AN APPLICATION OF PAULI'S METHOD OF COORDINATION TO ATOMS HAVING FOUR MAGNETIC PARTS

By G. Breit

Abstract

It is shown that the origin of spectral terms of an arc spectrum obtained by adding a highly excited electron to a certain term of the spark may be understood in terms of an application of the principle of mechanical transformability made by Pauli. According to this application it is sufficient to know (a) the strong and weak field magnetic quantum numbers of a level (b) which of the two vectors r or k is the faster in a magnetic field (c) whether the term is inverted or not in order to tell the value of j belonging to that level. The derivation of Pauli's results is based on sufficiently general principles to enable one to apply it to the Pauli-Hund method of tracing spectral terms. The possible groupings of the j_a's or the j_s's are discussed and it is shown that Pauli's principle is valid here also.

PAULI has shown that Ehrenfest's principle of mechanical transformability requires a definite arrangement of the magnetic orientations of the core and the electron into groups, each of the groups corresponding to a definite value of the inner quantum number j. This enables him to predict, from a knowledge of the strong and weak magnetic quantum numbers of a level, the value of the inner quantum number belonging to that level. It has been shown by Russel and Saunders, Pauli, Heisenberg, Goudsmit and Hund[1] that spectral terms in the periodic system can be predicted by adding the weak and strong magnetic quantum numbers of the constituent electrons. However, the origin of the particular magnetic sublevels of a term is not always clear. Hund has treated this point and has shown that the knowledge of the spark spectrum enables one to restrict the possibilities to a certain extent. It is shown below that Hund's coordination is logically connected with Pauli's and that by extending the latter, one may trace the origin of the terms.

The essential points of Pauli's theoretical reasoning are as follows. He considers an atom consisting of two magnetic parts to which he refers as the "core" (*Rumpf*) and the electron. The angular momentum of the

[1] S. Goudsmit, Zeits. f. Physik, **32**, 794 (1925),
F. Hund, Zeits. f. Physik, **34**, 296 (1925); **33**, 345 (1925);
W. Heisenberg, Zeits. f. Physik, **32**, 345 (1925),
W. Pauli, Zeits. f. Physik, **31**, 765 (1925),
H. N. Russell and F. A. Saunders, Astrophys. J. **61**, 38 (1925),
W. Pauli, Zeits. f. Physik, **20**, 371(1923),
also for detailed summary, H. N. Russell and O. Laporte, J. Opt. Soc. July, 1926.

first he calls r and of the second k. In a strong magnetic field r and k are orientated in the field independently of each other and each of them describes a circular cone around the direction of the applied field. Therefore in a strong field the state of the atom must be specified in addition to its ordinary quantum numbers also by two new ones giving the components of r and k along H. These components when expressed in $h/2\pi$ units are called m_r and m_k. If the external field is weakened the Zeeman level represented by (m_k, m_r) changes into another permissible quantum state in accordance with the principle of mechanical transformability. However, for weak fields r and k no longer describe circular cones around H. The angle between r and k remains fixed in very weak fields. To a good approximation both r and k may be said to precess around their resultant j which in turn precesses around H. Pauli shows that as the field H is weakened the Zeeman level specified in a strong field by (m_k, m_r) is transformed adiabatically into a Zeeman level having the "weak" magnetic quantum number $m = m_k + m_r$ and a definite inner quantum number j which is obtained most easily by means of a graphical representation of Pauli's results as follows.

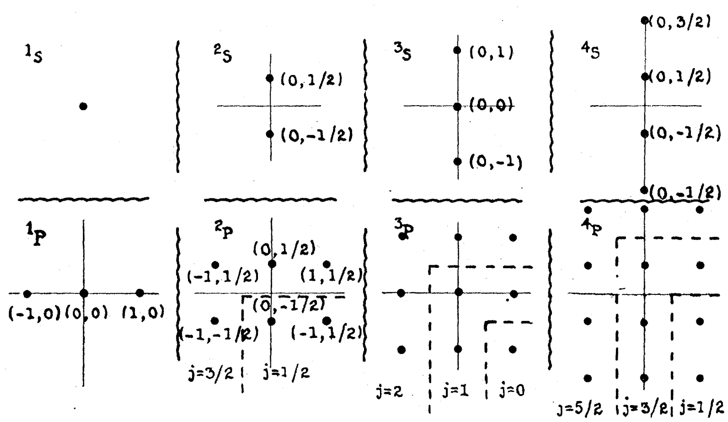

Fig. 1. Typical coordinations in multiplets.

We plot the quantity m_k which represents the component of the angular momentum of the electron along the magnetic field in units $h/2\pi$ as abscissas and m_r which gives the component of the angular momentum of the core as ordinates. Both are taken in a strong field. We represent some typical cases. The dotted lines in these pictures separate the Zeeman levels which unite into one j level in a weak field in accordance with Pauli's results for the case of j^+, i.e., for regular terms. If the terms are inverted the dotted coordination lines are obtained by reflecting the lines drawn in the origin $m_k = m_r = 0$. These pictures do not contain anything new but give simply a diagrammatic representation of Pauli's assignment of (m_k, m_r) to a given pair of values (j, m) in a Zeeman level.

According to Pauli and Hund if there should be two electrons one of which has by itself values (r_1, k_1) and the other (r_2, k_2) we must consider the results of independent addition of r_1 and r_2 and also those of the addition of k_1 and k_2. Thus two alkali electrons having $r_1 = \frac{1}{2}$, $r_2 = \frac{1}{2}$ can add themselves to a resultant $r = r_1 + r_2 = 1$ or to a $r = r_1 - r_2 = \frac{1}{2} - \frac{1}{2} = 0$ giving rise in the first case to a triplet term and in the second to a singlet. We suppose that the same rules of coordination which give resultant

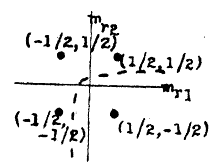

Fig. 2. r coordination for two electrons.

values of m in the above drawn diagrams apply also to the combination of the r's. This means that the following (Fig. 2) diagram gives the state of affairs, the dotted line separating the triplet combinations $(\frac{1}{2}, \frac{1}{2})$ $(-\frac{1}{2}, \frac{1}{2})$, $(-\frac{1}{2}, -\frac{1}{2})$ from the singlet $(\frac{1}{2}, -\frac{1}{2})$.

Such an hypothesis is a natural one to make if we are to think concretely of r_1, k_1, r_2, k_2 as four different magnetic parts because Pauli's reasoning with the exception of one point may be repeated word for word for the combination of r_1, r_2 even though it has been developed for r combining with k. The difference between the new case and the one shown in Fig. 1 lies in the fact that we have no *a priori* reason to regard either r_1 or r_2 as the faster vector while r is in all probability faster than k. However, it is shown later that such *a priori* reasons may be found in the relative positions of the electrons. The main object of this note is to propose the above hypothesis.

Thus the interpretation is ambiguous to the extent of not knowing which of the electrons should be labeled as 1. The empirical data discussed by Hund enable us to decide this. Consider ^2S and ^2P combining and let the total quantum number of ^2P remain fixed while that of ^2S increases indefinitely. We have then the relation shown in Fig. 3. Here the crosses represent the magnetic levels of ^2P belonging to $j = \frac{1}{2}$. The dots also belong to ^2P giving $j = \frac{3}{2}$. The circles give levels of the triplet and singlet resulting from the combination. It is readily seen that the arrows drawn heavily represent the origin of the singlet term. This means that the r of the ^2P electron must be labeled as 1 and the r of the ^2S as 2. Hence it would seem in this case that the r corresponding to the electron approaching ionization must be considered as analogous to the r of a single electron. Since the essential distinction between r and k in Pauli's derivation is that r in a strong field is the more rapidly precessing vector and since the coordination is inverted if the rotation of r,k about j is reversed we must consider the general position of the triplet with respect to the singlet before we can say which of the two r's is the faster. In Fig. 3 the coordination for the ^2P is that holding for Pauli's j^+ rotation. Fig. 3 shows that the singlet converges to the higher value of j while the

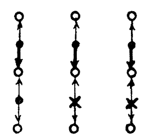

Fig. 3. Formation of ^1P and ^3P.

triplet converges partly to $j=\frac{1}{2}$ and partly to $j=\frac{3}{2}$. Hence the doublet formed by $(^1P,^3P)$ is inverted so that our previous conclusion must be changed to the opposite one, *viz.*, the r corresponding to the electron in the less ionized state precesses faster in a strong field than that of the more highly ionized electron.

Let us consider next the combination of two ^2P electrons leading as is well known to the formation of $^1S,^1P,^1D,^3S,^3P,^3D$. Here we are concerned not only with combinations of the r's but also of the k's or more correctly of the $j_a=k-1$. The coordination of the r's is the same as before and is

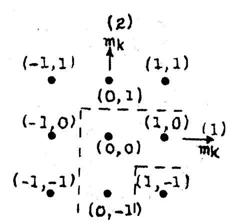

Fig. 4. k coordination for two P electrons.

given by Fig. 2. The vectors j_a can be imagined to combine in a strong field as in Fig. 4 by means of their strong magnetic field quantum numbers. The dotted lines divide those pairs of values of $(m_k^{(1)},m_k^{(2)})$ which in a weak field correspond to the same rigid vector configuration $j_a^{(1)}+j_a^{(2)}$ and which give rise to terms having the same resultant j_a—therefore terms designated by the same letter. We thus see from Fig. 4 that

$(1,-1)$ gives S terms
$(1,0)(0,0)(0,-1)$ gives P terms
$(1,1)(0,1)(-1,1)(-1,0)(-1,-1)$ gives D terms (A)

Before a comparison with experiment is made we cannot distinguish between this and the alternative

$(-1,1)$ for S
$(0,1)(0,0)(-1,0)$ for P
$\cdot(1,1)(1,0)(1,-1)(0,1)(--1,-1)$ for D (B)

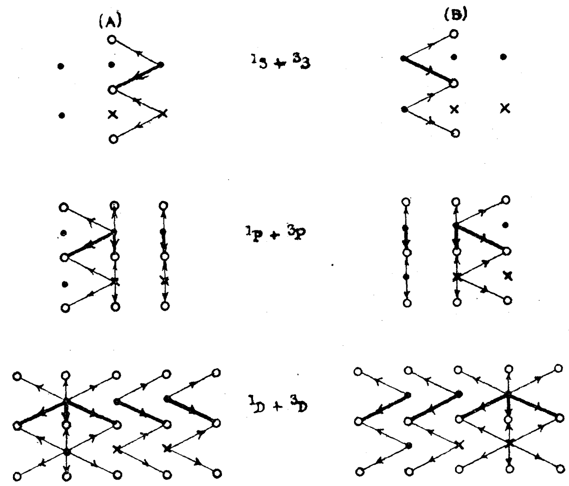

Fig. 5. Combination of two ^2P electrons.

Corresponding to these two possibilities we have the following formation using heavy arrows for the origin of singlets and light ones for triplets: This requires that if the resultant terms are regular for

A				B			
^1S	converges	towards	$j=\frac{3}{2}$.	^1S	converges	towards	$j=\frac{3}{2}$
^3S	"	"	$j=\frac{3}{2}$ and $j=\frac{1}{2}$	^3S	"	"	$j=\frac{3}{2}$
^1P	"	"	$j=\frac{3}{2}$	^1P	"	"	$j=\frac{3}{2}$
$^3P_0$	"	"	$j=\frac{1}{2}$	$^3P_0$	"	"	$j=\frac{1}{2}$
$^3P_1$	"	"	$j=\frac{1}{2}$	$^3P_1$	"	"	$j=\frac{1}{2}$
$^3P_2$	"	"	$j=\frac{1}{2}$ and $j=\frac{3}{2}$	$^3P_2$	"	"	$j=\frac{3}{2}$
A				B			
^1D	"	"	$j=\frac{3}{2}$	^1D	"	"	$j=\frac{3}{2}$
$^3D_1$	"	"	$j=\frac{1}{2},\ \frac{3}{2}$	$^3D_1$	"	"	$j=\frac{1}{2}$
$^3D_2$	"	"	$j=\frac{1}{2},\ \frac{3}{2}$	$^3D_2$	"	"	$j=\frac{1}{2}$
$^3D_3$	"	"	$j=\frac{3}{2}$	$^3D_3$	"	"	$j=\frac{3}{2}$

We see at once that no real convergence is possible in A while in G $j=\frac{1}{2}$ of the spark gives rise to $^3P_0$,$^3P_1$,$^3D_1$,$^3D_2$ all the other terms con_ verging to $j=\frac{3}{2}$. This is actually the arrangement considered probable by Hund. If the energy values corresponding to the S terms are higher than those for the P which in turn are higher than those for the D as they seem to be in the majority of cases (according to an informal statement of Dr. O. Laporte) we can regard the l multiplet represented in Fig. 4 as an inverted one and therefore we should actually expect that the coordination is given by the scheme B if $j_a^{(2)}$ is regarded as the faster vector in a strong field. Hence for the l coordination the outside electron must be regarded as the faster vector j_a while for the j_s^5 or r coordination the inside electron has the faster vector.

The writer has examined other cases than those considered above and in all of them the method leads to similar results. Thus if we combine ^3P and ^2S we get ^2P and ^4P. For ^2P, $j=\frac{1}{2}$ is assigned to $j=1$ of ^3P and $j=\frac{3}{2}$ to $j=2$. For ^4P the values $j=\frac{1}{2}$, ,$\frac{3}{2}$ $\frac{5}{2}$ assign themselves in order to $j=0$, 1, 2 of ^3P. The combination of ^3D and ^2S leads to ^2D and ^4D. For ^2D the values $j=\frac{3}{2}$, $\frac{5}{2}$ belong respectively to $j=2$, 3 of ^3D. For ^4D, $j=\frac{7}{2}$, $\frac{5}{2}$ belong respectively to $j=3$, 2 of ^3D while $j=\frac{3}{2}$, $\frac{1}{2}$ of ^4D both converge towards $j=1$ of ^3D. Again if ^4P and ^2S combine we get ^3P and ^5P. For ^3P the levels $j\equiv 0$, 1, 2 converge respectively to $j=\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ of ^4P, etc. Examples not involving ^2S terms may also be given. Thus if ^3P and ^2P combine to give rise to ^2S,^2P,^2D,^4S,^4P,^4D we get for example for ^4D $j=\frac{7}{2}$, $\frac{5}{2}$ converging to $j=2$, 1 of ^3P while $j=\frac{3}{2}$, $\frac{1}{2}$ converge to $j=0$. The whole assignment is consistent also for the convergence to ^2P and in some special types of combination one can prove that it always must be consistent. If the combining terms should be regular and the resultant terms inverted the method does not lead to a convergence of a j level in the result to one level in the spark spectrum.

In all of this we have assumed that the two electrons are not equivalent. If they are, no coordination is possible on the above principles because no preference can be given to either. Whether the impossibility of obtaining coordination for equivalent electrons is directly connected with Pauli's exclusion principle is difficult to say. However, an indirect connection must of course exist. If it should be granted that the origin of r lies in the internal spin of the electron[2] it is easy to understand Pauli's exclusion principle as due to the impossibility of two electrons occupying the same orbit because m_r and m_k define completely the position of the orbit in a strong field. Very strong perturbations between two equivalent orbits would set in and would make their simultaneous existence impossible. If it should be legitimate to pay attention here to

[2] G. E. Uhlenbeck and S. Goudsmidt, Nature, Feb. 20, 1926;
F. R. Bichowsky and H. C. Urey, Proc. Nat. Acad. Sci., **12**, 80–75 (Feb. 1926).

the relatively small variation of mass with velocity the magneto mechanical ratio for the external electron should be somewhat higher than for the inside one and thus its precession in a strong field would be faster. This is in the right direction for what we have found for the l coordination. The r coordination requires that the inside electron so far as its spin is concerned should be the faster one and thus for its spin the magneto-mechanical ratio should be greater than for the outside electron.*

The writer is greatly indebted to Dr. O. Laporte for numerous discussions of this subject.

DEPARTMENT OF TERRESTRIAL MAGNETISM,
CARNEGIE INSTITUTION OF WASHINGTON,
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* One might attempt to see a reason for this in the relativity transformations

$$h_x'=h_x,\ h_y'=h_y+\beta d_z/\sqrt{1-\beta^2},\ h_z'\ h_z-\beta d_y/\sqrt{1-\beta^2}$$

according to which a change in the magnetic field h of the stationary system brings about a greater change in h' and consequently causes a greater change in the precession of a fast moving electron. However a more precise theory of the spinning electron than those available so far is needed for a certain consideration of the question.