On the Connexion between the Completion of Electron Groups in an Atom with the Complex Structure of Spectra

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Especially in connexion with Millikan and Landé's observation that the alkali doublet can be represented by relativistic formulae and with results obtained in an earlier paper, it is suggested that this doublet and its anomalous Zeeman effect expresses a classically non-describable two-valuedness of the quantum theoretical properties of the optically active electron [Germ: *Leuchtelektron*], without any participation of the closed rare gas configuration of the atom core in the form of a core angular momentum or as the seat of the magneto-mechanical anomaly of the atom. We then attempt to pursue this point of view, taken as a temporary working hypothesis, as far as possible in its consequences also for atoms other than the alkali atoms, notwithstanding its difficulties from the point of view of principle. First of all it turns out that it is possible, in contrast to the usual ideas, to assign for the case of a strong external magnetic field, which is so strong that we can neglect the coupling between the atomic core and the optically active electrons, to those two systems, as far as the number of their stationary states, the values of their quantum numbers, and their magnetic energy is concerned, no other properties than those of the free atomic core of the optically active electron of the alkalis. On the basis of these results one is also led to a general classification of every electron in the atom by the principal quantum number n and *two* auxiliary quantum numbers k_1 and k_2 to which is added a further quantum number m_1 in the presence of an external field. In conjunction with a recent paper by E. C. Stoner this classification leads to a general quantum theoretical formulation of the completion of electron groups in atoms.

1. The Permanence of Quantum Numbers (Principle of Gradual Construction [Germ: *Aufbauprinzip*]) in Complex Structures and the Zeeman Effect

In a previous paper[1] it was emphasised that the usual ideas, according to which the inner, completed electron shells of an atom play an essential part in the complex structure of optical spectra and their anomalous Zeeman effect in the shape of core angular momenta and as the real seat of the magneto-mechanical anomaly, are subject to several serious difficulties. It seems therefore plausible to set against these ideas that especially the doublet structure of the alkali spectra and their anomalous Zeeman effect are caused by a classically undescribable two-valuedness of the quantum theoretical properties of the optically active electron. This idea is particularly based upon the results of Millikan and Landé that the optical doublets of the alkalis are similar to the relativity doublets in X-ray spectra and that their magnitude is determined by a relativistic formula.

If we now pursue this point of view, we shall assign -- as was done by Bohr and Coster

for the X-ray spectra -- to the stationary states of the optically active electron involved in the emission of the alkali spectra two auxiliary quantum numbers k_1 and k_2 as well as the principal quantum number n. The first quantum number k_1 (usually simply denoted by k) has the values 1, 2, 3, ... for the s, p, d, . . . terms and changes by unity in the allowed transition processes; it determines the magnitude of the central force interaction forces of the valence electron with the atom core. The second quantum number k_2 is for the two terms of a doublet (e.g., p_1 and p_2) equal to $k_1 - 1$ and k_1, in the transition processes it changes by Â±1 or 0 and determines the magnitude of the relativity correction (which is modified according to LandÃ© to take into account the penetration of the optically active electron in the atom core). If we follow Sommerfeld to define the total angular momentum quantum number j of an atom in general as the maximum value of the quantum number m_1 (usually simply denoted by m) which determines the component of the angular momentum along an external field, we must put $j = k_2 - 1$ for the alkalis. The number of stationary states in a magnetic field for given k_1 and k_2 is $2j + 1 = 2k_2$, and the number of these states for both doublet terms with given k_1 is altogether $2(2k_1 - 1)$.

If we now consider the case of strong field (Paschen-Back effect), we can introduce apart from k_1 and the just mentioned quantum number m_1, instead of k_2 also a magnetic quantum number m_2 which determines directly the energy of the atom in the magnetic field, that is, the component of the magnetic moment of the valence electron parallel to the field. For the two terms of the doublet it has, respectively, the values $m_1 + 1/2$ [N.B one-half] and $m_1 - 1/2$. Just as in the doublet structure of the alkali spectra the "anomaly of the relativity correction" is expressed (the magnitude of which is mainly determined by another quantum number, as is the magnitude of the central force interaction energy of the optically active electron and the atom core), so appears in the deviations of Zeeman structure from the normal Lorentz triplet the "magnetomechanical anomaly" which is similar to the other anomaly (the magnitude of the magnetic moment of the optically active electron is mainly determined by another quantum number, as is the angular momentum). Clearly, the appearance of half-odd-integral (effective) quantum numbers and the thereby formally caused value $g = 2$ of the splitting factor of the s-term of the alkalis is closely connected with the twofoldness of the energy level. We shall here, however, not attempt a more detailed theoretical analysis of this state of affairs and use the following considerations of the Zeeman effect of the alkalis as empirical data.

Without worrying about the difficulties encountered by our point of view, which we shall mention presently, we now try to extend this formal classification of the optically active electron by four quantum numbers n, k_1, k_2, m_1 to atoms, more complex than the alkalis. *It now turns out that we can retain completely on the basis of this classification the principle of permanence of quantum numbers (Aufbauprinzip) also for the complex structure of the spectra and the anomalous Zeeman effect in contrast to the usual ideas.* This principle, due to Bohr, states that when a further electron is added to a -- possibly charged -- atom, the quantum numbers of the electrons which are already bound to the atom retain the same values as correspond to the appropriate state of the free atom core.

Let us first of all consider the alkaline earths. The spectrum consists in this case of a singlet and a triplet system. The quantum states with a well-defined value of the quantum number k_1 of the optically active electron correspond then for the first system to altogether $1(2k_1 - 1)$ and in the last system to $3(2k_1 - 1)$ stationary states in an external magnetic field. Up to now this was interpreted as meaning that in strong fields the optically active electron in each case could take up $2k_1 - 1$ positions, while the atom core was able to take up in the first case one, and in the last case three positions. The number of these positions is clearly different from the number 2 of the positions of the free atom core (alkali-like s-term) in a field. Bohr[2] called this state of affairs a "constraint" [Germ: *Zwang*] which is not analogous to the action of external fields of force. Now, however, we can simply interpret the total $4(2k_1 - 1)$ states of the atom as meaning that the atom core always has two positions in a field, and the optically active electron as for the alkalis $2(2k_1 - 1)$ states.

More generally, a branching rule formulated by Heisenberg and Landé[3] states that a stationary state of the atom core with N states in a field leads through the addition of one more electron to two systems of terms, corresponding to altogether $(N + 1)(2k_1 - 1)$ and $(N- 1)(2k_1 - 1)$ states in a field, respectively, for a given value of the quantum number k_1 of the last electron. According to our interpretation, the $2N(2k_1 - 1)$ states of the complete atom in a strong field come about through N states of the atom core and $2(2k_1 - 1)$ states of the optically active electron. In the present quantum theoretical classification of the electrons the term multiplicity required by the branching rule is simply a consequence of the "Auf bauprinzip". According to the ideas presented here Bohr's constraint expresses itself not in a violation of the permanence of quantum numbers when the series electron is coupled to the atom core, but only in the peculiar two-valuedness of the quantum theoretical properties of each electron in the stationary states of an atom.

We can, however, from this point of view use the "*Aufbauprinzip*" *to calculate* not only the number of stationary states, but also *the energies in the case of strong fields* (at least that part which is proportional to the field) *additively from those of the free atom core and of the optically active electron,* where the latter can be taken from the alkali spectra. Because, in this case, both the total component $\overline{m}_1$ of the angular momentum of the atom along the field (in units [h-bar]) as well as the component $\overline{m}_2$ of the magnetic moment of the atom in the same direction (in Bohr magnetons) are equal to the sum of the quantum numbers m_1 and m_2 of the single electrons:

$$\overline{m}_1 = Sm_1, \quad \overline{m}_2 = Sm_2. \qquad (1)$$

The latter can independently run through all values corresponding to the values of the angular momentum quantum numbers k_1 and k_2 of the electrons in the stationary state of the atom considered. ($\overline{m}_2 oh$ is here thus the part of the energy of the atom proportional to the field strength; o = Larmor frequency.)

Let us consider as an example the two s-terms (singlet- and triplet S-term) of the alkaline earths. To begin with it is sufficient to consider only the two valence electrons, as the contribution of the other electrons to the sums in (1) vanish when taken

together. According to our general assumption we must for each of the two valence electrons take (independently of the other electron) the values $m_1 = -1/2$, $m_2 = -1$ and $m_1 = 1/2$, $m_2 = 1$ of the s-terms of the alkalis. According to (1) we then get the following values for the quantum numbers $\overline{m}_1$ and $\overline{m}_2$ of the total atom:

$$\overline{m}_1 = -1/2\ -1/2,\ -1/2\ +1/2,\ +1/2\ -1/2,\ +1/2\ +1/2$$
$$\overline{m}_2 = \quad -1\ -1, \qquad -1\ +1, \qquad 1\ -1, \qquad 1\ +1,$$

or

$\overline{m}_1 = -1$	0	1
$\overline{m}_2 = -2$	0, 0	2

[Corresponding to one term with $j = 0$ and one with $j = 1$ in weak fields.][a] To obtain the p-, d-, . . . terms of the alkaline earths, one must combine in (1) the unchanged contribution of the first valence electron (S-term) in an appropriate manner with the m_1- and m_1-values of the p-, d-, . . . terms of the alkalis for the second electron.

The rule (1) leads in general exactly to the procedure for calculating the energy values in strong field proposed recently by Landé[4] which has been shown by this author to give correct results also in complicated cases. According to Landé this procedure leads, for instance, to the correct Zeeman terms of neon (at least in the case of strong fields) if one assumes[b] that in the atom core there is one active electron in a p-term (instead of in an s-term as above) and if one lets the optically active electron go through s-, p-, d-, f-, . . . terms.

This result now suggests that we *characterise in general each electron in an atom not only by a principal quantum number n, but also by the two auxiliary quantum numbers k_1 and k_2*, even when several equivalent electrons or completed electron groups are present. Moreover, we shall allow (also in the just-mentioned cases) in our thoughts *such a strong magnetic field that we can assign to each electron, independently of the other electrons not only the quantum numbers n and k_1, but also the two quantum numbers m_1 and m_2* (where the last one determines the contribution of the electron to the magnetic energy of the atom). The connexion between k_2 and m_2 for given k_1 and m_1 must be taken from the alkali spectra.

Before we apply in the next section this quantum theoretical classification of the electrons in an atom to the problem of the completion of the electron groups, we must discuss in more detail the difficulties encountered by the here-proposed ideas of the complex structure and the anomalous Zeeman effect and the limitations of the meaning of our ideas.

First of all, these ideas do not pay proper regard to the, in many respects independent, separate appearance of the different term systems (e.g., the singlet and the triplet systems of the alkaline earths), which also play a role in the position of the terms of these systems and in the Landé interval rule. Certainly, one cannot assume two

different causes for the energy differences of the triplet levels of the alkaline earths, both the anomaly of the relativity correction of the optically active electron and the dependence of the interaction between the electron and the atom core on the relative orientation of these two systems.

A more serious difficulty, raising a matter of principle, is however the connexion of these ideas with the correspondence principle which is well known to be a necessary means to explain the selection rules for the quantum numbers k_1, j, and m and the polarisation of the Zeeman components. It is, to be sure, not necessary according to this principle to assign in a definite stationary state to each electron an orbit uniquely determined in the sense of usual kinematics; however, it is necessary that the totality of the stationary states of an atom corresponds to a collection (class) of orbits with a definite type of periodicity properties. In our case, for instance, the above-mentioned selection and polarisation rules require according to the correspondence principle a kind of motion corresponding to a central force orbit on which is superposed a precession of the orbital plane around a definite axis of the atom to which is added in weak external magnetic fields also a precession around an axis through the nucleus in the direction of the field. The dynamic explanation of this kind of motion of the optically active electron, which was based upon the assumption of deviations of the forces between the atom core and the electron from central symmetry, seems to be incompatible with the possibility to represent the alkali doublet (and thus also the magnitude of the corresponding precession frequency) by relativistic formulae. The situation with respect to the kind of motion in the case of strong fields is similar.

The difficult problem thus arises *how to interpret the appearance of the kind of motion of the optically active electron which is required by the correspondence principle independently of its special dynamic interpretation which has been accepted up to now but which can hardly be retained.* There also seems to be a close connexion between this problem and the question of the magnitude of the term values of the Zeeman effect (especially of the alkali spectra).

As long as this problem remains unsolved, the ideas about the complex structure and the anomalous Zeeman effect suggested here can certainly not be considered to be a sufficient physical basis for the explanation of these phenomena, especially as they were in many respects better reproduced in the usually accepted point of view. It is not impossible that in the future one will succeed in merging these two points of view. In the present state of the problem it seemed of interest to us to pursue as far as possible also the first point of view to see what its consequences are. This is the sense in which one must consider our discussions in the next section of the application of the tentative point of view, presented here to the problem of the completion of electron groups in an atom, notwithstanding the objections which can be made against it. We shall here draw conclusions only about the number of possible stationary states of an atom when several equivalent electrons are present, but not about the position and relative order of the term values.

2. On a General Quantum Theoretical Rule for the Possibility of the Occurrence of Equivalent Electrons in an Atom

It is well known that the appearance of several equivalent electrons, that is, electrons

which are fully equivalent both with respect to their quantum numbers and with respect to their binding energies, in an atom is possible only under special circumstances which are closely connected with the regularities of the complex structure of spectra. For instance, the ground state of the alkaline earths in which the two valence electrons are equivalent corresponds to a singlet S-term, while in those stationary states of the atom which belong to the triplet system the valence electrons are never bound equivalently, as the lowest triplet *s*-term has a principal quantum number exceeding that of the ground state by unity. Let us now as second example consider the neon spectrum. This consists of two groups of terms with different series limits, corresponding to different states of the atom core. The first group, belonging to the removal of an electron with the quantum numbers $k_1 = 2$, $k_2 = 1$ from the atom core can be considered to be composed of a singlet and a triplet system, while the second group, belonging to the removal of an electron with $k_1 = k_2 = 2$ from the atom core, can be said to be a triplet and quintet system. The ultraviolet resonance lines of neon have not yet been observed, but there can hardly be any doubt that the ground state of a Ne-atom must be considered to be a *p*-term as far as its combination with the known excited states of the atom is concerned; in accordance with the unique definiteness and the diamagnetic behaviour of the inert gas configuration there can be only *one* such term, namely with the value $j = 0$.[c] As the only *p*-terms with $j = 0$ are the (lowest) triplet terms of the two groups, we can thus conclude that for Ne for the value 2 of the principal quantum number only those two triplet terms exist and moreover are identical for both groups of terms.

In general we can thus expect *that for those values of the quantum numbers n and k_1 for which already some electrons are present in the atom, certain multiplet terms of spectra are absent or coincide.* The question arises what quantum theoretical rules decide this behaviour of the terms.

As is already clear from the example of the neon spectrum, this question is closely connected with the problem of the completion of electron groups in an atom, which determines the lengths 2, 8, 18, 32, . . . of the periods in the periodic table of the elements, This completion consists in that an *n*-quantum electron group neither through emission or absorption of radiation nor through other external influences is able to accept more than $2n^2$ electrons.

It is well known that Bohr in his theory of the periodic table, which contains a unified summary of spectroscopic and chemical data and especially a quantum theoretical basis for the occurrence of chemically similar elements such as the platinum and iron metals and the rare earths in the later period of the table, has introduced a subdivision of these electron groups into subgroups. By characterising each electron in the stationary states of the atom by analogy with the stationary states of a central force motion by a symbol n_k with k [less than or equal to] *n,* he obtained in general for an electron group with a value *n* of the principal quantum number *n* subgroups. In this way Bohr was led to the scheme of the structure of the inert gases given in Table 1. He has, however, emphasised himself[5] that the equality, assumed here, of the number of electrons in the different subgroups of a maingroup is highly hypothetical and that for the time being no complete and satisfying theoretical explanation of the completion of the electron groups in the atom, and especially of the period lengths 2, 8, 18, 32, . . . in the periodic table

could be given.

Table 1. Original Bohr Scheme of Inert Gas Configurations

Element	Atomic number	Number of n_k electrons														
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	6_1	6_2
Helium	2	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Neon	10	2	4	4	-	-	-	-	-	-	-	-	-	-	-	-
Argon	18	2	4	4	4	4	-	-	-	-	-	-	-	-	-	-
Krypton	36	2	4	4	6	6	6	4	4	-	-	-	-	-	-	-
Xenon	54	2	4	4	6	6	6	6	6	6	-	4	4	-	-	-
Emanation	86	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4

Recently essential progress was made in the problem of the completion of the electron groups in an atom by the considerations of E. C. Stoner.[6] This author suggests first of all a scheme for the atomic structure of the inert gases in which in contrast to Bohr no opening of a completed subgroup is allowed by letting other electrons of the same main group be added to it, so that the number of electrons in a closed subgroup depends only on the value of k, but not on the value of n, that is, on the existence of other subgroups in the same main group. This means already a large simplification which could, moreover, be supported by several experimental data. One must here assume for $k = 1$ two, for $k = 2$ six, for $k = 3$ ten, and in general for a given value of k $2(2k - 1)$ electrons in the closed state of the corresponding subgroup to remain in agreement with the empirically known numbers of electrons in the inert gases.

Stoner remarked further that *these numbers of electrons agree with the number of the stationary states of the alkali atoms in an external field for the given value of k.* He therefore pushes further the analogy with the stationary states of the alkali spectra by assuming a further subdivision of the subgroups, corresponding to the complex structure of these spectra (and of the X-ray spectra), which are characterised by the two numbers k_1 and k_2 where k_1 is the same as Bohr's k, while we must put $k_2 = k_1 - 1$ or $k_2 = k_1$ (except for $k_1 = 1$, where in accordance with the simple nature of the s-term, $k_2 = 1$ only). Corresponding to the number $2k_2$ of the stationary states into which a stationary state of an alkali atom with given values of the quantum numbers k_1 and k_2 decomposes in an external field, Stoner assumes $2k_2$ electrons in a completed part-subgroup corresponding to the quantum numbers n, k_1, k_2. Table 2 gives the scheme of the atomic structure of the inert gases, to which Stoner was led in this way.

Table 2. Scheme of Inert Gas Configurations According to Stoner

Element	Atomic number	Number of n_k electrons														
		1_1	2_1	2_2, (1+2)	3_1	3_2, (1+2)	3_3, (2+3)	4_1	4_2, (1+2)	4_3, (2+3)	4_4, (3+4)	5_1	5_2, (1+2)	5_3, (2+3)	6_1	6_2, (1+2)
Helium	2	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Neon	10	2	2	2+4	-	-	-	-	-	-	-	-	-	-	-	-	-
Argon	18	2	2	2+4	2	2+4	-	-	-	-	-	-	-	-	-	-	-
Krypton	36	2	2	2+4	2	2+4	4+6	2	2+4	-	-	-	-	-	-	-	-
Xenon	54	2	2	2+4	2	2+4	4+6	2	2+4	4+6	-	2	2+4	-	-	-	-
Emanation	86	2	2	2+4	2	2+4	4+6	2	2+4	4+6	6+8	2	2+4	4+6	2	2+4	

We can now make this idea of Stoner's more precise and more general, if we apply the ideas about the complex structure of the spectra and the anomalous Zeeman effect, discussed in the previous section, to the case where equivalent electrons are present in an atom. In that case we arrived, on the basis of an attempt to retain the permanence of quantum numbers, at a characterisation of each electron in an atom by both the principal quantum number n and the two auxiliary quantum numbers k_1 and k_2. In strong magnetic fields also an angular momentum quantum number m_1 was added to this for each electron and, furthermore, one can use apart from k_1 and m_1 also a magnetic moment quantum number m_2, instead of k_2. First of all, we see that the use of the two quantum numbers k_1 and k_2 for each electron is in excellent agreement of Stoner's subdivision of Bohr's subgroup.[d] Secondly, by considering the case of strong magnetic fields we can reduce Stoner's result, that the number of electrons in a completed subgroup is the same as the number of the corresponding terms of the Zeeman effect of the alkali spectra, to the following more general rule about the occurrence of equivalent electrons in an atom:

There can never be two or more equivalent electrons in an atom for which in strong fields the values of all quantum numbers n, k_1, k_2, m_1 (or, equivalently, n, k_1, m_1, m_1) are the same. If an electron is present in the atom for which these quantum numbers (in an external field) have definite values, this state is "occupied".

We must bear in mind that the principal quantum number occurs in an essential way in this rule; of course, several (not equivalent) electrons may occur in an atom which have the same values of the quantum numbers k_1, k_2, m_1, but have different values of the principal quantum number n.

We cannot give a further justification for this rule, but it seems to be a very plausible one. It refers, as mentioned, first of all to the case of strong fields. However, from thermodynamic arguments (invariance of statistic weights under adiabatic transformations of the system)[e] it follows that the number of stationary states of an atom must be the same in strong and weak fields for given values of the numbers k_1 and k_2 of the separate electrons and a value of $\overline{m}_1 = S m_1$ (see (1)) for the whole atom. We can therefore also in the latter case make definite statements about the number of stationary states and the corresponding values of j (for a given number of equivalent electrons belonging to different values of k_1 and k_2). We can thus find the number of possibilities of realising various incomplete electron shells and give an unambiguous answer to the question posed at the beginning of this section about the absence or coincidence of certain multiplet terms in spectra for values of the principal quantum number for which several equivalent electrons are present in an atom. We can, however, only say something about the number of terms and the values of their

quantum numbers, but not about their magnitude and about interval relations.

We must now show that the consequences of our rule agree with experiment in the simplest cases. We must wait and see whether it will also prove itself in comparison with experiment in more complicated cases or whether it will need modifications in that case; this will become clear when complicated spectra are sorted out.

First of all, we see that Stoner's result and with it the period lengths 2, 8, 18, 32, . . . are immediately included in a natural way in our rule. Clearly, for given k_1 and k_2 there cannot be more equivalent electrons in an atom than the appropriate value of m_1, (that is, $2k_2$) and in the completed group there corresponds exactly *one* electron to each of these values of m_1.

Secondly, it turns out that our rule has an immediate consequence that the triplet *s*-term with the same principal quantum number as the ground state is absent for the alkaline earths. If we investigate the possibilities for the equivalent binding of two electrons in *s*-terms (in that case we have thus $k_1 = 1$ and k_2 can also only have the value 1), according to our rule the cases are excluded in strong fields where both electrons have $m_1 = 1/2$ or both have $m_1 = -1/2$; rather, we can only have $m_1 = 1/2$ for the first electron and $m_1 = -1/2$ for the second electron, or the other way round[f] so that the quantum number $\overline{m}_1 = Sm_1$ for the total atom can only have the value 0. Therefore also in weak fields (or when there is no field) only the value $j = 0$ is possible (singlet S-term).

We now investigate the case that *one* electron is removed from a closed shell, as will occur in X-ray spectra. Clearly when an electron is missing from one of Stoner's part-subgroups, the case is always possible that *no* electron is present with the value m_1; we call this the "hole-value" of m_1. The other electrons are then uniquely divided over the other values of m_1 so that for each of those values we have one electron. The sum of these other values of m_1 and thus the quantum number $\overline{m}_1$ of the total atom is clearly in each case equal to the opposite of the hole-value of m_1. If we let it go through all possible values and take into account that an electron can be removed from every part-subgroup, we see that in strong fields the multiplicity of the hole-values of m_1 and thus also that of the values of $\overline{m}_1$ is the same as that of the m_1 value of a single electron. Due to the invariance of statistical weights it follows thus also for weak fields that the numbers of stationary states and of *j*-values of single ionised closed electron shells (X-ray spectra) are the same as in the alkali spectra, in accordance with experiment.

This is a special case of a general *reciprocity law: For each arrangement of electrons there exists a conjugate arrangement in which the hole-values of m_1 and the occupied values of m_1 are interchanged.* This interchange may refer to a single part-subgroup while the other part-subgroups are unchanged, or to a Bohr subgroup, or to the whole of a main group, since the different part-subgroups are completely independent of one another as far as possible arrangements are concerned. *The electron numbers of the two conjugate arrangements add up to the number of electrons in the completed state of the group (or subgroup) considered, while the j-values of the two arrangements are the same.* The latter follows from the fact that the sum of the hole-values of m_1 of an

arrangement always is the opposite of the sum of the occupied m_1-values. Therefore, the quantum numbers $\overline{m}_1$ of the whole atom are the opposite of one another for conjugate arrangements. As the j-values are defined as the upper limit of the set of $\overline{m}_1$-values, and as this set is symmetric around zero, it follows that the j-values are the same (compare the examples discussed below). Because of this periodicity law to some extent the relations at the end of a period of the periodic table reflect those at the beginning of a period. We must emphasise, however, that this for the time being refers only to the number of stationary states of the shell in question and the values of their quantum numbers, whereas we can say nothing about the magnitude of their energies or about interval relations.[g]

As an application of our rule we shall discuss now the special case of the gradual formation of the eight-shell (where of the principal quantum number considered no electrons with $k = 2$ are present in the ground state); this gives us at the same time another example of the just-derived reciprocity rule. The binding of the first two electrons in this shell has already been discussed and in what follows we shall assume for the sake of simplicity that no electron is missing from the $k_1 = 1$ subgroup so that it is closed (compare Table 2 with Stoner's scheme). According to Stoner, for the following elements until the completion of the eight-shell (e.g., from B to Ne) the ground state will always be a p-term, in agreement with all experimental data up to now. Especially follows the alkali-like spectrum, corresponding to the binding of the third electron of the eight-shell, with the well-known absence of the s-term with the same principal quantum number as the ground state.

We can thus immediately go over to the binding of the fourth electron of the eight-shell, which appears in the not-yet analysed arc spectrum of carbon and the partially already unraffled arc spectrum of lead. According to the Landé-Heisenberg branching rule (see previous section) the corresponding spectrum should have in general the same structure as the neon spectrum, that is, consist of a singlet-triplet group and a triplet-quintet group with different series limits, corresponding to the $2p_1$- and the $2p_2$-doublet term of the ion considered. We shall show, however, that according to our rules these spectra must differ essentially, as far as the number and f-values of the p-terms of the maximum principal quantum number ($n = 2$ for C, $n = 6$ for Pb) is concerned, from the Ne-spectrum (where, as we mentioned at the beginning of this section, apart from the ground state with $j = 0$ no further p-term exists with principal quantum number 2); this is in contrast to the structure of the excited states which we expect to be similar.

We must distinguish three cases, according to the number of electrons in the two part-subgroups with $k_1 = 2$, $k_2 = 1$ and with $k_1 = 2$, $k_2 = 2$ over which we must distribute two electrons (we have already assumed that the first two electrons are bound in s-terms, $k_1 = k_2 = 1$).

(a) Two equivalent n_{21}-electrons: Corresponding to the p_1-term of the alkalis m_1 can for this part-subgroup only take on the two values $m_1 = \pm 1/2$. It is thus closed in this case with $\overline{m}_1 = 0$ and $j = 0$.

(b) One n_{21}- and one n_{22}-electron: For the second partsubgroup m_1 can, corresponding

to the p_2-term of the alkalis take on the four values $\pm 1/2$, $\pm 3/2$ and these can be combined in all possible ways with the above-mentioned values $m_1 = +1/2$ of the first electron, since the two electrons are in different part-subgroups and are thus not equivalent.[h] We have thus

$$\overline{m}_1 = (-3/2, -1/2, 1/2, 3/2) + (-1/2, 1/2)$$
$$= \pm(3/2 + 1/2), \pm(3/2 - 1/2), \pm(1/2 + 1/2), \pm(1/2 - 1/2)$$
$$= \pm 2, \pm 1, \pm 1, 0, 0$$

From this we see immediately that the terms split in two series with [absolute value] $\overline{m}_1$ [less than or equal to] 2 and with $\overline{m}_1$ [less than or equal to] 1. In the field free case these correspond clearly to two terms: one with $j = 2$, and one with $j = 1$.

(c) Two equivalent n_{22}-electrons: According to our rule the m_1-values of the two electrons must be different and we find for the possible values of $\overline{m}_1$:

$$\overline{m}_1 = \pm(3/2 + 1/2), \pm(3/2 - 1/2), (3/2 - 3/2), (1/2 - 1/2) = \pm 2, \pm 1, 0, 0.$$

If there is no magnetic field we find thus one term with $j = 2$ and one with $j = 0$.

Altogether we find thus for the four-shell five different p-terms with maximum principal quantum number, of which two have j = 2, one j = 1, and two j = 0.

We can say nothing about the energies or the interval relations of this group of terms. However, we can make definite statements about the Zeeman splittings of these terms to be expected.

By substituting the m_2-values (taken from the Zeeman terms of the alkalis in strong fields) for the separate electrons corresponding to the given m_1-values, we find from rule (1) the Zeeman splittings for the five p-terms of the four-shell in strong fields:

$\overline{m}_1$	-2	-1	0	1	2
$\overline{m}_2$	-3, -2	-2, -1, 0	0, 0, 0, 0, 0	1, 1, 2	2, 3

Using the same rule applied by Landé[4] to higher-order multiplets, one obtains from this for the determination of the sum of the g-values for the two $j = 2$ terms (denoted by Sg_2) and for the g-value for the $j = 1$ term (denoted by g_1) the equations

$$2Sg_2 = 2 + 3 = 5, \qquad Sg_2 + g_1 = 1 + 1 + 2 = 4,$$

or

$$Sg_2 = 5/2, \qquad g_1 = 3/2.$$

The earliest test of this theoretical result for the four-shell is possible for lead. Observations certainly show four p-terms, while the existence of a fifth p-term is

doubtful.[7] So far unpublished measurements by E. Back of a few lead lines make it, moreover, very likely that the first four p-terms have j-values 2, 2, 1, 0, and that the g-values of these terms also agree with the theoretically expected ones.

Let us now return to the discussion of the gradual construction of the eight-shell. By means of the reciprocity rule, applied to the whole of the Bohr subgroup with $k = 2$, which contains in its closed state six electrons, we can immediately apply the results obtained for the four-shell to the number of possibilities to realise the six-shell (from electrons with $k_1 = 2$), which occurs, for instance, for O. The following cases of the six-shell are clearly conjugate to the cases (a), (b), and (c):

(a) Four equivalent n_{22}-electrons (two empty spaces in the n_{21}-group). This part-subgroup is closed; hence as before sub (a) one term with $j = 0$.

(b) One n_{21}-, three equivalent n_{22}-electrons (one empty space in the n_{21}-, and one empty space in the n_{22}- group). As before: one term with $j = 2$ and one term with $j = 1$.

(c) Two equivalent n_{21}- and two equivalent n_{22}-electrons (two empty spaces in the n_{22}-group). The first partsubgroup is closed. As before: one term with $j = 2$, one term with $j = 0$.

We must thus also here, for instance for oxygen, expect five p-terms with the smallest principal quantum number. So far only three such terms have been observed for O and S, with j-values of 2, 1, 0.[8] We must wait and see whether two more p-terms of the same principal quantum number can be found from the observations, or whether our rule must be modified in this case.

As yet there are no observations about the five-shell (3 electrons with $k_1 = 2$) and we shall therefore give only the result of the discussion; according to our rule this shell gives rise to five p-terms, one term with $j = 5/2$, three terms with $j = 3/2$, and one term with $j = 1/2$. For the seven-shell, realised in x-ray spectra we get -- as we mentioned before -- terms similar to the alkalis.

We shall not discuss here further special cases, before experimental data are available, but it should be clear from the examples given that in each case our rule is able to give a unique answer to the question about the possibilities of realising the different shells for a given number of equivalent electrons. To be sure, only in the simplest cases was it possible to verify that the results obtained in this way are in agreement with experiment.

In general we may note that the discussions given here are in principle based, as far as the transition from strong to weak or vanishing fields is concerned, upon the invariance of the statistical weights of quantum states. However, on the basis of the results obtained there seem to be no reasons for a connexion between the problem of the completion of electron groups in an atom and the correspondence principle, as Bohr suspected to be the case, It is probably necessary to improve the basic principles of quantum theory before we can successfully discuss the problem of a better foundation of the general rules, suggested here, for the occurrence of equivalent electrons in an atom.

Footnotes

[N.B. A few footnotes have been omitted in this translation.]

[a] One notes that one must assign to the two cases $m_1 = -1/2$ for the first and $m_2 = 1/2$ for the second electron, or $m_1 = +1/2$ for the first and $m_2 = -1/2$ for the second electron two different terms (as far as the part of the energy independent of the field is concerned). This is perhaps a blemish of the classification given here. It will later on, however, turn out that if the inner and the outer valence electron are equivalent, these two terms are in fact identical.

[b] The replacement here of a seven-shell (atom core of neon) by one electron will be given a theoretical basis in the next section.

[c] As already indicated, the value of j is defined here and henceforth as the maximum value of the quantum number m_1.

[d] It follows directly from Millikan and Landé's results about the relativistic doublets of the X-ray spectra that this subdivision and the question about the number of electrons in the part-subgroups also makes sense for completed electron groups. These numbers appear clearly in the expression for the energy of the whole groups as function of the order number in the shape of factors of the Moseley-Sommerfeld expressions involving definite values of the screening numbers (determined by k_1) and the relativity correction (determined by k_2).

[e] This invariance is independent of the validity of classical mechanics under the transformation.

[f] The second case corresponds to an interchange of the two equivalent electrons and gives us therefore here no new stationary state (compare the footnote lettered a). However, in this two-fold realisability of the quantum state considered is contained the fact that its statistical weight with respect to the exchangeability of the two electrons must be multiplied by two (compare also the discussion of statistical weights by Stoner)[6].

[g] However, because of the equality of the number of m_2-values for conjugate arrangements it follows that also in weak fields the "g-sums" (taken over terms with the same j) of the appropriate terms are the same.

[h] Because of this we must count the case $m_1 = +1/2$ for the first and $m_1 = -1/2$ for the second electron different from the case $m_1 = -1/2$ for the first and $m_1 = +1/2$ for the second electron. Compare the footnote lettered a.

References

[1] W. Pauli, *Z. Physik* **31,** 373 (1925).

[2] N. Bohr, *Ann. Physik* **71,** 228 (1923); especially p. 276.

[3] W. Heisenberg and A. Landé, *Z. Physik* **25,** 279 (1924).

[4] A. Landé, *Ann. Physik* **76,** 273 (1925); see especially section 2.

[5] See N. Bohr, *Drei Aufsätze über Spektren und Atombau,* Brunswick, 1924.

[6] E. C. Stoner, *Phil. Mag.* **48,** 719 (1924).

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