/n''')\right]. \end{aligned}$$

The non-diagonal terms of the energy, $H(n''/n''')$, etc., are by hypothesis different from zero only if n'' and n''' refer to states with different electron quantum numbers, and even so they are small of the first order. If the right side were precisely zero, we should have obviously the result that $M_S^x(n'/n''')$ was different from zero only if $H(n'''/n''')$ was equal to $H(n'/n')$ which is what we wished to show. As it is, this result is true only to the first order of small quantities: M_S^x can have other, small components, and $H(n'''/n''')$ can differ from $H(n'/n')$ by small quantities. Thus we should expect that our approximate wave functions for a multiplet would give only approximately equal energies. This is not true, however, when we actually calculate by our method; the energies are precisely equal. The reason can be easily seen. Let the states n' and n''' be both connected with the same electron quantum number. Then the matrix components on the left side of the equation above are all found in terms of integrals over wave functions of those particular electron quantum numbers. The matrices on the right, however, involve other states, n'', which must refer to different electron quantum numbers, so that the right side would involve different, independent integrals. The two sides could not be in general equal unless each was zero. Hence the result is: if the approximate wave functions are computed by our method, the angular momentum has components, between two states of the same electron quantum numbers, only if both states have the same energy. Its components between states of different electron quantum number are small of the first order. From now on, we can neglect the latter terms, as we did with the energy. Thus the matrix of the angular momentum is of the form shown in Fig. 5. This can be compared with Fig. 3, showing the matrix of the energy in the final wave functions; but Fig. 3 should now be numbered to show that the diagonal terms of energy within one of the small squares of Fig. 5 (that is, in a multiplet) are all equal.

We have shown that the wave functions connected with a set of n's and l's are divided into groups, each wave function of a group having the same energy value, and the angular momentum having components only between different wave functions of a group, not from one group to another. We wish now to show that the matrix components of angular momentum within such a group are really such as to indicate a vector of magnitude L, and another S. To do this, we first note that $M_L{}^x$, $M_L{}^y$, $M_L{}^z$, $M_S{}^x$, $M_S{}^y$, $M_S{}^z$ satisfy the commutation relations

$$M_L{}^y M_L{}^z - M_L{}^z M_L{}^y = -\frac{h}{2\pi i} M_L{}^x, \text{ etc.},$$

$$M_S{}^y M_S{}^z - M_S{}^z M_S{}^y = -\frac{h}{2\pi i} M_S{}^x, \text{ etc.},$$

$$M_L{}^x M_S{}^x - M_S{}^x M_L{}^x = 0, \text{ etc.}$$

We show these by proving them for the separate m_l's and m_s's of the separate electrons, and then combining by the relations $M_L{}^x = \sum m_l{}^x$, etc. For the separate electrons, the results for the m_l's are well known; for the m_s's, the results come directly from Pauli's theory of the electron spin. We also note; that $M_L{}^z$ and $M_S{}^z$ have diagonal matrices, with diagonal values M_L and M_S (in units of $h/2\pi$). Now it can be proved[20] that if we have a set of matrices related by the commutation rules $M_L{}^y M_L{}^z - M_L{}^z M_L{}^y = -(h/2\pi i) M_L{}^x$, etc.; if these have components only between a limited set of states, and if $M_L{}^z$ forms a diagonal matrix; then the whole matrix is uniquely determined, except for a phase constant; further, $M_L{}^z$ must have integral, or half integral, characteristic values M_L, ranging from a value $-L$ to L; the states can be described by the values of M_L, so that can be taken as a quantum number. Then the matrix components prove to be given by

$$M_L{}^x(M_L/(M_L+1))M_L{}^x((M_L+1)/M_L) = \frac{1}{4}\left(\frac{h}{2\pi}\right)^2 [L(L+1) - M_L(M_L+1)] \cdots$$

$$M_L{}^z(M_L/M_L) = M_L$$

$$[(M_L{}^x)^2 + (M_L{}^y)^2 + (M_L{}^z)^2](M_L/M_L') = \left(\frac{h}{2\pi}\right)^2 L(L+1)\delta(M_L/M_L').$$

Such a set of matrix components is the unique description of a vector L, in its $(2L+1)$ possible orientations. Similar results apply to M_S.

In our case, these relations lead immediately to the following results. In the first place, the $M_L{}^x$'s depend only on orbital coordinates, the $M_S{}^x$'s only on spins. Thus the $M_L{}^x$'s can have components only between two wave functions in which the spin appears in the same way (and which thus have the same M_S). Similarly $M_S{}^x$'s can have components only between states of the same M_L. Therefore for each M_S there are a number of states of the multiplet, with different M_L's and having matrix components of the $M_L{}^x$'s between them as given above. These different sets of states, on the other hand, can differ only in the spin function, so that the components of $M_L{}^x$'s are the same for each set with each M_S. Similarly, for each M_L, there are a number of states, with different spin functions but with the same orbital functions, different M_S's, and components of $M_S{}^x$'s just as above. The result is an array of terms which can be plotted in precisely the rectangular form used in the paper, and corresponding to the $(2L+1)$ orientations of the vector L, combined with the $(2S+1)$ orientations of S.

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[20] Born, Heisenberg, and Jordan, Zeits. f. Physik **35**, 557 (1926).