From "Atomic Spectra and Atomic Structure by Herzberg

Background reading for Op...al Pumping

which in the above case is given simply by $\sum e_i x_i^2$, where x is the axis along which the charges are located. It is immediately seen that this expression is *not* zero. In general a quadrupole is more complicated than the one given in Fig. 23, and likewise the quadrupole moment is usually more complex. The general case will not, however, be discussed here.

Just as a variable dipole moment leads to radiation (*dipole radiation*), so also does a variable quadrupole moment lead to radiation (*quadrupole radiation*). The latter is, however, considerably weaker. The transition probability, similarly to the above, is obtained by substituting $e_i\psi_n\psi_m^* d\tau$ for e_i in $\sum e_i x_i^2$, and integrating. Therefore quadrupole radiation depends upon the integral $\int x^2\psi_n\psi_m^* d\tau$, whereas dipole radiation depends upon $\int x\psi_n\psi_m^* d\tau$. Because of this difference, *transitions which are strictly forbidden for dipole radiation may occur—though quite weakly—due to quadrupole radiation.* The ratio of the transition probabilities of ordinary dipole radiation to ordinary quadrupole radiation is found to be about $1 : 10^{-8}$.

Finally, it may happen that, for a transition, the variation of the electric dipole moment will disappear, whereas that of the *magnetic* dipole moment does not (cf. Chapter II, p. 111). According to classical theory, a variable magnetic dipole moment such as that produced, for instance, by an alternating current in a coil gives rise to electromagnetic radiation. Correspondingly, in wave mechanics, it gives rise to a transition probability which may be different from zero even if the ordinary dipole transition probability is zero. Again, the transition probability due to *magnetic dipole radiation* is small compared with that due to electric dipole radiation ($1 : 10^{-5}$).

Actually, cases have been observed in which transitions that are strictly forbidden by the electric dipole selection rules take place due to quadrupole or magnetic dipole radiation. (See Chapter IV.)

5. Alkali Spectra

The principal series. The absorption spectra of alkali vapors (Fig. 2) appear quite similar in many respects to the absorption spectrum of the H atom (Lyman series). They are only displaced, to a considerable extent, toward longer wave lengths.[19] These spectra also consist of a series of lines with regularly decreasing separation and decreasing intensity. This series is called the *principal series.* It

cannot, however, be represented by a formula completely analogous to the Balmer formula. On the other hand, since the lines converge to a limit, we must be able to represent them as differences between two terms. One of these terms is a constant T_{Ps} (known as the *fixed term*) and has the frequency of the *series limit.* The other (known as the *running term*) must depend on a running number (order number) m in such a way that the term disappears as $m \rightarrow \infty$.

It has been found that the series can be satisfactorily represented with $R/(m + p)^2$ as the running term. R is the Rydberg constant, and p is a constant number < 1; p is called the *Rydberg correction.* It is the correction that, for the alkalis, must be applied to the Balmer term ($p = 0$ gives the Balmer term). The running number m takes values from 2 to ∞. The quantity $n^* = m + p$ is called the *effective principal quantum number.* Thus the formula for the absorption series (principal series) for the alkalis[20] is:

$$\nu = T_{Ps} - \frac{R}{(m + p)^2}$$

A continuous spectrum follows at the series limit, as shown in Fig. 2.

Other series. In emission, other series in addition to the principal series may be observed for the alkalis. These series partly overlap one another. Fig. 3 (p. 5) shows the Na emission spectrum. The three most intense of the additional series have been given the names *diffuse*, *sharp*, and *Bergmann series.* The last is also sometimes called the *fundamental* series. The lines of the diffuse and the sharp series frequently appear diffuse and sharp, as their names indicate. The Bergmann series lies further in the infrared and consequently does not appear in the spectrogram in Fig. 3. The limits of these series and, therefore, their limiting terms differ from the limiting term of the principal

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[19] We disregard for the moment the splitting of the lines of the heavier alkalis, with which we shall deal in Chapter II. This splitting is still so small for Li that it cannot be noticed with the usual spectroscopic apparatus.

[20] This formula does not hold so exactly as that for the H spectrum. More exact agreement with experiment can be obtained by adding to the denominator an additional term which depends on m.

series, but the sharp and the diffuse series have a common limit (see Fig. 3). T_{ss} is the common limiting term for the sharp and the diffuse series; T_{bs}, for the Bergmann series. The running terms are quite analogous to those of the principal series, but the Rydberg correction has a different value for each series. Thus we have:

$$\text{Principal Series:}\quad \nu = T_{ps} - \frac{R}{(m+p)^2} \qquad (m = 2, 3, \cdots)$$

$$\text{Sharp Series:}\quad \nu = T_{ss} - \frac{R}{(m+s)^2} \qquad (m = 2, 3, \cdots)$$

$$\text{Diffuse Series:}\quad \nu = T_{ss} - \frac{R}{(m+d)^2} \qquad (m = 3, 4, \cdots)$$

$$\text{Bergmann Series:}\quad \nu = T_{bs} - \frac{R}{(m+f)^2} \qquad (m = 4, 5, \cdots)$$

The values found empirically show that $T_{ps} = R/(1 + s)^2$, $T_{ss} = R/(2 + p)^2$, $T_{bs} = R/(3 + d)^2$; that is, the limiting terms belong to one of the series of running terms. If we put mP as a symbol for $R/(m + p)^2$, mS for $R/(m + s)^2$, and so on, the series may be written:

$$\text{Principal Series:}\quad \nu = 1S - mP \qquad (m = 2, 3, \cdots) \qquad (\text{I}, 35)$$

$$\text{Sharp Series:}\quad \nu = 2P - mS \qquad (m = 2, 3, \cdots) \qquad (\text{I}, 36)$$

$$\text{Diffuse Series:}\quad \nu = 2P - mD \qquad (m = 3, 4, \cdots) \qquad (\text{I}, 37)$$

$$\text{Bergmann Series:}\quad \nu = 3D - mF \qquad (m = 4, 5, \cdots) \qquad (\text{I}, 38)$$

Theoretical interpretation of the alkali series. From the four series of the alkalis it is evident that four different term series or four sets of energy levels exist, and these can be designated by S, P, D, F. In Fig. 24 these series are given for Li in the manner explained in an earlier section. The ground state of the alkali atom is $1S$, since in absorption only the principal series appears and this has $1S$ as the lower level. The S terms $2S$, $3S$, $\cdots$ follow after it. The lowest P state occurring is $2P$, and it lies above the $1S$ term by an amount equal to the wave number of the first line of the principal series $1S - 2P$. The series of P terms follow after it. The principal series in absorption corresponds to transitions from the ground state to the various P states; the converse holds for emission. The sharp series corresponds to transitions from the higher S terms to the lowest P state. The lowest D term lies still higher than the lowest P term (namely, by $2P - 3D$), and, analogously, the $4F$ term is higher than $3D$. All term series go to the same limit, whereas of course the line series have different limits (cf. above).

The similarity of this energy level diagram (Fig. 24) to the generalized energy level diagram of H (Fig. 13, p. 26) is obvious. The main difference is that the members of the

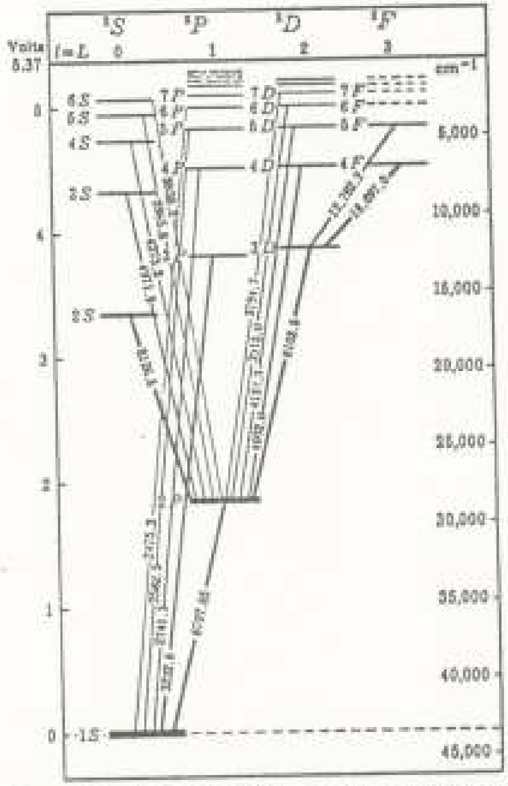

Fig. 24. **Energy Level Diagram of the Li Atom [after Grotrian (8)].** The wave lengths of the spectral lines are written on the connecting lines representing the transitions. Doublet structure (see Chapter II) is not included. Some unobserved levels are indicated by dotted lines. The true principal quantum numbers for the S terms are one greater than the empirical running numbers given (see p. 61); for the remaining terms, they are the same.

different adjacent term series no longer have almost exactly the same height. This is to be expected, theoretically, for the terms of a single electron moving in a field which is not the Coulomb field of a point charge. The structure of the alkali spectrum therefore leads to the conclusion that, for the alkali atoms, *a single outer electron moves about an atomic core*[21] whose field shows marked deviations from the Coulomb field of a point charge, which are due to the finite extent of the core. Furthermore, it follows that the S, P, D, F *terms are distinguished* from one another *by the value of the quantum number* l ($l = 0, 1, 2, 3, \cdots$); that is, by the orbital angular momentum of the outer electron. On the basis of the old Bohr theory, each term series would correspond to a series of elliptical orbits, as in Fig. 10 (p. 18). The fact that the series of P terms begins with $m = 2$, the D terms with $m = 3$, and the F terms with $m = 4$ is also in agreement with this assumption, since, if the order number m is identified with the principal quantum number n, m must be $\geqq l + 1$ (see p. 38). The selection rule $\Delta l = \pm 1$ is also fulfilled; only neighboring term series combine with one another.

The Rydberg correction (the deviation from the hydrogen terms) is greater, the nearer the electron comes to the core in its orbit according to the old Bohr idea. The correction is greater still if the orbit penetrates the core (so-called *penetrating orbits*), as then the effective nuclear charge Z_{eff} acting on the electron is appreciably altered. In the immediate neighborhood of the nucleus the whole nuclear charge acts, but at a great distance it is shielded by the core electrons down to $Z_{\text{eff}} = 1$. Accordingly, the Rydberg correction should be greatest for S terms, smaller for P terms, still smaller for D terms, and so on (see Fig. 10). This is actually the case. The Rydberg correction is extremely small for F terms; that is, they are practically Balmer terms. In contrast, the Rydberg correction for S terms is so large (for Li, 0.59) that we are not certain what the *true principal quantum number* is—that is, whether the ground term for Li has $n = 1$ or 2. The numbers in Fig. 24 are not the true principal quantum numbers of the emission electron. We shall find out later what these are.

The common limit of all term series (Fig. 24) corresponds to the removal of the outer electron (the *emission electron*), which is moving about the atomic core. Beyond this limit, as in the case of hydrogen, extends a *continuous term spectrum* which corresponds to the removal of the electron with more or less kinetic energy. The existence of this continuous term spectrum is proved from observation of continuous spectra extending beyond the limit of the line series (cf. Figs. 2 and 3). The height of the limit of the term series above the ground state $1S$ gives the *energy of ionization* (*ionization potential*) of the alkali atom. From Fig. 24 we can see directly that this is equal to the wave number of the limit of the principal series (see also p. 23); for Li, the ionization potential is 43,486 cm^{-1} or 5.363 volts.

Alkali-like spark spectra. Just as the spectra of He^+, Li^{++}, and Be^{+++} are similar to that of hydrogen, the spectra of the alkali-like ions (ions with the same number of electrons) are very similar to the alkali spectra (Paschen, Fowler, Bowen, Millikan, Edlen, and others). The spectra of ions are usually called *spark spectra* and those of neutral atoms *arc spectra*, since the former are generally produced in an electric spark (or condensed discharge), and the latter in arcs. This corresponds to the fact that the excitation potential of the spectra of ions is much greater than for the spectra of neutral atoms, on account of the necessity of producing ionization or multiple ionization of the atom in the former case. The spectra of singly, doubly, etc., charged ions are called *spark spectra of the first, second, etc., order*. The arc spectrum is indicated by the Roman numeral I placed after the symbol for the element; the first spark spectrum is indicated by the Roman numeral II; and

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[21] The stable electron group obtained by removal of the outermost electron or electrons is called the *core* or *kernel*.