

The lowest term of the ortho system, however, is a 3P term—not a 3S term. (Cf. the Ca energy level diagram, Fig. 32, p. 77.) Just as with He, the two term systems converge to the same limit. From the splitting of the energy level diagram into two partial systems, we may conclude that, as for He, there are only *two electrons outside the atomic core* of the alkaline earths. The same conclusion holds for the alkaline-earth-like ions. The energy level diagram and the difference between the two term systems will be considered in greater detail in Chapter II.

Background reading for ~~Section~~ Effect of Optical Pumping

CHAPTER II

Multiplet Structure of Line Spectra and Electron Spin

1. Empirical Facts and their Formal Explanation

Doublet structure of the alkali spectra. As shown in Chapter I, the quantum numbers n and l just suffice to characterize the different term series of the alkalis (Fig. 24, p. 57). However, they no longer are adequate for He and the alkaline earths, since for these there are twice as many term series as for the alkalis—that is, there are two complete term systems, which are distinguished by a left upper index 1 or 3 on the term symbol. The physical meaning of this method of distinction will be made clear in the subsequent discussion. Even if we provide an explanation by assuming that the atom under consideration exists in two different forms (for example, orthohelium and parahelium), the insufficiency of the quantum numbers thus far introduced becomes still more obvious when we examine the alkali spectra with spectral apparatus of greater dispersion. It is then found that each of their lines is double, as is generally known for the D line of Na. The line splitting increases rapidly in the series Li, Na, K, Rb, and Cs. It can be detected for Li only by using spectral apparatus of very high dispersion. However, for the D line of Na, the splitting is 6 Å. Fig. 29(a), page 74, shows this and some other Na doublets. The line splitting can naturally be traced back to a *term splitting*. Either the upper or the lower, or both of the terms involved are double, that is, split into two levels of slightly different energy.

To illustrate, Fig. 28 gives the energy level diagram of potassium. The scale used in the diagram is just sufficient

to show the splitting. The ground state and other S terms are single; the P terms are split, the splitting decreasing with increasing order number. The components are drawn side by side. If the ground state were split and the P states were single, all the lines in the principal series ($1S - mP$) would have the same splitting (in cm^{-1}); but this is not the case. On the other hand, all lines of the sharp series ($2P - mS$) have the same splitting, since the common lower state $2P$ is split while the upper states mS are not split. The lines of the diffuse series ($2P - mD$) have the same splitting, for the same reason. The D terms themselves are split, but the splitting is so much smaller that it makes scarcely any difference in the case of potassium (see below).

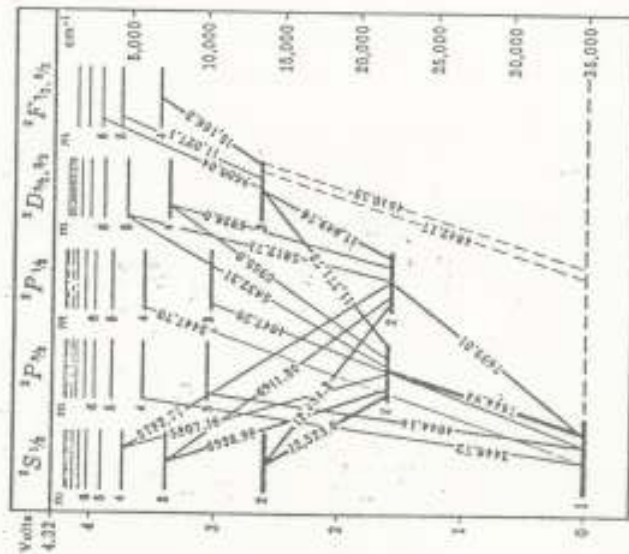


Fig. 28. Energy Level Diagram for Potassium [Grotrian (8)]. Here m is the empirical order number of the terms (see p. 55). For S terms, the true principal quantum number of the emission electron (p. 62) is 3 greater than m ; for P terms, it is 2 greater; for D and F terms, it is equal to m .

Quantum number J . Since the quantum numbers thus far introduced do not suffice, we distinguish, at first formally, the components of the doublets by an index number—that is, a new quantum number. We could write: P_1 and P_2 . But, instead, we use as indices: for the P terms, $\frac{1}{2}$ and $\frac{3}{2}$; for the D terms, $\frac{3}{2}$ and $\frac{5}{2}$; and so on. The reason for this nomenclature will become apparent later. In Fig. 28 these symbols are written over the corresponding term series. In addition, a left upper index 2 (doublet) is given to all the term symbols (see below). The S terms are given a subscript $\frac{1}{2}$, although they are actually single. This new quantum number (subscript) is designated as J , and was called the inner quantum number by Sommerfeld. The different values of J occurring are summarized in Table 3.

TABLE 3

 J VALUES FOR DOUBLET TERMS

Term	L	J
S	0	
P	1	$\frac{1}{2}$, $\frac{3}{2}$
D	2	$\frac{3}{2}$, $\frac{5}{2}$
F	3	$\frac{5}{2}$, $\frac{7}{2}$
G	4	$\frac{7}{2}$, $\frac{9}{2}$

Each individual term of the alkalis is now characterized by the three quantum numbers n , l , and J . In the future we shall write L instead of l when we wish to characterize the whole atom and not a single electron. The selection rule is the same as for l (Chapter I, section 4):

$$\Delta L = \pm 1$$

Selection rule for J ; compound doublets. The splitting of the D terms for potassium is so small that, for most purposes, they can be treated as if they were single. Accordingly, the D terms are not drawn separately in Fig. 28. Thus there will be practically no difference in the splitting

of the sharp (${}^2P - {}^2S$) and the diffuse (${}^2P - {}^2D$) series. This also holds for Na, of which a few of the diffuse and the sharp doublets are shown in Fig. 29(a). The splitting of the D terms becomes noticeable for Rb and Cs, as well as for the alkali-like ions Ca^+ , Sr^+ , and so on. If the individual doublet term components could combine with one another without restriction, four components would be expected for each of the lines of the diffuse series (since each



Fig. 29. Examples of Line Doublets. (a) Some Na doublets (part of the Na emission spectrum reproduced in Fig. 3, taken with larger dispersion). (b) Compound doublet of Ca^+ . Thus principal quantum numbers are used to designate the terms.

component of the upper D term should combine with each of the two components of the lower P term). Actually, only three components are observed, as is shown in the spectrogram for a ${}^2P - {}^2D$ transition of Ca^+ , in Fig. 29(b). Using the J values given above, we obtain agreement with experiment if we assume for the new quantum number J the selection rule:¹

$$\Delta J = 0 \text{ or } +1 \text{ or } -1 \quad (\text{II, 1})$$

Fig. 30 shows the energy level diagram (not drawn to scale) corresponding to the Ca^+ doublet reproduced in Fig. 29(b). Transitions allowed by the selection rule are given as solid vertical lines, the horizontal distance between the lines corresponding to their frequency difference. The

¹ If we had distinguished the components of the P and D terms simply by the indices 1 and 2, a representation of the observed transitions would not have been possible with such a simple selection rule.

spectrum produced in this way is drawn schematically in the lower part of Fig. 30. For the transition, ${}^2D_{3/2} - {}^2P_{1/2}$, $\Delta J = 2$. This transition is forbidden by the selection rule, and actually does not appear in Fig. 29(b); however, it is shown by a dotted line in Fig. 30. As already stated, the splitting of the upper D term is relatively small, and thus, using low dispersion, we obtain doublets only, as for the sharp series, since ${}^2P_{3/2} - {}^2D_{3/2}$ and ${}^2P_{1/2} - {}^2D_{1/2}$ practically coincide. Using greater dispersion, as in Fig. 29(b), we find that one component of the doublet, and only one, is double. However, this group of lines is called, not a triplet, but a *compound doublet*, since it results from the combination of doublet terms. The lines of the Bergmann series (${}^2D - {}^2F$) similarly consist of such compound doublets, which are incompletely resolved still more often than those of the diffuse series. Allowed combinations for the different series are also indicated in Table 3.

Triplets and singlets of the alkaline earths and helium. A more accurate investigation of the two systems of lines of the alkaline earths, using high dispersion, shows that the *para* system consists of single lines (*singlets*), whereas the *ortho* system consists of threefold lines (*triplets*). The splitting of the latter increases rapidly with increasing atomic number of the element in the second column of the periodic system. For Hg, the splitting is so great that different lines of one and the same multiplet lie in different regions of the spectrum.

Similar to the spectrum of the alkaline earths, even under large dispersion, the lines of the *para* system of He appear single, whereas those of the *ortho* system appear as very

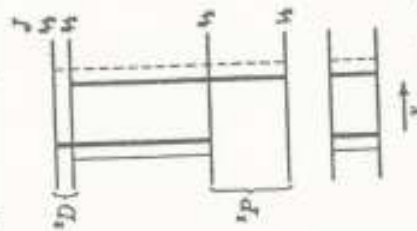


Fig. 30. Origin of a Compound Doublet ${}^2P - {}^2D$. [Cf. Fig. 29 (b).] Intensities are indicated by the thickness of the lines.