

alternation of multiplicities may therefore be expressed in the following generalized form:

The terms of atoms or ions with an even number of electrons have odd multiplicities; the terms of atoms or ions with an odd number of electrons have even multiplicities. This rule holds also for elements not fitting into one of the eight columns of the periodic system; for example, the rare earths.

2. Physical Interpretation of the Quantum Numbers

Meaning of L for several emission electrons. For the H atom and the alkalis (which have one emission electron), L is the same as l , which is itself proportional to the orbital angular momentum of the electron. For elements with a larger number of emission electrons, such as the earths or the elements of the oxygen group, the quantum number L was at first introduced purely empirically to distinguish the different term series (S, P, D, \dots) of a term system. Its numerical value and, from this, the symbol for the corresponding term were obtained from the combination properties, the same selection rule being assumed for L as for l , that is, $\Delta L = \pm 1$. Further information was obtained from the investigation of multiplet structure and of the Zeeman effect. In more general cases, transitions with $\Delta L = 0$ are also observed (see Chapter IV). The question is: In the more general cases what meaning does L have in our model of the atom?

If we recall that a definite, constant orbital angular momentum l is ascribed to the emission electron of the H atom or of the alkali atoms, it appears very plausible, even in a complicated atom, to ascribe to each individual electron a definite, constant orbital angular momentum l_i , where l_i is a vector of magnitude $0, 1, 2, \dots$ in units $h/2\pi$.

That this assumption is true to a first approximation follows from the consideration that in complicated atoms each electron may be thought of as moving in the smeared-out field of the other electrons. This smeared-out field is approximately spherically symmetrical, and an electron

moving in a spherically symmetric field has, according to wave mechanics, quantum numbers n and l , where l is proportional to the angular momentum (see p. 46f.).

The individual angular momenta produce, when added vectorially, a resultant which depends on the number, magnitude, and direction of the respective vectors. Classically, since these can take all possible directions, the resultant momentum can, in general, take all values up to $\sum |l_i|$, the last when all l_i are in the same direction.⁴ Quantum mechanics, however, shows that for atomic systems the resultant orbital angular momentum, as well as the individual angular momenta l_i , can be only an integral multiple of $h/2\pi$.⁵ The resultant orbital angular momentum is thus $L'(h/2\pi)$, or more accurately $\sqrt{L'(L'+1)} h/2\pi$ where L' is taken temporarily as the corresponding quantum number. The individual l_i can therefore be oriented only in certain discrete directions to one another. For the case of two electrons with orbital angular momenta l_1 and l_2 , the possible resultant L' values are given by:

$$L' = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2), \dots, |l_1 - l_2|$$

Fig. 35 (p. 84) shows the possible resultants for $l_1 = 2$, $l_2 = 1$. Thus we obtain as many different states of the atom as there are different L' values. They are distinguished by the orientation of the orbital planes to one another (to use the old Bohr mode of expression).

However, the individual electrons do not move even approximately independent of one another, as do, for example, the planets in the solar system; rather, they exert strong forces on one another (interactions), due partly to their electric repulsion and partly to the magnetic moments resulting from their angular momenta (see section 3). These interactions have magnitudes which depend on the particular circumstances. For example, if the two electrons

⁴ In general, the smallest possible value for the resultant is 0. But it will be greater than 0 if one l_i is larger than the sum of the magnitudes of all the others.

⁵ The basis for this conclusion is quite analogous to the basis for the integral value of l , given on page 41.

have very different principal quantum numbers, the interactions are relatively small on account of the large mean separation; whereas they will, in general, be rather large when the principal quantum numbers are equal.

This interaction now has the effect that the direction of the individual angular momenta is no longer constant with time (as in the case of the one-electron problem) but carries out a *precessional movement* (just as the direction of the earth's axis carries out a very slow precession due to the interaction with the gravitational field of the sun, which seeks, on account of the flattening of the earth at the poles, to set the earth's axis perpendicular to the orbital plane). In classical as well as in wave mechanics, the resultant angular momentum L' remains, however, constant in magnitude and direction during this precession of the individual momenta. The precession for the case of two electrons is shown in Fig. 36. The greater the interaction, the greater will be the velocity of precession.* If this velocity is of the same order as the angular velocity corresponding to the individual angular momenta themselves, the latter lose their meaning completely, since then the electron does not describe, even to a first approximation, a rotational motion about the individual angular momentum vector as axis, but rather a much more complicated motion. For very strong coupling (very high velocity of precession), this motion reduces, in a first approximation, to a simple

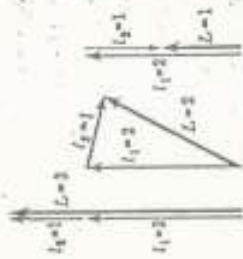


Fig. 35. Addition of l_1 and l_2 to Give a Resultant Orbital Angular Momentum L for $l_1 = 2$, $l_2 = 1$, and $L = 3$, 2, 1.

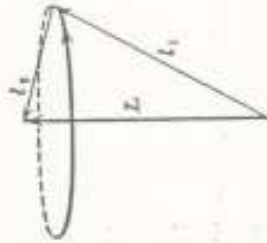


Fig. 36. Precession of l_1 and l_2 about the Resultant L . Replacing l_1 , l_2 , and L by L , S , and J gives a picture of the precession of L and S about J . (See p. 90.)

* In the case of the precession of the earth's axis, the interaction is so small that the period of precession is 25,000 years.

rotation about the precessional axis (the axis of the resultant angular momentum). In this case only the resultant L' has an exactly defined meaning.

If the selection rules for the quantum number L' of the resultant orbital angular momentum are derived in the way outlined in Chapter I, section 4, it is found that the selection rule $\Delta L' = \pm 1$ usually holds, although $\Delta L' = 0$ can also occur. L' therefore has just the properties observed for the empirically introduced L . Therefore L' must be identified with L . Thus the *different term series* S , P , D , ... of an atom with more than one emission electron are distinguished by different values (0, 1, 2, ...) for the resultant orbital angular momentum L of the electrons. Hence the selection rule

$$\Delta L = 0, \pm 1 \quad (\text{II, 3})$$

holds. In addition, there is the rule that, so long as the interaction of the electrons is not very large, only those quantum transitions take place for which only one of the emission electrons makes a jump—that is, only one alters its l value, the alteration being in accordance with the selection rule (I, 29): $\Delta l = \pm 1$. For example, a state of an atom with two emission electrons with $L = 1$, $l_1 = 1$, $l_2 = 0$ cannot combine with a state $L = 2$, $l_1 = 3$, $l_2 = 3$, although this combination would be allowed according to (II, 3) alone.

For strong coupling of the angular momentum vectors, the energy of the entire system will obviously differ according to the orientation of the individual angular momenta to one another. Thus in the case of two electrons (considered above), the energies of the states

$$L = (l_1 + l_2), \quad (l_1 + l_2 - 1), \quad \dots, \quad |l_1 - l_2| \quad (\text{II, 4})$$

differ—the difference being greater, the stronger the coupling (interaction). The observed magnitude of the energy difference is a direct measure of the strength of the coupling.

As we have shown above, when there is strong interaction in an atom, the individual angular momenta l_i no longer

have any exact meaning as angular momenta; only their resultant L has an exact meaning. The momenta l_i are, however, still of importance in determining the number and type of the terms. Both in the Bohr theory and in quantum mechanics, *Ehrenfest's adiabatic law* holds: *For a virtual, infinitely slow alteration of the coupling conditions, the quantum numbers of the system do not change*⁷ and, in particular, the number of terms does not vary. Hence, if we "uncouple" the individual orbital angular momenta by assuming their interactions removed, we come, in the limiting case, to the state in which each individual l_i actually has the meaning of an angular momentum and in which we can carry out the above vector addition. Thus we obtain the correct number and type of the resulting terms.

Consequently, for the case of a number of electrons in an atom, we ascribe to each electron an l value that would correspond to the angular momentum of this electron for infinitely small or vanishing coupling. Electrons with $l = 0$ are called *s-electrons*; those with $l = 1$, *p-electrons*; those with $l = 2$, *d-electrons*; and so on (small letters being used in contrast to capital letters, which represent terms of a complete atom or ion). The principal quantum number of the electron is added to this, and we have such symbols as $1s$, $2p$, $4d$, and so on. At all events, even in the actual atom, the quantum numbers l_i still retain their importance for deriving the number and type of terms, but do not always correspond to angular momenta—at least not in the strict sense of the word.

Table 5 shows the term types given by various electron configurations (cf. Table 10, p. 132).

If all but one of the l_i are zero, the resulting L value will naturally be that of the single l_i . This single l then retains literally its physical meaning of an angular momentum.

⁷ The converse of this law is: Only such magnitudes can be quantized as remain constant (invariant) for adiabatic changes. According to Ehrenfest, this converse may be considered the fundamental law of the old quantum theory.

Such, for example, is the case for most (normal) terms of the alkaline earths and He. The term type S, P, D, \dots then depends only upon the l value of this one emission electron, just as for the alkalis. However, even for the alkaline earths there are terms—the so-called *anomalous terms* (see Chapter IV, section 2)—for which two electrons have $l \neq 0$. For elements of the carbon group and beyond, the occurrence of such terms with more than one electron having $l \neq 0$ is quite general.

TABLE 5

L VALUES AND TERM SYMBOLS FOR TERMS WITH DIFFERENT ELECTRON CONFIGURATIONS

Electron Configuration	L	Term Symbol
s	0	S
p	1	P
pp	0 1 2	$S P D$
pd	1 2 3	$P D F$
dd	0 1 2 3 4	$S P D F G$
ppp	0 1 1 1 2 2 3	$S P P D D P$

When there are three electrons for which $l \neq 0$, the vector addition may be carried out simply by combining the l values of two electrons and then combining each of the resulting L values with the l of the third electron.

Physical interpretation of J : cause of multiplet splitting. On the basis of the foregoing, a term with a given L is single. How can we then explain the observed splitting into multiplets of the terms with a given value of L ? As we shall anticipate here (cf. the following section), investigations of the anomalous Zeeman effect have shown that the individual components of a multiplet are distinguished from one another by the *total angular momentum of the atom*. In fact, using the above nomenclature for distinguishing the sub-levels (empirical quantum number J), the total angular momentum is found to be equal to $J \times h/2\pi$, where, as will be remembered, J is the quantum number at first intro-

duced purely formally in order to distinguish the sub-levels. According to quantum mechanics, the exact value of the total angular momentum is, not $J(\hbar/2\pi)$, but $\sqrt{J(J+1)} \times \hbar/2\pi$, as in the case of l . As before, the difference can in many cases be disregarded.

The total angular momentum of the atom is thus not equal to the resultant (integral) orbital angular momentum L , which is the same for all components of a multiplet term, but can take as many different values as the multiplicity of the term. Thus, to obtain the total angular momentum J , one has to add vectorially to L an additional integral or half-integral angular momentum vector S , whose exact meaning we shall leave undefined for the moment. According to the quantum theory, L and S cannot be oriented to each other in any arbitrary direction but only in certain directions (similar to the case of the individual l_i), and therefore only certain discrete values of the resultant J are possible. The largest and the smallest values of J for a given pair of values L and S are obtained by a simple addition and subtraction of the corresponding quantum numbers L and S .⁸ In this calculation only the magnitude of the resultant vector is of importance, since J , naturally, can only be positive. Intermediate values of J are also possible, and these differ from the extreme values (sum and difference) by integral amounts, just as in the addition of the l_i to form a resultant L . In this case we have therefore:

$$J = (L + S), (L + S - 1), (L + S - 2), \dots, |L - S| \quad (\text{II, 5})$$

In other words, the rule is: the vector addition of L and S is such that the different possible values of their vector sum have integral differences. Fig. 37 illustrates this rule for the cases $L = 1, S = \frac{1}{2}; L = 1, S = 1; L = 2, S = 1; L = 1, S = \frac{3}{2}; L = 2, S = \frac{3}{2}$. When $L > S$, it is easily

⁸ This S , naturally, has nothing to do with the S of the S terms. The former is a quantum number; the latter, a symbol for $l = 0$. This nomenclature is intentionally used and must therefore be used here, although it may lead to confusion.

seen from (II, 5) that the number of possible J values for a given value of L is

$$2S + 1$$

On the other hand, if $L < S$, the number of possible J values for a given value of L is

$$2L + 1$$

In particular, for S terms ($L = 0, 2L + 1 = 1$) there is only one value of J ; namely, $J = S$.

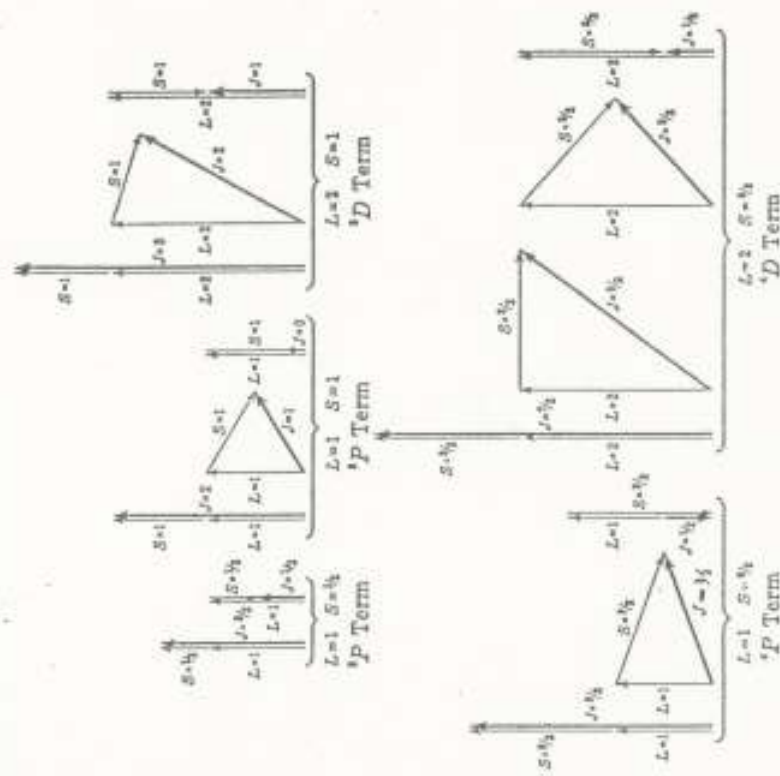


Fig. 37. Vector Addition of L and S to Give a Resultant J for Different Examples. For a given combination of L and S , all the possible orientations of L and S with respect to one another and the corresponding total angular momenta are illustrated. The vector J is indicated by a heavy line. Its direction is fixed in space. The magnitude of the vector J (and, correspondingly, of L and S) is taken as $J(\hbar/2\pi)$, and not $\sqrt{J(J+1)}\hbar/2\pi$, as it should be strictly speaking.

Note that, in drawing such figures, the direction of the first vector is quite arbitrary. It is only for simplicity that all these have been drawn vertically.

The number of possible J values—that is, possible values of the total angular momentum—is equal to the number of components into which a term of given L is split. Evidently when the angular momentum is different for two states, the energy will, in general, also be different, as we have already seen when dealing with the vector addition of the l_i . Now, we had previously associated some terms with a system of higher multiplicity, though they themselves actually had a smaller number of components; for example, we had 2S terms, although the S terms are always single. The reason for this apparent inconsistency is now clear. The important thing for the behavior of a term is not the number of its components but the *magnitude of its additional angular momentum vector S*. For 2S terms, the quantum number of the additional angular momentum S equals 1, as for 3P and 3D terms. This value of S gives three components for $^3P, ^3D, \dots$ terms (cf. Fig. 37), but only one component for S terms since $L = 0$. In spite of this fact, the 3S term behaves like $^3P, ^3D, \dots$ terms since for all of them $S = 1$. The value $2S + 1$ is generally called the *multiplicity* of a term, which gives the number of possible J values or the number of components only when $L > S$.

According to the above discussion, the vector additions in Fig. 37 represent the cases of $^3P, ^3P, ^3D, ^3P, ^3D$ terms. The 3P term has only three components (since $L < S$), but in spite of that is called a *quartet* term. Table 6 gives the multiplicities ($2S + 1$) for different values of S .

As Table 6 shows, the multiplicity $2S + 1$ is even when S is half integral (for example, for the alkalis, $S = \frac{1}{2}$, and doublets result), but is odd when S is integral (for example, for the alkaline earths, $S = 1$ or 0 , and triplets and singlets result). Conversely, in order to explain an observed even number of components (for example, doublets), we must necessarily assume that S is half integral; whereas, for an odd number of components, S must be integral.

Just as in the combination of the l_i to give L , a precession of the components L and S takes place about the resultant J

TABLE 6
MULTIPLICITIES FOR DIFFERENT VALUES OF S

S	Multiplicity of the Terms
0	Singlets
$\frac{1}{2}$	Doublets
1	Triplets
$\frac{3}{2}$	Quartets
2	Quintets
$\frac{5}{2}$	Sextets
...	...

(cf. Fig. 36, p. 84). The greater the interaction of L and S , the faster will be the precession and the greater will be the difference in energies of the states with different J ; that is, the greater will be the multiplet splitting. Furthermore, according to Dirac's wave mechanical theory of the electron spin, Sommerfeld's fine structure formula (I, 12) still holds if k is replaced by $j + \frac{1}{2}$, where j corresponds to J for the case of one electron. It thus follows from (I, 12) that, for the case of one emission electron, the doublet splitting is proportional to Z^4 . Strictly speaking, this conclusion should hold only for hydrogen-like ions, but qualitatively this rapid increase in multiplet splitting with increasing Z will also hold for all other cases. This result is in agreement with experiment. For example, for Li ($Z = 3$), the splitting of the lowest 3P level is 0.34 cm^{-1} , for Ca ($Z = 55$), it is 5540 cm^{-1} ; for Be ($Z = 4$), the total splitting of the first 3P level is 3.03 cm^{-1} ; for Hg ($Z = 80$), 6397.9 cm^{-1} . On the other hand, according to (I, 12), the splitting should decrease with increasing n and L . This effect is also observed. For a not too high atomic number, the multiplet splitting is, in general, relatively small; that is, the velocity of the precession of L and S about J is small. L and S therefore retain, to a good approximation, their meaning as angular momenta, even when the interaction is allowed for. However, for heavy elements, sometimes only

J retains its meaning as an angular momentum (see Chapter IV, section 3).

If the components in a multiplet term lie energetically in the same order as their J values (smallest J value lowest) the term is called *regular* or *normal* and, in the converse case, *inverted*. For example, most of the P and D terms of the alkalis and the alkaline earths are regular doublets or triplets (Figs. 30 and 33). Similarly, the quartet terms of C^+ in Fig. 34 (p. 80) are also regular. Fig. 38 gives a D term as an example of an inverted term. The reason for the appearance of the inverted order of the terms will not be discussed here [cf. White (12) and Condon and Shortley (13)].

J	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
—————	—————	—————	—————	—————
$L=2, S=\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$

Fig. 38. Example of an inverted term D . Corresponding to the interval rule (see p. 178), the separation of the components increases from top to bottom, contrary to a normal term.

Selection rule for J . Wave mechanical calculation of the transition probability (cf. Chapter I, section 4) shows that the selection rule $\Delta J = 0, \pm 1$ holds for the quantum number J of the total angular momentum of an atomic system. In addition, it is found that a level with $J = 0$ does not combine with another level with $J = 0$. These results agree exactly with the selection rules (II, 1) and (II, 2), which were derived purely empirically from spectroscopic observations (see p. 74 and p. 79).

Physical interpretation of S . What meaning can we now give to the additional angular momentum S in our atomic model? Historically, the first assumption held that this angular momentum was the angular momentum of the atomic core. The assumption has proved untenable, since for the alkalis, for example, the atomic core is formed by the ground state of the corresponding alkali ion and, according to the spark spectrum, this is a 1S_0 state (just as for the inert gases, according to the Sommerfeld-Kossel displacement law) and thus has $J = 0$, $L = 0$, and $S = 0$. That is to say, an angular momentum of the atomic core

cannot be present in the case of a neutral alkali atom. Apart from this, it is difficult to see why the angular momentum of the atomic core should be half integral. But that J and therefore the additional angular momentum S really must be half integral for even multiplicities is also confirmed definitely by the investigation of the anomalous Zeeman effect, as will be seen later. Goudsmit and Uhlenbeck were thus led to the assumption that the additional angular momentum S is due to the electron or electrons themselves. According to this assumption, each electron performs a rotation about its own axis as well as a motion about the nucleus. This rotation is such that the angular momentum s has the same magnitude for each electron, $\frac{1}{2}(\hbar/2\pi)$; the rotation is usually called the *spin*, or the *electron spin*.⁹ The assumption of electron spin has been verified by an extraordinarily large amount of experimental material and must be regarded today as entirely correct.¹⁰

When several electrons are present, the individual spin vectors s , combine with one another just as in the case of the l , previously discussed. It is the *resultant spin vector* which, according to Goudsmit and Uhlenbeck, is identical with the above empirically derived, additional angular momentum vector S . Analogous to L , the resultant spin vector S can take only certain discrete values according to the quantum theory, the maximum value being obtained when all the s , are parallel. In that case, if N is the number of electrons, the corresponding quantum number S is equal to $N/2$, since each electron contributes $\frac{1}{2}$. For other orientations of the s , the following S values are possible:

$$N/2 - 1, N/2 - 2, \dots, \frac{1}{2} \text{ or } 0$$

The smallest value is $\frac{1}{2}$ or 0 according as $N/2$ is half integral

⁹The rigorous quantum mechanical formula for the magnitude of the vector s would be $\sqrt{s(s+1)}\hbar/2\pi$; that is, with $s = \frac{1}{2}$, $\frac{1}{2}\sqrt{3}\hbar/2\pi$.
¹⁰The assumption appears as a necessary result of Dirac's relativistic wave mechanics. However, this theory has thus far been completely worked out only for the one-electron problem.

or integral. It follows that S is *half integral or integral according as the number of electrons is odd or even*. The empirically obtained alternation law of multiplicities follows directly from this result, since the multiplicity is equal to $2S + 1$ and will therefore be even or odd, according as the number of electrons is odd or even (see p. 81).

The same conclusions that we have derived for the spin from analogy and consideration of the old quantum theory may also be reached by an accurate wave mechanical treatment [Condon and Shortley (13)]. Also, we can obtain these conclusions rather more simply and schematically (but less rigorously) by assuming that the spins of the individual electrons in an atom will be either parallel or antiparallel to one another. It is then obvious that the resultant will be half integral or integral according to whether the number of electrons is odd or even.

The exact theoretical derivation shows that, to a first approximation, states with different S (different multiplicities) do not combine with one another. This prohibition of intercombinations has also been observed empirically (p. 79). We therefore have the selection rule for S :

$$\Delta S = 0 \quad (\text{II, 6})$$

Both theory and experiment show that this selection rule is adhered to less and less strictly as the atomic number increases.

The alkalis have one electron outside the atomic core (see Chapter III). Consequently $S = \frac{1}{2}$, and doublet terms result, in agreement with experiment.

The alkaline earths and He have two electrons outside the atomic core. Their spins can be either parallel $\uparrow\uparrow$ or antiparallel $\uparrow\downarrow$ to one another; that is, $S = 1$ or 0 , and there result triplet as well as singlet states. Each state with a given L can, in general, occur as a triplet state as well as a singlet state. The ground state, which occurs only as a singlet state, forms an exception (cf. the energy level diagrams of Figs. 27 and 32), which will be explained in the next chapter.

With three electrons outside the core, S can have the values $\frac{3}{2}$ and $\frac{1}{2}$, corresponding to $\uparrow\uparrow\uparrow$ and $\uparrow\uparrow\downarrow$. This gives quartets and doublets.

Table 7 lists the possible term multiplicities for various numbers of electrons.

TABLE 7

POSSIBLE MULTIPLICITIES FOR VARIOUS NUMBERS OF ELECTRONS

Number of Electrons	Possible Multiplicities
1	Doublets
2	Singlets, triplets
3	Doublets, quartets
4	Singlets, triplets, quintets
5	Doublets, quartets, sextets
6	Singlets, triplets, quintets, septets
7	Doublets, quartets, sextets, octets
8	Singlets, triplets, quintets, septets, nonets

According to the preceding discussion, the spectrum of the H atom should also be a doublet spectrum. Actually, it has been shown that the hydrogen fine structure can only be explained quantitatively by taking account of this fact. The relations are, however, complicated in this case by the fact that the separation of terms with different l (and equal n) is of the same order as the doublet splitting. We shall not go into these complications [see White (12)] but merely note that, according to this interpretation, the lines of the Lyman series are not single, as assumed in Fig. 13, but consist of two components like the lines of the principal series of the alkalis. (The experimental investigation of the fine structure of the Lyman lines offers many difficulties because the lines lie in the vacuum region, and has therefore not yet been carried out.)

The fact that multiplet splitting does occur shows that an interaction between L and S exists. It is, in general, small for a not too great atomic number. This interaction is due to the fact that a *magnetic moment* is associated with the electron spin, just as with any rotation of charges. The magnetic moment of the spin is influenced by the magnetic moment associated with the orbital angular mo-

mentum L , the magnitude of this interaction depending upon their orientation to each other. Therefore, as already mentioned, a precession of L and S about the direction of the total angular momentum J takes place (cf. Fig. 36, p. 84).

For the magnitude of the magnetic moment of the electron, Goudsmit and Uhlenbeck made the assumption that it is twice as great as follows from the classical connection between magnetic moment and angular momentum. The meaning of this assumption will be amplified in section 3 of this chapter.

As already noted, states with different S (different multiplicities but with other quantum numbers the same) have appreciably different energies (cf. Figs. 27 and 32). For a not too high atomic number, the energy difference is appreciably greater than the energy difference between the individual components of a multiplet. Although it might appear that this energy difference of terms with different multiplicities is due to the different interactions of the spins resulting from their different orientations, the interaction of the spin vectors s_i due to their magnetic moments cannot possibly be very much greater than that of L and S . In fact, theoretically it should be appreciably smaller. The energy difference of the various multiplet systems must, therefore, have another origin, which will be dealt with in Chapter III.

3. Space Quantization, Zeeman Effect and Stark Effect

General remarks on Zeeman Effect and Stark Effect. The necessity for the assumption of an angular momentum or spin of the electron itself and, in particular, its double magnetism is made especially clear in the explanation of the Zeeman effect of spectral lines. This effect may be described as follows. When a light source is brought into a magnetic field, each emitted spectral line is split into a number of components. To a first approximation, the splitting is proportional to the strength of the magnetic field. Fig. 39 shows three examples of such splitting.

The splitting of the lines is evidently due to a splitting of the terms in the magnetic field. The influence of a magnetic field on energy levels is, perhaps, most clearly under-

stood by considering how a magnetic needle behaves in a magnetic field. The potential energy of the magnetic needle depends upon its direction with respect to the magnetic field. Therefore, if the needle is displaced from the



Fig. 39. Examples of Line Splitting in a Magnetic Field (Zeeman Effect) [after Back and Landé (6)].

(a) Normal Zeeman triplet of the Cd line 6438.47 Å ($^1P - ^1D$ transition). Above, the exposure was so made that only light polarized parallel to the field direction could reach the plate (single component at the position of the original line). Below, the components were polarized perpendicular to the field; they lie symmetrical to the original line.

(b) Anomalous Zeeman splitting of the two D lines of Na, 5880.96 Å and 5895.03 Å ($^3S - ^3P$ transition). Above, with magnetic field. Below, without magnetic field.

(c) Anomalous splitting of the Zn line 4722.16 Å ($^1P_1 - ^1S_0$ transition).

direction of the field and then released, it will vibrate back and forth about its equilibrium position (the position of minimum potential energy—that is, when the needle is in the direction of the field) and can be brought to rest only by the dissipation of its energy. Like the magnetic needle, the atom generally has a magnetic moment μ . The rotation of electric charges which, even according to wave mechanics, takes place in the atom always leads to the production of a magnetic moment in the direction of the axis of rotation. This effect follows the same laws that operate when a current flows through a wire ring (circular electric current). The greater the angular momentum of the atom, the greater will be the magnetic moment μ . Because of the inherent connection between magnetic moment and angular momentum, we have to take into account the gyroscopic forces when we discuss the behavior of an atom in a magnetic field.

The effect of these gyroscopic forces is that the rotational axis of the atom (direction of ψ) does not vibrate back and forth about the position of minimum energy, but executes a *precessional motion* with uniform velocity about the direction of the field (so-called *Larmor precession*). This precession is shown diagrammatically in Fig. 40.

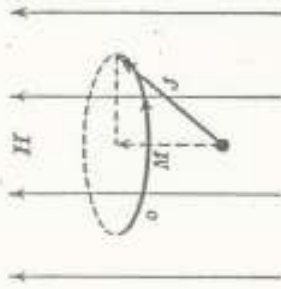


Fig. 40. Precession of the Total Angular Momentum J in a Magnetic Field H about the Field Direction as the vibration frequency of a mag-

net.) So long as no energy is dissipated, the precession continues at a constant angle to the field direction; that is, J has a constant component M in the direction of the field. The energy in a magnetic field (as for the magnetic needle) is:

$$W = W_0 - H\psi_H \quad (\text{II, 7})$$

where ψ_H is the component of the magnetic moment in the field direction and W_0 is the energy in the field-free case. When ψ or J is perpendicular to the field direction, $W = W_0$.

Just as two angular momentum vectors in an atomic system cannot, according to quantum mechanics, take any arbitrary direction with respect to one another but only certain discrete directions, so an angular momentum vector can take only certain discrete directions in a magnetic field. This means that J (and therefore ψ) is space quantized in a magnetic field. Just as the resultant in the aforementioned case of two angular momentum vectors can take only integral or half-integral values, so in this case the component M of the angular momentum J in the direction of the field can be only an integral or half-integral multiple of $h/2\pi$. It will be

integral when J is integral, or half integral when J is half integral. Thus the following relation holds:

$$M = J, J - 1, J - 2, \dots, -J \quad (\text{II, 8})$$

This gives $2J + 1$ different values.

The left half of Fig. 41 illustrates the possible orientations of J to the direction of the magnetic field H for $J = 2$ and $J = \frac{3}{2}$. The precession which J carries out about the field direction, as in Fig. 40, can take place only at one of the given angles to the field direction. For $J = \frac{3}{2}$, only the directions parallel or antiparallel to the field are possible.

Corresponding to this space quantization, the energy of the system in a magnetic field cannot take any value

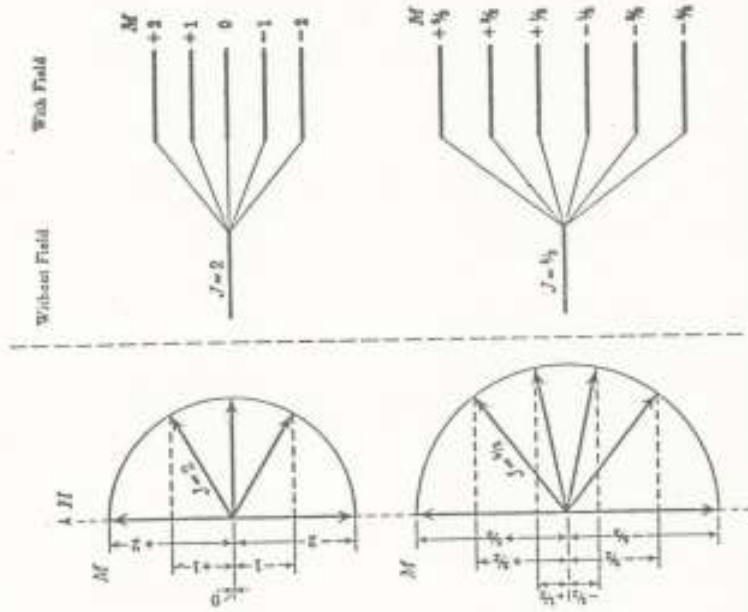


Fig. 41. Space Quantization of the Total Angular Momentum J in a Magnetic Field H for $J = 2$ and $J = \frac{3}{2}$. To the left are the possible orientations to the magnetic field. To the right, in an energy level diagram, the corresponding energy values are indicated.

between $W_0 + H|\psi\rangle$ and $W_0 - H|\psi\rangle$; but it can take only $2J + 1$ discrete values. The right half of Fig. 41 shows this term splitting in a magnetic field. According to (II, 7), the splitting is proportional to the field strength. It is, in first approximation, symmetrical about the undisplaced term. All the energy differences between the individual components are the same, since $H\psi_M$ is proportional to M (cf. below) and the possible M values have whole-number differences.

The space quantization itself is independent of the field strength. It remains even when the field strength decreases to zero, although then all the $2J + 1$ different states, differing in orientation, have equal energy: they are degenerate.

This degeneracy in the field-free case is the same as that already mentioned for the H atom (p. 47). There we had a $2l + 1$ fold space degeneracy. Now, in the general case, J replaces l . Without field, there are consequently $2J + 1$ different eigenfunctions which belong to the same eigenvalue; with field, there are $2J + 1$ slightly different eigenvalues or energy values belonging to these $2J + 1$ different eigenfunctions.¹¹

The existence of space quantization is shown most strikingly by the Stern-Gerlach experiment in which a beam of atoms is sent through an inhomogeneous magnetic field. In such a field, a body with a magnetic moment is subject, not only to a force tending to turn the direction of the magnetic moment into the field direction, but also to a deflecting force due to the difference in field strength at the two poles of the body. Depending on its orientation, the body will therefore be driven in the direction of increasing or decreasing field strength. Suppose we now send through

¹¹ In the field-free case, any linear combination of the $2J + 1$ eigenfunctions is an eigenfunction of the same energy value. The eigenfunctions with field will be approximately equal to those without field only when one has chosen the "correct" linear combinations of the field-free eigenfunctions that are appropriate for the problem; that is, when one has placed the z -axis of formulas (I, 28) in the direction of the field.

such an inhomogeneous field atoms possessing a magnetic moment (Fig. 42). If atoms with all possible orientations to the field are present, a sharp beam should be drawn out into a band. Actually, a splitting of the beam into $2J + 1$ different beams takes place. In Fig. 42, J is assumed to be $\frac{1}{2}$ and a splitting into two beams results. This experiment shows unambiguously that in a magnetic field not all orientations to the field, but only $2J + 1$ discrete directions, are possible.



Fig. 42. Schematic Representation of the Stern-Gerlach Experiment. A beam of atoms possessing a magnetic moment ($J = \frac{1}{2}$) comes from the left, passes through an inhomogeneous magnetic field between the poles N and S , and falls on the receiving plate A . The directions of the angular momenta of the atoms are indicated by the small arrows.

It must be noted that, whereas the rigorous quantum theoretical value for the magnitude of J is $\sqrt{J(J+1)} \hbar/2\pi$ (cf. p. 88), the rigorous value for the component M of J is $M(\hbar/2\pi)$, not $\sqrt{M(M+1)} \hbar/2\pi$. Therefore the maximum component of the vector J in the direction of the field is $J(\hbar/2\pi)$ and not $\sqrt{J(J+1)} \times \hbar/2\pi$. This may at first seem rather puzzling because in classical mechanics the maximum component of a vector in a given direction is equal to the magnitude of the vector. In fact the magnitude of a vector in classical mechanics may be defined either (a) by the usual square root of the sum of the squares of the three components, or (b) as the largest value its component can have on some fixed axis. In classical mechanics, the two definitions are equivalent and hence the distinction between (a) and (b) is never made explicit. In quantum mechanics, the two are not equivalent—the magnitude being $\sqrt{J(J+1)} \hbar/2\pi$ in the sense of (a), and $J(\hbar/2\pi)$ in the sense of (b), as stated above.

Thus in quantum mechanics the component of J is always smaller than its magnitude, which means that the angular momentum vector cannot point exactly in the direction of the field (fixed axis). This is illustrated on the right in Fig. 43 for $J = \frac{1}{2}$ and

$J = 1$, whereas on the left the more naive representation of Fig. 41 is given. For larger values of J the difference between the two ways of representation—that is, between definitions (a) and (b)—becomes smaller and smaller in accordance with the correspondence principle (see p. 28). For the cases where only the components of the angular momentum matter, definition (b) is sufficient even in quantum mechanics. For some calculations, however, it is necessary to use definition (a). (See below.)

The difference between (a) and (b) in quantum mechanics is intimately connected with Heisenberg's uncertainty relation. If the angular momentum could point exactly in the direction of the field, it would of course mean that the other two components were equal to zero. As then all the three components of the angular momentum would have exact values, it follows from Heisenberg's uncertainty relation that the three corresponding co-ordinates (the angles about the x -, y -, and z -axes) are completely undetermined. This is only possible if the probability distribution is spherically symmetrical—that is, if the angular momentum is zero (' S ' state; cf. p. 135). As soon as the angular momentum J is different from zero, only one of the three components p_x, p_y, p_z can have an exact value, $p_z = M(h/2\pi)$; whereas, for the other two, only the sum of the squares is known, $p_x^2 + p_y^2 = J^2 - p_z^2 = J(J+1)(h/2\pi)^2 - M^2(h/2\pi)^2$, which can never be equal to zero.

With increasing magnetic field strength and therefore increasing velocity of precession, J loses its meaning of angular momentum. This is similar to the previously considered

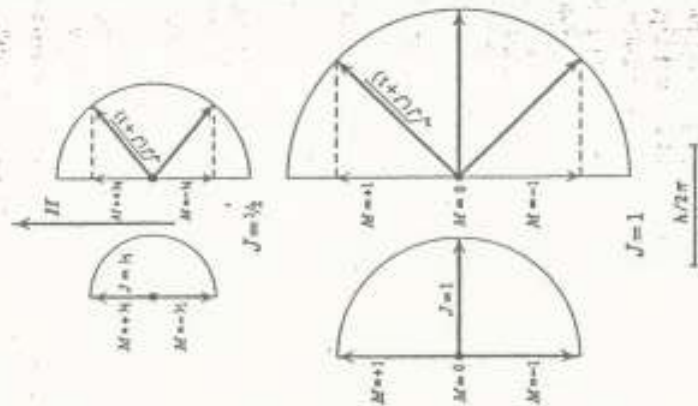


Fig. 43. Space Quantization for $J = \frac{1}{2}$ and $J = 1$. To the left is the naive representation (see Fig. 41) taking the magnitude of the total angular momentum equal to $J(h/2\pi)$. To the right is the exact representation taking the magnitude equal to $\sqrt{J(J+1)}h/2\pi$.

components p_x, p_y, p_z can have an exact value, $p_z = M(h/2\pi)$; whereas, for the other two, only the sum of the squares is known, $p_x^2 + p_y^2 = J^2 - p_z^2 = J(J+1)(h/2\pi)^2 - M^2(h/2\pi)^2$, which can never be equal to zero.

With increasing magnetic field strength and therefore increasing velocity of precession, J loses its meaning of angular momentum. This is similar to the previously considered

case of the vectors l_i . For strong fields, only M retains a strict physical meaning, since there results what is essentially a rotation of the system about the direction of the field.

Normal Zeeman effect. The magnetic moment resulting from the revolution of a negative electric point charge is given classically by:

$$\mu = -\frac{e}{2mc}\dot{\rho} \quad (\text{II, 9})$$

where $\dot{\rho}$ = angular momentum and m = mass of the charged particle. Because of the negative sign of the charge, the magnetic moment has the opposite direction to the angular momentum. For atoms, the angular momentum is $J(h/2\pi)$ [or more accurately, $\sqrt{J(J+1)}h/2\pi$]. The magnitude of the magnetic moment is thus:

$$\mu = -\frac{e}{2mc}\frac{h}{2\pi}J \quad \left[\text{or more exactly, } -\frac{e}{2mc}\frac{h}{2\pi}\sqrt{J(J+1)} \right]$$

For $J = 1$, the magnetic moment is accordingly:

$$\mu_0 = \frac{e}{2mc}\frac{h}{2\pi}$$

which is known as the *Bohr magneton* and has the value 0.9273×10^{-20} erg oersted. The component of μ in the field direction is:

$$\mu_W = -\frac{e}{2mc}\frac{h}{2\pi}M \quad (\text{II, 10})$$

Substituting this value of μ_W in (II, 7), we find that the energy in a magnetic field is:

$$W = W_0 + h\omega M, \quad \text{where } \omega = \frac{1}{2\pi}\frac{eH}{2mc} \quad (\text{II, 11})$$

Here ω is the so-called *Larmor frequency*, which may be shown to be the frequency of precession. From (II, 11) we see that the state with smallest energy has its angular momentum antiparallel to the field direction ($M < 0$). Because of the negative sign in (II, 9), the magnetic moment is then in the field direction.

From (II, 11) it follows that terms with different J values will have different numbers of components ($2J + 1$) in a

magnetic field, but that the separation of consecutive components must be the same for all terms of an atom for a given field strength. This separation is $h\nu$. If two terms combine, it may be shown theoretically (cf. below) that the selection rule for M is:

$$\Delta M = 0, \pm 1 \quad (\text{II, 12})$$

with the addition that the combination

$$M = 0 \rightarrow M = 0 \text{ is forbidden for } \Delta J = 0 \quad (\text{II, 13})$$

Because there is equal splitting for all terms, the number of line components is always 3 since all lines with equal ΔM coincide (see Fig. 44). Lines with $\Delta M = 0$ fall in the position of the original field-free line; lines with $\Delta M = \pm 1$ lie to the right and left at a distance

$$\Delta \nu_{\text{Zeem}} = \frac{0}{c} = 4.0099 \times 10^{-5} \times H$$

This kind of splitting is called the *normal Zeeman effect*. It is observed only for singlet lines ($S = 0$). [Cf. Fig. 39(a), p. 97.]

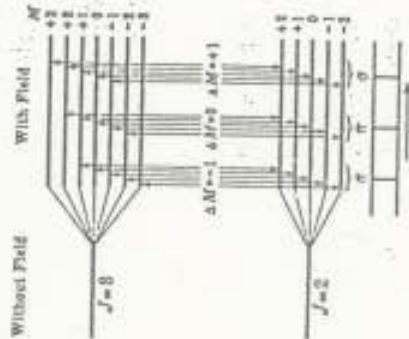


Fig. 44. Normal Zeeman Effect for a Combination $J = 3 \rightarrow J = 2$. The arrows representing the transitions form three groups (indicated by brackets). The arrows in each group have equal length and give rise, therefore, to one and the same line in the splitting pattern (lower part of figure).

It should perhaps be added that, for observations made in a direction perpendicular to the field, the lines with $\Delta M = 0$ are polarized parallel to the field (π -components); the lines with $\Delta M = \pm 1$, perpendicular to the field (σ -components). [Cf. Fig. 39(a).] These results are in agreement with more detailed calculations, as given below.

The selection rule for the magnetic quantum number M will now be briefly derived, according to the methods previously mentioned (p. 51 f.), as a simple example of the wave mechanical derivation of selection rules. Let $\psi' = \chi' e^{iM'\varphi}$ and $\psi'' = \chi'' e^{iM''\varphi}$ be the eigenfunctions of the upper and lower states, respectively.

With the field direction taken as the z -axis, the dependence of the eigenfunction on the azimuthal angle φ is completely allowed for in the factor $e^{iM\varphi}$. [The form of the dependence on φ given previously for the H atom is generally true (p. 39).] Thus φ does not occur in χ . The matrix element R , associated with the transition, has components

$$\int \psi' \psi^{*''} x \, d\tau = \int \chi' \chi^{*''} e^{i(M'-M'')\varphi} x \, d\tau$$

and similarly for y and z .

We introduce co-ordinates x, ρ (distance from z -axis), and φ . Then $d\tau = \rho \, d\varphi \, dz \, d\rho$; $x = \rho \cos \varphi$; $y = \rho \sin \varphi$. Considering first the x component of the matrix element, it is:

$$\begin{aligned} \int \psi' \psi^{*''} x \, d\tau &= \iiint \chi' \chi^{*''} e^{i(M'-M'')\varphi} x \, \rho \, d\varphi \, dz \, d\rho \\ &= \iiint \chi' \chi^{*''} x \, \rho \, dz \, d\rho \int e^{i(M'-M'')\varphi} \, d\varphi \end{aligned}$$

This integral is different from zero only when

$$\int_0^{2\pi} e^{i(M'-M'')\varphi} \, d\varphi$$

does not vanish. Such is the case only when $M' = M''$. Thus the x component of the transition moment will always vanish unless $M' = M''$ or, in other words, light polarized in the x direction (direction of the field) will be emitted only when the selection rule $\Delta M = M' - M'' = 0$ is obeyed.

The z component of the matrix element becomes:

$$\begin{aligned} \int \psi' \psi^{*''} z \, d\tau &= \iiint \chi' \chi^{*''} e^{i(M'-M'')\varphi} \rho \cos \varphi \, \rho \, d\varphi \, dz \, d\rho \\ &= \iiint \chi' \chi^{*''} \rho^2 \, dz \, d\rho \int e^{i(M'-M'')\varphi} \cos \varphi \, d\varphi \end{aligned}$$

which is different from zero only if the second integral does not vanish. By using $\cos \varphi = \frac{1}{2}(e^{i\varphi} + e^{-i\varphi})$, the second integral becomes:

$$\frac{1}{2} \int_0^{2\pi} e^{i(M'-M''+1)\varphi} \, d\varphi + \frac{1}{2} \int_0^{2\pi} e^{i(M'-M''-1)\varphi} \, d\varphi$$

This vanishes unless the exponent in at least one of the two integrals = 0; that is, we have the selection rule $\Delta M = +1$ or -1 . The same result is obtained for the y component. For both components of the transition moment perpendicular to the field direction, we therefore have the selection rule $\Delta M = \pm 1$. In this way we obtain not only the selection rules but also the polarization rules. The components of the splitting pattern with

$\Delta M = 0$ are polarized parallel to the field direction; those with $\Delta M = \pm 1$, perpendicular to the field direction. These results are in agreement with experiment. [Cf. Fig. 39(a).] A more detailed treatment, which we shall not discuss here, leads to the additional rule that the transition $M = 0 \rightarrow M = 0$ is forbidden for transitions with $\Delta J = 0$.

Anomalous Zeeman effect. For all lines that are not singlets, the so-called *anomalous Zeeman effect* is observed. [See Fig. 39(b) and (c), p. 97.] It consists of a splitting into many more than three components with separations that are rational multiples of the normal splitting $\Delta\nu_n$ (Runge's rule). This effect can be explained only by assuming that the magnitude of the term splittings for a given field strength is not the same for all terms but differs according to the values of L and J . We may account for this formally by replacing equation (II, 11) by:

$$W = W_0 + h\sigma M g \quad (\text{II, 14})$$

where g , which is called *Landé's g -factor*, is a rational number which depends upon J and L . It is quite obvious that, even if we retain the above selection rule $\Delta M = 0, \pm 1$, the number of line components obtained in a magnetic field will now depend upon the number of term components ($2J + 1$).

Consider, for example, the D lines of sodium, which correspond to the transitions ${}^3P_{1/2} \rightarrow {}^3S_{1/2}$ and ${}^3P_{3/2} \rightarrow {}^3S_{1/2}$. Since M has only two values for each of the terms ${}^3P_{1/2}$ and ${}^3S_{1/2}$, and has four values for ${}^3P_{3/2}$, it is clear that with a different g value for each of the three terms the number of components of the splitting pattern for one D line of Na will be different from that for the other. As Fig. 45 shows, we obtain four and six components, respectively, in agreement with experiment. [Cf. Fig. 39(b).] Conversely, the observed difference in the splitting patterns of D_1 and D_2 shows that the two P levels, ${}^3P_{1/2}$ and ${}^3P_{3/2}$, differ from each other in the magnitude of their total angular momentum (the orbital momentum being the same), since it is this which is space quantized. Thus J is actually to be identified with the total angular momentum, as we have already

assumed in the foregoing discussion. Finally, the fact that ${}^3P_{1/2} \rightarrow {}^3S_{1/2}$ gives exactly four components shows that, M, J, g

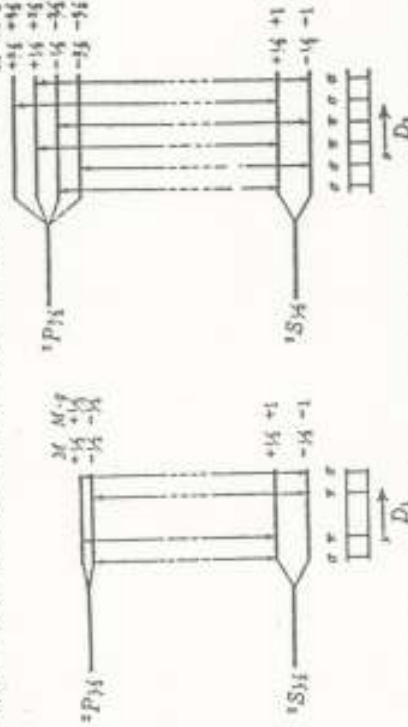


Fig. 45. Anomalous Zeeman Effect of the Sodium D Lines, ${}^3P_{1/2} \rightarrow {}^3S_{1/2}$ and ${}^3P_{3/2} \rightarrow {}^3S_{1/2}$. [Cf. Fig. 39(b), p. 97.] The components designated by σ have $\Delta M = \pm 1$; those designated by π have $\Delta M = 0$. It should be noted that, contrary to Fig. 44, arrows indicating transitions with equal ΔM no longer have the same length, because of the difference in the splitting in the upper and lower states.

actually, J must be taken equal to $\frac{1}{2}$ in both cases. With no other choice of J values is it possible to obtain a splitting of each of the terms into two components. For example, if J were equal to 1 for both terms, the terms would split into three components each, and the line into six components (cf. Fig. 46).

In a similar manner, the correctness of the other J values in Tables 3 and 4 can be shown (p. 73 and p. 78). Fig. 46 gives the explanation of the splitting for a ${}^3S_1 \rightarrow {}^3P_1$ transition, a spectrogram of which is reproduced in Fig. 39(c).

We saw above (II, 14) that the anomalous Zeeman effect

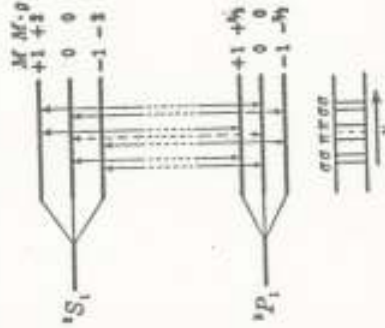


Fig. 46. Anomalous Zeeman Splitting of a ${}^3S_1 \rightarrow {}^3P_1$ Transition. [Cf. Fig. 39(c), p. 97.] According to the selection rule (II, 13), the transition $M = 0 \rightarrow M = 0$ is forbidden, since at the same time $\Delta J = 0$. This transition is indicated by a dotted line.

can be explained formally by introducing the factor $g \neq 1$ into formula (II, 11) for the splitting of a term in a magnetic field, where g depends on L and J . The original formula (II, 11) with $g = 1$ for all terms was based on the assumption that the magnetic moment was given by the classical formula (II, 9). This assumption must, therefore, be incorrect for atoms showing an anomalous Zeeman effect (for which $g \neq 1$). So long as we consider only a revolution of point-like electrons about the atomic nucleus, it is difficult to understand any deviation from formula (II, 9). But even on the basis of the classical theory, the rotation of a non-point electron about its own axis would lead to a ratio of mechanical angular momentum to magnetic moment different from that given by (II, 9). Thus we can well imagine that the magnetic behavior of the spin of the electron is not the same as that arising from orbital motion.

The extent of the departure from the normal orbital type can be obtained, for example, when the behavior of the ground state 2S of the alkalis in a magnetic field is considered, since in this state J results wholly from the spin of one electron. It is found empirically that, for this 2S state,

$$\Delta W = \pm h\omega_1$$

that is, $g = 2$, whereas, if $J = s = \frac{1}{2}$ had a normal magnetic behavior, we ought to have:

$$\Delta W = \pm h\omega_1$$

or $g = 1$. However, the empirical splitting $\Delta W = h\omega_1$ is obtained for the 2S term if we assume that the magnetic moment of the electron due to its spin is one whole Bohr magneton,

$$-\frac{e}{2mc} \frac{h}{2\pi} 1$$

and not

$$-\frac{e}{2mc} \frac{h}{2\pi} 2$$

as would be the case if the electron behaved normally. The assumption that the electron has a magnetic moment of one whole Bohr magneton (whose direction is opposite to that of the spin), in spite of the fact that its spin is only $\frac{1}{2}h/2\pi$,

was first put forward by Goudsmit and Uhlenbeck, simultaneously with the hypothesis of electron spin, and leads to a complete explanation of the splitting in all other cases as well as in the special case considered above. It is clear that in the general case g depends on the values of L , S , and J , and will differ from the limiting values $g = 1$ for $S = 0$, and $g = 2$ for $L = 0$. Theoretically it is found (cf. below) that the following formula holds (Landé):

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (\text{II, 15})$$

Suppose an atom has the values of L , S , and J given in Fig. 47. The length of these vectors is proportional to $\sqrt{L(L+1)}$, $\sqrt{S(S+1)}$, and $\sqrt{J(J+1)}$, respectively, if we take the rigorous formula. The magnetic moments μ_L and μ_S associated with L and S are included in the same figure. The resulting magnetic moment would lie in the direction of J if the magnetic moment μ_S connected with the spin were normal, since then μ_S/S would equal μ_L/L . Actually, the magnetic moment of the spin is twice as large as if it were normal; that is,

$$\frac{\mu_S}{S} = \frac{2\mu_L}{L}$$

The resultant μ therefore falls, not in the direction of J , but in the direction shown, which is different from J and precesses with L and S about the direction of the total angular momentum. Since this precession is, in general, much faster than the Larmor precession, usually only the component of μ in the J direction, μ_J , need be considered in calculating the magnetic effect. This is (see Fig. 47):

$$\mu_J = \mu_L \cos(L, J) + \mu_S \cos(S, J) \quad (\text{II, 16})$$

In this,

$$\mu_L = -\frac{e}{2mc} \frac{h}{2\pi} \sqrt{L(L+1)} \quad \text{and}$$

$$\mu_S = -\frac{2e}{2mc} \frac{h}{2\pi} \sqrt{S(S+1)} \quad (\text{II, 17})$$

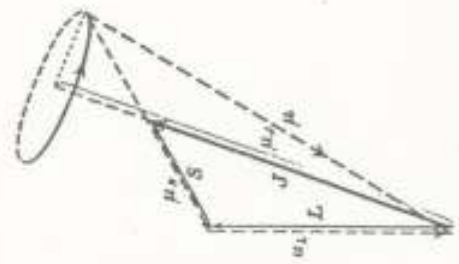


Fig. 47. Addition of Magnetic Moments in an Atom (in Explanation of the Landé g-formula). The length of the vector μ_L is taken equal to L . Therefore μ_S is double the length of S . It should be noted that the direction of the angular momentum vectors is opposite to that of the corresponding magnetic moments.

Here the minus sign indicates, as before, that the magnetic moment has the opposite direction to the corresponding angular momentum vector.

In the calculation of the magnetic splitting, it is ψ_H , the component of ψ_J in the direction of the field, which matters. In order to obtain (II, 14) instead of (II, 11) for the energy in a magnetic field, we have to replace formula (II, 10) for ψ_H formally by

$$\psi_H = -\frac{e}{2mc} \frac{h}{2\pi} M \vartheta$$

This substitution means we have to take as definition for g

$$\psi_J = -\frac{e}{2mc} \frac{h}{2\pi} \sqrt{J(J+1)} g \quad (\text{II, 18})$$

The factor g can be calculated from (II, 16) when both cos terms are known. From Fig. 47, using the obtuse-angled triangle formed by L , S , and J , we obtain, with the help of the cosine law:

$$\begin{aligned} \cos(L, J) &= \frac{J(J+1) + L(L+1) - S(S+1)}{2\sqrt{J(J+1)}\sqrt{L(L+1)}} \\ \cos(S, J) &= \frac{J(J+1) + S(S+1) - L(L+1)}{2\sqrt{J(J+1)}\sqrt{S(S+1)}} \end{aligned} \quad (\text{II, 19})$$

Substituting (II, 17), (II, 18), and (II, 19) in (II, 16), and omitting the factor $\frac{e}{h} \frac{h}{2\pi}$, we find:

$$\begin{aligned} g &= \frac{\sqrt{L(L+1)}}{\sqrt{J(J+1)}} \cos(L, J) + \frac{2\sqrt{S(S+1)}}{\sqrt{J(J+1)}} \cos(S, J) \\ &= \frac{J(J+1) + L(L+1) - S(S+1)}{2\sqrt{J(J+1)}} \\ &\quad + \frac{2[J(J+1) + S(S+1) - L(L+1)]}{2\sqrt{J(J+1)}} \end{aligned} \quad (\text{II, 20})$$

This last expression shows clearly the meaning of the factor 2 in the second term. If the factor 2 were not present, that is, if the electron spin were magnetically normal, g would obviously equal 1. But, by including the factor 2, we obtain from (II, 20) the Landé formula already given in (II, 15). Thus g is a rational number which is generally different from 1, in agreement with experiment. For $J = S$ and $L = 0$, $g = 2$, a value that we have already used.

If, in the derivation of the g -formula, we had used simply $J(h/2\pi)$, $L(h/2\pi)$, $S(h/2\pi)$ for the magnitudes of the vectors, instead of the accurate quantum mechanical values, obviously a different formula would have been obtained. The fact that the Landé g -formula gives extraordinarily close agreement with

experiment is further evidence of the correctness of the quantum mechanical formula for the magnitudes of the angular momentum vectors.

From (II, 15) the g values for ${}^2P_{1/2}$ and ${}^2P_{3/2}$ are $\frac{3}{2}$ and $\frac{5}{2}$. Using these values, the energy level diagram for the Zeeman splitting of the sodium D lines has been drawn in Fig. 45, and is in quantitative agreement with experiment. [Cf. Fig. 39(b).]

It might at first appear remarkable that the term ${}^2P_{1/2}$ shows any splitting at all. According to our earlier discussion, for ${}^2P_{1/2}$ the vectors L and S are in opposite directions [cf. Fig. 37, p. 89] and, since $L = 1$ and $S = \frac{1}{2}$, we would expect zero magnetic moment because of the double magnetism of S ; correspondingly, no splitting should result. The above formula gives, however, $g \neq 0$. A magnetic moment will therefore be present.

When the accurate wave mechanical values for the angular momentum vectors are taken, J , L , and S for ${}^2P_{1/2}$ do not fall in a straight line but produce the diagram shown in Fig. 48. It is seen that the two magnetic moments of $L = 1$ and $S = \frac{1}{2}$ do not compensate each other. When the length of L represents at the same time the magnitude of μ_L , μ_S is twice as long as S , and ψ has the indicated direction and magnitude. The whole system of vectors precesses about J . The magnetic behavior depends only upon ψ_J , the component of ψ in the direction of J . We can easily see from Fig. 48 that ψ_J is not zero and, correspondingly, the splitting differs from zero. The difference between the old quantum theory and the new quantum mechanics is particularly striking in this case.

The foregoing considerations have shown that when L and S in a stationary state differ from zero, the magnetic moment ψ is not constant, but continually changes its direction (precesses about J). The possibility of magnetic dipole radiation, mentioned previously, depends on this fact.

In addition to the term splitting, the relative intensities of the individual components in the transitions can also be predicted theoretically. [Cf. Hund (7); Condon and Shortley (13).]

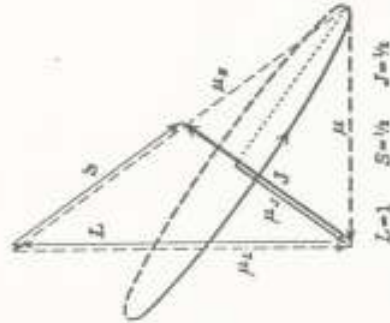


Fig. 48. Origin of the Magnetic Moment for a ${}^2P_{1/2}$ State. (Cf. Fig. 47.)

The line splitting will vary according to the values of J , L , and S in the upper and lower states—that is, according to the term type in the upper and lower states. Conversely, the investigation of the Zeeman effect forms a very effective means of establishing the type of term taking part in a transition. This is particularly useful for complicated line spectra. For example, it enables us to find which lines belong to a Rydberg series since they must all show the same Zeeman effect. [Further details may be found in Back and Landé (6).]

From the above discussion it is clear that the *double magnetism of the electron is fundamental to the explanation of the anomalous Zeeman effect* and phenomena related to it. Actually, the double magnetism of the electron, as well as the spin of the electron itself, may be derived from Dirac's relativistic wave mechanics without the use of any additional assumptions. The fact that such a large body of complicated phenomena (Fig. 39, p. 97, shows only the simplest examples) can be dealt with completely and quantitatively must be regarded as one of the remarkable achievements of wave mechanics.

Paschen-Back effect. With increasing field strength, when the magnetic splitting becomes greater than the multiplet splitting, Paschen and Back found that the *anomalous Zeeman effect changes over to the normal*. This has the following reason: When the magnetic splitting becomes greater than the multiplet splitting, the precessional velocity ω of J in the magnetic field about the field direction becomes greater than the precessional velocity of S and L about J (see above). The resultant motion is, therefore, better described as an independent precession of S about the field direction and a similar precession of L about the field direction, the motion being somewhat disturbed by the coupling of L and S . Hence we say that L and S are *uncoupled* by the magnetic field. To a first approximation, each of these vectors is therefore space quantized in the magnetic field

independently of the other with components M_L and M_S , respectively. For each value of $M_L = L, L - 1, L - 2, \dots, -L$, M_S can take each of the values $S, S - 1, \dots, -S$. The magnitude of the term splitting is then, to a first approximation:

$$\Delta W = h\omega M_L + 2h\omega M_S \quad (\text{II, 21})$$

(S has double magnetism) and is, therefore, again an integral multiple of the *normal* splitting, as in (II, 11).

For M_L , we have the same selection rules as for M , and for the same reasons as those given earlier:

$$\Delta M_L = 0, \pm 1 \quad (\text{II, 22})$$

For M_S , the following selection rule is obtained from theory:

$$\Delta M_S = 0 \quad (\text{II, 23})$$

Taking into account these selection rules and using (II, 21), a normal Zeeman triplet is obtained for a transition between two multiplet terms in a strong magnetic field. Fig. 49 shows this for a ${}^3P \rightarrow {}^2S$ transition (for example, the D lines of Na). It should be compared with Fig. 45

(p. 107), which applies to the same transition in a weak field. In a more rigorous treatment a correction term of the form $ahM_S M_L$ must be added to ΔW in (II, 21), because of the interaction of L and S which is naturally still present. As a result of this, each component of the normal line triplet will generally give a narrow doublet, triplet, etc., according as the original field-free transition was a doublet, triplet, etc.,

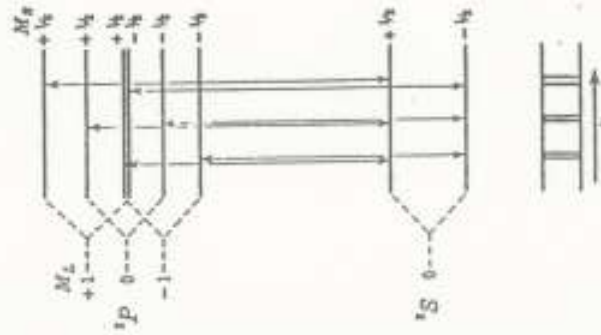


Fig. 49. Paschen-Back Effect for a ${}^3P \rightarrow {}^2S$ Transition. Here transitions with equal ΔM or ΔM_S nearly coincide, whereas in the normal Zeeman effect they exactly coincide. [Cf. Fig. 44, p. 104.] Thus, in the figure shown here, each component of the "normal" triplet has two components.

transition. The reason for this line splitting is apparent from Fig. 49 for the case of a doublet transition.¹⁴ More complicated splitting patterns are obtained by using intermediate fields. [Incomplete Paschen-Back effect. See Back and Landé (6); White (12).]

It is readily seen that the total number of term components is the same in both strong and weak fields: $(2L + 1) \times (2S + 1)$, in agreement with the Ehrenfest adiabatic law (mentioned previously).

Stark effect. As Stark first discovered, a *splitting of the spectral lines* also takes place *in an electric field*. Fig. 50 illustrates the splitting of the He line $\lambda 4388$ in the two directions of polarization (parallel and perpendicular to the field). In each pattern the strength of the field increases from top to bottom. [For experimental details, see Foster (132).] As will be seen, the patterns are not symmetrical

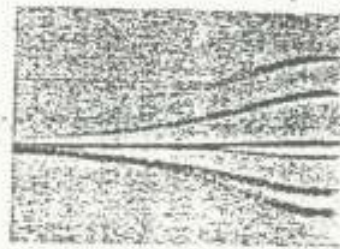
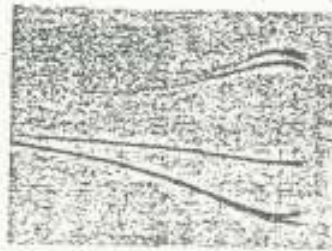


Fig. 50. Stark Effect Splitting of the Helium Line $\lambda 4388$ [after Foster (132)]. Above, the exposure was so made that only light polarized parallel to the field direction could reach the plate. Below, only light polarized perpendicular to the field could reach the plate. In each pattern the field increases from top to bottom.

intrinsic interest and as an application of quantum theory the Stark effect plays a very important part in the theories of molecular formation from atoms, of the broadening of spectral lines, and of dielectric constants.

¹⁴ The two components of the central "line" in this case coincide almost exactly since ahM_sMc is zero for both upper states; but in higher approximation they would not coincide.

The components of the angular momentum J can take only the values $+J, J - 1, J - 2, \dots, -J$ with respect to any preferred direction. This rule holds also for the direction of an electric field. Thus *space quantization takes place also in an electric field*. If, and how, the states with different M differ from one another energetically depends upon the kind of field acting.

An electric field does not act on the magnetic moment associated with J . The result of the action of an electric field is, rather, that the atom becomes electrically polarized, as shown schematically in Fig. 51.

The positively charged nucleus K becomes separated from the center of gravity S of the negative charges by an electric field E . There results an *electric dipole moment*, proportional to the field, whose magnitude depends upon the orientation of the orbit, that is, of the angular momentum J , to the field. The atom seeks to set itself in the direction of smallest energy, just as in the case of a magnetic field. Because of the gyroscopic forces, this produces a precession of J about the field direction such that the component M of J is constant (see Fig. 51). The stronger the field, the more rapid will be the velocity of precession. The energy shift is given by the product of the field strength and the dipole moment—a result analogous to that of the magnetic case. However, since the dipole moment is itself proportional to the field strength, the term shift in the Stark effect is proportional to the *square* of the field strength. Closely connected with this relation is the fact that, in an electric field, the term components, which differ only in the sign of M , have

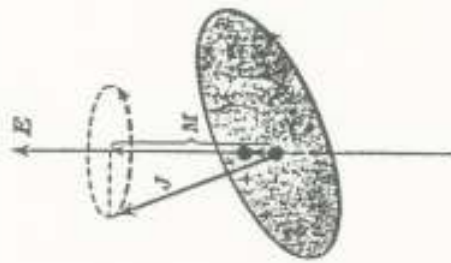


Fig. 51. Production of an Electric Dipole Moment in an Electric Field (Stark Effect) and Precession of J about the Field Direction. The shaded surface represents the orbital plane of the atom. The angular momentum vector is perpendicular to that plane.