CHAPTER VII

LINE SPECTRA

7-1. Introduction.-Our study of atomic physics up to this point has dealt largely with the physical characteristics of material particles and radiation and to some extent with their interaction. The next two chapters will be concerned with the emission and absorption of radiation by atoms. A study of spectra leads to a theory of atomic systems as composed of elementary particles, namely a massive positively charged nucleus surrounded by an elaborate and complex structure of electrons. We shall be unable to pursue the theoretical developments to their recent culmination, but certain of the fundamental advances will indicate how the enormously involved mass of experimental data has been correlated into a consistent whole.

We shall confine ourselves to the study of the radiation from monatomic gases and vapors, the so-called line spectrum, in distinction to the radiation from a polyatomic gas which is known as a band spectrum. A study of spectra leads to a theory of atomic systems as composed of elementary particles, namely a massive positively charged nucleus surrounded by an elaborate and complex structure of electrons. We shall be unable to pursue the theoretical developments to their recent culmination, but certain of the fundamental advances will indicate how the enormously involved mass of experimental data has been correlated into a consistent whole.

We shall postpone the discussion of the theoretical developments through which the experimental facts are interpreted until we have made a brief resume of the empirical spectroscopic knowledge up to the time of the concepts introduced by Bohr. The entire subject of line spectra is, of course, far too large to be dealt with adequately in this book. We shall have to content ourselves with an outline of the experimental facts and an indication of how they have been coordinated mathematically. For a thorough understanding of the subject the reader should acquaint himself with its early developments as given by Sommerfeld or Andrade. The standard works on the so-called vector model of the atom are those of Back and Landé, and Hund. The more recent theoretical developments of the subject are to be found in the accounts of Condon and Morse, and Sommerfeld, and in the original papers. A complete bibliography of the experimental work from 1920 to 1931 has been given by Gibbs. The symbolic notation used in spectroscopy has undergone many confusing variations; a table of the systems used by various authors has been given by Ruark and Urey. Fortunately, as the theoretical interpretation of the phenomena has now become quite stable, a unified notation is coming into use. In this book we shall endeavor to keep consistently to the system which has been codified by Russell, Shenstone, and Turner.

7-2. Early Empirical Spectroscopy.-When it is desired to obtain the spectrum of a given source the light which it emits is concentrated upon a very narrow slit by means of a lens that is transparent to the region of the spectrum which is being observed or photographed. An image of this illuminated slit is formed by means of a series of lenses or concave mirrors upon a photographic plate, the images of the different colors corresponding to the different wave lengths being displaced sideways by the dispersion of a prism or grating. These images constitute the “lines” of the spectrum. A long narrow slit is used rather than an opening of any other shape for several reasons: the narrowness of the image permits the separation of colors only slightly different; extremely faint long images are easier to see than would be the images of a circular opening whose diameter equaled the slit width; it is easier to make a good slit than any other shape of adjustable diaphragm. The method of correlating the positions of these slit images with the wave lengths which they represent will be taken up in a subsequent section.

2 ANDRADE, “The Structure of the Atom,” Bell (1930).
8 GIBBS, Rev. Mod. Phys., 4, 278 (1932).
From the earliest days of spectroscopy it was realized that the line spectrum given off by an incandescent vapor was characteristic of the vapor in question and to a certain extent of its temperature. The work of Bunsen and Kirchhoff brought the subject of spectrum analysis into prominence about 1859, and in the following years certain elements were actually discovered by this method. As the technique of measuring the wave length of light was improved, principally through the work of Fraunhofer, Angström, and Rowland, interesting but baffling relationships between the characteristic lines of certain of the elements were noted. The presence of series of close pairs of lines in the spectra of the alkali metals was among the first of these interesting characteristics to be observed. It was also thought that certain numerical relationships had been found between the lines of the hydrogen spectrum, but these proved illusory. The first well-substantiated quantitative relation was discovered by Hartley, who found that if frequencies were used instead of wave lengths, the frequency differences between the lines in certain recurring groups known as multiplets were the same for all similar multiplets occurring in the spectrum of the element. This was a very important observation and its significance will be seen when the empirical spectroscopic scheme is more fully developed.

Principally, however, attention was concentrated on the apparently simpler spectra such as those of hydrogen and the alkali metals. Certain series of lines were observed for these elements. From their similar behavior under various excitation conditions the members of these series, which were apparently single in the case of hydrogen and double in the cases of the alkalis, were evidently closely related to one another. The obvious method of attack was to search for numerical relationships between their wave lengths or frequencies. Contrary to the expectations of those pioneers in the study of spectra who were familiar with the properties of vibrating mechanical systems, neither the frequencies nor the wave lengths of the lines of a series could be made to fit any scheme of fundamental vibrations and their overtones or harmonics. A large amount of fruitless effort was expended in a search for these harmonic relations, which were expected by analogy with acoustical systems. The first successful representation of a series was achieved empirically by Balmer in 1885. He showed that the lines in the visible spectrum of atomic hydrogen, as well as five lines in the ultra-violet (up to that time observed only in the spectra of the stars), could be represented very accurately by the equation

\[ \lambda = \frac{3,645.6}{n^2 - \frac{4}{4}} \times 10^{-8} \text{ cm}. \]  

where \( n = 3, 4, 5, \ldots, 11 \). This discovery was the most fundamental step in advance which had been taken up to that time. However, due to its expression in terms of wave length rather than frequency, a great deal of its significance was not apparent. Balmer's success caused an abandonment of the search for harmonics and stimulated investigations for other series of a similar kind.

In 1890 Rydberg discovered several of the most important characteristics of spectral series. He suggested formulating the expression for the series members in terms of the reciprocal of the wave length, i.e., in terms of the wave number. Equation (7-1) then becomes

\[ \frac{1}{\lambda} = \frac{1}{\lambda} = 27,430 \left( 1 - \frac{1}{n^2} \right) \]

where \( R \) is a constant, known as the Rydberg constant, whose value for hydrogen in accordance with the most modern measurements is \( R = 109,677.759 \text{ cm}^{-1} \). This expression for the wave number of a line as the difference between two quantities, which bears a suggestive relation to the frequency differences observed by Hartley, was very important, but its significance was not fully realized at the time. Rydberg also recognized the existence of three series in the spectra of the alkali metals to which he gave the names sharp, principal, and diffuse as being somewhat characteristic of the different series. He further suggested that they could be approximately represented by an expression of the form

\[ \tilde{\nu} = \tilde{\nu}_\infty - \frac{R}{(n + \mu)^3} \]

where \( n \) is a running number which takes successive integral values for the members of a series, \( \mu \) is a small constant, and \( \tilde{\nu}_\infty \) is the series limit, i.e., the value of \( \tilde{\nu} \) when \( n \) becomes infinite. This is only an approximation, and \( \mu \) is not strictly constant, particularly for certain types of series. If \( \mu \) is put equal to zero the expression reduces to the form of Eq. (7-2) which is thus included as a special type.

1 Hartley, J. Chem. Soc. 43, 390 (1883).
1 Balmer, Ann. Physik, 25, 80 (1885).
1 Rydberg, Kongl. Svenska Vet.-Akad. Handlingar, 23, No. 11 (1890); Phil. Mag. 29, 331 (1890).
Equation (7-3) may be written more symmetrically and in a way which brings out further possibilities as

\[ \tilde{\nu} = R \left( \frac{1}{(n_1 + \mu_1)^2} - \frac{1}{(n_2 + \mu_2)^2} \right) \]  

(7-4)

where \( R/(n_1 + \mu_1)^2 \) takes the place of \( \tilde{\nu}_m \). Rydberg found that \( n_1 \) was generally unity, but he suggested that series might be found having different values of this constant. This idea was further developed by Ritz who found that lines which would be predicted by taking differences between certain of the second terms of the Rydberg expressions [Eq. (7-3)] for different series were actually observed. Such differences are obviously of the form of Eq. (7-4). These observed lines were known as combination lines, and the principle of their prediction as the combination principle. To improve further the representation of series, many other forms of these terms whose differences represent lines were suggested. The only other type of equation for a term which we shall consider is that proposed by Ritz, which contains an additional constant and also the term value itself in the denominator. This is capable of describing most series much more accurately than either the Balmer or Rydberg forms, but the process of series representation is more laborious, as there is the additional constant to determine. We may list the three types of term formulas, differences between which give the wave numbers of observed lines, as

- Balmer: \( \tilde{\nu} = \frac{R}{n^2} \)
- Rydberg: \( \tilde{\nu} = \frac{R}{(n + \mu)^2} \)
- Ritz: \( \tilde{\nu} = \frac{R}{(n + \mu + \alpha z)^2} \)

It has been found that the lines in a spectrum such as that of sodium occur in close pairs. A double series is formed by pairs of lines having a constant wave-number difference between them; both the sharp and the diffuse series are of this type. On the other hand, the principal series is formed of double lines whose wave-number difference becomes continually less as the series limit is approached. There are certain interesting relationships between these series. The constant wave-number difference of the sharp and diffuse doublets is the same as that of the first doublet in the principal series, and the differences between the common limits of the sharp and diffuse series and the limit of the principal series are equal to the wave numbers of the lines of the first doublet of the principal series. These facts find a ready explanation in the Ritz combination principle and are most clearly brought out by the use of a Grotrian diagram, in which the values of the terms are plotted vertically, those terms that belong together in a family being plotted in separate columns for convenience. Such a column forms a series of terms and may be described by a formula such as the Rydberg or Ritz type. The number \( \mu \) has a different value for each column; the \( P \) group of terms is double,
from the lowest pair of $P$ terms the successive $S$ terms, is composed of pairs of lines of constant wave-number difference. A similar consideration applies to the double lines of the diffuse series, where the $D$ terms are subtracted from the low pair of $P$ terms. The origin of the other relationships that have been mentioned is easily understood from an inspection of the diagram.

Such a diagram can be constructed for any element, as it depends merely on the combination principle. For most other elements the series of terms are not double but show some other multiplicity. For example in the alkaline earths, mercury, etc., the terms are single and triple. For still other substances, many higher multiplicities, up to eight levels per term, are observed. It was found by Zeeman, as will be mentioned later, that if the light source is placed in a magnetic field, the lines of the spectrum are each separated into several very close components. This implies a splitting of certain terms in the diagram so that the complexity of the system is greatly increased. It is this enormous mass of empirical material represented by these plots for all the elements which must be accounted for by any satisfactory theory. We shall be able to indicate only a few of the simpler of these theoretical developments. For this purpose the Grotrian type of diagram will prove a very convenient basis for discussion. Its interpretation will be greatly enlarged and clarified through the theoretical significance which its terms receive.

7-3. The Atomic Theory of Bohr.-The experiments on photoelectricity, thermonics, and cathode rays had shown that electrons were a universal constituent of matter. The electromagnetic theory definitely stated that the acceleration of an electric charge must cause the emission of radiation. The obvious conclusion was that the atoms of each element contained electrons which could oscillate with certain frequencies and thus give off the spectrum characteristic of the element. The immediate stumbling block to such a theory was that this system of oscillators should exhibit the classical phenomena of harmonics, and these were not to be found, as has been mentioned before. Furthermore the experiments of Rutherford and Chadwick on the scattering of $\alpha$ particles by matter indicated that the positively charged part of the atom must be very small compared to the region occupied by the negative charge, whereas the oscillator type of atom suggested by Thomson required a large region of positive charge through which the electrons passed in order that their motion might be simple harmonic. If on the other hand the motion were circular and the radiation were caused by the continual acceleration toward the small nucleus demanded by Rutherford, we are faced with the difficulty that the light given off should form a continuous spectrum. The electron would spiral in faster and faster toward the nucleus, radiating away all its original potential energy until it eventually coalesced with the central positive charge. Thus the classical electromagnetic theory could provide no satisfactory structure for the atom. These difficulties were swept away and a satisfactory theory of the simple hydrogen atom was obtained at one grand stroke by Bohr. This was done at the expense of violating the electrodynamic laws when convenient, accepting Planck's suggestion that radiation is emitted and absorbed only in discrete units, and by inventing an extremely arbitrary rule governing angular momentum.

Other series of lines besides that of Balmer are known for hydrogen. One was discovered by Lyman in the ultra-violet, which can be represented by a formula similar to Eq. (7-2) but with $1/3^2$ as the first term in the bracket. Others have been found by Paschen, Brackett, and Pfund in the infra-red, for which the first terms are of the forms $1/3^2$, $1/4^2$, and $1/5^2$, respectively. Thus we may write a general expression for all the atomic hydrogen series as follows:

$$v = R \left( \frac{1}{n'^2} - \frac{1}{n^2} \right)$$

(7-5)

where $n'$ may have the values from 1 to 5, and $n$ runs through a series of values beginning with $n' + 1$. It is to an expression of this form that any satisfactory theory of the hydrogen atom must lead. We may arrive at one such theory in a very simple manner as follows.

Imagine the nucleus to possess an infinite mass and a charge of $+e$ and that there is one electron with a mass $m$ and a charge $-e$ which rotates around the nucleus in a circular orbit of radius $r$. Let us assume that it does not radiate any energy in spite of its central acceleration. If it is in equilibrium in the orbit, the centrifugal force $mv^2/r$ is balanced by the electrostatic attraction $e^2/r^2$. We may write this condition as

$$\frac{mv^2}{r} = \frac{e^2}{r^2}$$

(7-6)

Hence the kinetic energy may be written as

$$T = \frac{mv^2}{2} = \frac{e^2}{2r}$$

The potential energy, which is taken as zero when $r$ is infinite, is a negative quantity and may be written as $U = -e^2/r$. The total energy $E$, which is given by the sum of $T$ and $U$, may thus be written as

$$E = -\frac{e^2}{2r}$$

1 Bohr, Phil. Mag., 26, 1, 476, 857 (1913).
2 Lyman, Astrophys. J., 9, 181 (1906); 43, 89 (1916).
Here we make the further assumption that only those orbits are possible for which the angular momentum is an integral multiple of the quantity $\hbar/2\pi$, where $\hbar$ is Planck's constant. This is possible because $\hbar$ has the dimensions of either energy times time or momentum times distance. This so-called quantization of the angular momentum is a vital assumption of the theory. Thus

$$mv\rho = \frac{n\hbar}{2\pi}$$  \hspace{1cm} \text{(7-7)}

where $n$ is an integer known as the total quantum number. Eliminating $\rho$ between Eqs. (7-6) and (7-7) we obtain

$$r = \frac{n^2\hbar^2}{4\pi^2m_e^2}$$  \hspace{1cm} \text{(7-8)}

which gives us the radius of these possible orbits. Substituting this value of $r$ in the expression for $E$, we obtain the possible values for the total energy in a "stationary state"

$$E = -\frac{2\pi^2m_e^4}{n^2\hbar^2}$$  \hspace{1cm} \text{(7-9)}

Now let us suppose that the electron suddenly changes to a smaller orbit characterized by the quantum number $n'$. Its energy in this new position is less than before (a larger negative quantity). Here we make the assumption, following the lead of Planck and Einstein, that the excess energy of the electron, over and above that needed for the new orbit, is radiated away as a quantum or photon whose frequency is proportional to its energy, the constant of proportionality being $\hbar$. We are thus led to the fundamental Bohr frequency relation

$$hv = E - E'$$  \hspace{1cm} \text{(7-10)}

Substituting the values of Eq. (7-9) in Eq. (7-10) we obtain

$$h\nu = \frac{2\pi^2m_e^4}{\hbar^2}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

The frequency of the radiation is found by dividing both sides through by $h$, or the wave number by dividing by $hc$. Thus

$$\nu = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

This is of the same form as Eq. (7-5) which we wished to obtain, and the numerical value of the constant $R$ is given by

$$R = \frac{2\pi^2m_e^4}{\hbar^2c}$$

We thus see that these assumptions, which are largely due to Bohr, permit the derivation of a general expression for the entire spectrum emitted by atomic hydrogen. This is not surprising, however, in view of the revolutionary character of the assumptions made. The point that demands the greatest attention is the agreement, within about 0.1 per cent, of the empirical value of the constant $R$ with that calculated from Bohr's equation when the values of $e$, $m$, $\hbar$, and $c$ are substituted in it. This constituted a great step forward in the understanding of atomic radiation. The conception of the transference from one orbit to another of an electron rotating about a nucleus, as the essence of the mechanism of radiation, formed the basis of most of the subsequent development of spectroscopic theory during the decade after its introduction. We may very briefly consider some of its further successes.

The preceding theory can be extended very simply to the case of other hydrogen-like atoms, i.e., one-electron atoms such as singly ionized helium or doubly ionized lithium. It is merely necessary to represent the charge on the nucleus by $Ze$ instead of by $e$, where $Z$ is the atomic number of the element. The energy in a stationary state is then given by:

$$E = -\frac{2\pi^2Ze^4}{n^2\hbar^2} = Z^2R\frac{hc}{n^2}$$

The wave number of the emitted light is given by

$$\nu = RZ^2\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

This explains at once why some lines of the helium spectrum can be represented by the Balmer equation when it is multiplied by 4, which is a well-known experimental fact. If these lines are due to singly ionized helium, i.e., helium atoms which have lost one of their two electrons, the emitting system is a nucleus with a charge $2e$ ($Z = 2$) with a single planetary electron revolving around it. This is electrically equivalent to a hydrogen atom with a double charge on the nucleus.

Let us now consider the effect of removing some of the simplifying assumptions which we introduced. In the first place let us assume that the mass of the nucleus is not infinite but is equal to $M$. We then know that the electron and nucleus rotate about the common center of gravity. If they are distant $r$ and $R$, respectively, from the center of gravity, we have by definition: $mr = MR$. Multiplying this equation by the angular velocity of rotation $\omega$, we have

$$mr\omega = MR\omega \text{ or } m\overline{v} = MV$$

where $\overline{v}$ and $V$ are the tangential velocities of the electron and nucleus, respectively. The total kinetic energy is given by

$$T = \frac{1}{2}mv^2 + \frac{1}{2}MV^2 = \frac{1}{2}m\overline{v}^2\left(1 + \frac{m}{M}\right)$$
Since the separation of the nucleus and the electron is equal to \( r + \frac{mR}{M} \) the potential energy, if the nucleus has a charge \( Ze \), is given by

\[
U = -\frac{Ze^2}{r\left(1 + \frac{m}{M}\right)^2}
\]

The equations analogous to Eqs. (7-6), and (7-7) are then

\[
\frac{m\nu^2}{r} = -\frac{Ze^2}{2r\left(1 + \frac{m}{M}\right)}
\]

\[
E = T + U = -\frac{Ze^2}{2r\left(1 + \frac{m}{M}\right)}
\]

\[
m\nu r + M\nu R = m\nu r\left(1 + \frac{m}{M}\right) = \frac{nh}{2\pi} \tag{7-7}
\]

These lead to the following equation for the total energy, \( E \):

\[
E = -\frac{2\pi^2\mu^4Z^2}{n^6h^6\left(1 + \frac{m}{M}\right)} = -\frac{2\pi^2\mu^4Z^2}{n^6h^6} = -\frac{Z^2Rhc}{n^2} \tag{7-9}
\]

where the so-called reduced mass \( \mu \) and the Rydberg constant for the case of a nucleus with a finite mass are given by the relations

\[
\mu = \frac{m}{1 + \frac{m}{M}} \quad \text{and} \quad R = \frac{2\pi^2\mu^4}{\hbar^6}
\]

We see from the above relations that the Rydberg constant depends on the mass of the particular nucleus with which we are concerned. The largest value that \( R \) can have theoretically is that obtained when \( M \) is infinite; we shall write this as \( R_\infty \). The value of the Rydberg constant for hydrogen is evidently given by

\[
R_H = \frac{R_\infty}{1 + \frac{m}{M_H}}
\]

and for singly ionized helium:

\[
R_{He} = \frac{R_\infty}{1 + \frac{m}{M_{He}}}
\]

Eliminating \( R_\infty \) from these two relations and solving for \( m/M_H \) we obtain:

\[
\frac{m}{M_H} = \frac{R_{He} - R_H}{R_H - \frac{M_H}{M_{He}}R_H}
\]

From the atomic weights measured with a mass spectrograph or by chemical methods we know that the ratio of \( M_{He} \) to \( M_H \) is given by

\[
\frac{M_{He}}{M_H} = 4.0022 \quad \text{and} \quad \frac{M_H}{M_{He}} = 1.00784
\]

Experimental measurements of the Rydberg constants for hydrogen and helium, by methods which will be explained later, yield the following values:

\[
R_H = 109,677.759 \pm 0.05 \text{ cm}^{-1}
\]

\[
R_{He} = 109,722.403 \pm 0.05 \text{ cm}^{-1}
\]

whence we see that

\[
\frac{M_B}{m} = 1837.8
\]

This agrees to within 0.5 per cent with the value 1,846 found from deflection measurements of \( e/m \) and \( e/M \) in Chapter IV. This is a very reassuring result. Since \( R \) approaches \( R_\infty \) very rapidly, the value \( R_\infty \) may be used with a negligible error for all but the very lightest elements. The value of \( R_\infty \) calculated from the experimental values of \( R_H \) and \( R_{He} \) is

\[
R_\infty = 109,737.42 \pm 0.06 \text{ cm}^{-1}
\]

Largely in the hands of Sommerfeld, the Bohr atom was developed in more general terms. The possibility of elliptic orbits was dealt with by introducing the general quantum condition:

\[
\oint pdq = \tau \hbar
\]

for each coordinate necessary to specify the position of the electron. Here \( p \) is the momentum or angular momentum associated with the coordinate \( q, \tau \) is an integer known as the quantum number, and the integration is over a complete cycle of the variable. For a circular orbit, \( q \) is the angle \( \theta \) through which the radius vector turns, and \( p \) is equal to \( m\nu r \). Since the angular momentum is constant in a central force field, the integral of \( m\nu rd\theta \) over a complete cycle is equal to \( 2\pi m\nu \), and this formulation of the quantum conditions gives us the same result as Bohr's treatment of a circular orbit. Sommerfeld applied this condition to the momentum associated with both of the variables necessary to specify an ellipse, i.e., the radius \( r \) and the angle \( \theta \). This introduces two quantum numbers; the azimuthal quantum number \( k \) and the radial quantum number \( n \). The resultant expression for the energy of an elliptical orbit is found to be

\[
E = -\frac{2\pi^2\mu^4Z^2}{(n^2 + k^2)} \quad -\frac{Z^2Rhc}{(n^2 + k^2)} \tag{7-11}
\]

It is seen that this gives the same value for the energy as in the case of a circular orbit for which the total quantum number \( n + k \) is the sum of \( n \) and \( k \). Since a knowledge of the energy levels of an atom does not suffice
to distinguish between the various possible electron orbits which have the same value of \( n_r + k \), we may consider that we have a number of elliptical orbits and one circular one coalescing to give only one term. Such a situation received the appellation “degenerate.” Sommerfeld also showed that if the relativistic variation of mass with velocity were taken into account for the electron the degeneracy would be removed, and each particular combination of \( n_r \) and \( k \) would give rise to a different term. This would give each line of the spectrum a fine structure, i.e., each line would in reality be two or more lines very close together. This is actually found to be the case for hydrogen, and the term separations found experimentally agree very well with those predicted by Sommerfeld.

Equation (7-11) bears a striking resemblance to the empirical expression of Rydberg, but there is an important difference. Here the denominator is the sum of two integers, whereas in a Rydberg term it is an integer plus a small quantity which is in general a fraction. A qualitative explanation of how the denominator of Eq. (7-11) may not be an integer can be obtained in the following way. For elements other than hydrogen the nucleus is surrounded by several electrons. These will disturb the electric field of the nucleus, and the electron responsible for the emitted light will no longer be moving in the Coulomb field of a point charge. It has been shown by Sommerfeld\(^1\) that if the field is derivable from a potential function of the form

\[
U = -\frac{Ze^2}{r} + \left( \alpha_0 + \frac{\alpha_1}{r} + \frac{\alpha_2}{r^2} + \cdots \right)
\]

where the expression in brackets represents the non-Coulomb nature of the field, the terms are given to a first approximation by the Balmer form, to a second approximation by that of Rydberg, and to a third approximation by that of Ritz. The quantity in the bracket of the term denominator can be considered as an effective quantum number \( n^* \). The difference between this and the corresponding hydrogen quantum number \( n \), which for a Ritz term is of the form

\[
n^* \rightarrow n = \mu + \alpha \tilde{v}
\]

is known as the quantum defect and is a measure of the non-Coulomb nature of the field. This was a very great success for the older form of the quantum theory, but the quantitative agreement between the empirical constants of a Ritz term and reasonable values of the \( \alpha \)'s, which represent perturbing terms on the Coulomb field, was much less satisfactory.

While these early developments provided merely the opening wedge for the theoretical treatment of spectra from the point of view of the electron structure of an atom, they introduced certain fundamental conceptions. The most important of these was the identification of spectroscopic terms with the energy levels of an atom. Upon this idea the Grotrian diagram is immediately interpretable as a plot of atomic energy states through the Bohr frequency relation. The direct experimental verification of this important point will be taken up in the following chapter. The quantitative success of these early developments stopped with the simple hydrogen or ionized helium atom, i.e., with an atom which contains only one electron in addition to the nucleus. Its success in those cases and its partially satisfactory description of certain other simple atomic phenomena led to the feeling that these ideas were qualitatively correct. This conception of an atom may be briefly summarized as a heavy nucleus surrounded by an external electron structure, the configuration of which can be specified by certain parameters known as quantum numbers; the atoms emit radiation of the frequency given by the Bohr relation when the internal energy determined by this configuration decreases from one allowed value to another.

7-4. The Vector Model. The first grasp of the general principles underlying the description of spectra came from the work of Catalan\(^1\) on the highly complex multiplets of the manganese spectrum rather than from the simple spectra which might at first sight have been considered to afford better possibilities for the observation of broad generalities. Next, in importance was the introduction by Russell and Saunders\(^2\) of the conception of spectral terms as properties of the atom or of the electron configuration as a whole rather than of a single radiating electron. This was followed very shortly by the theoretical developments due to Pauli\(^3\), Goudsmit,\(^4\) Heisenberg,\(^5\) Hund,\(^6\) and Uhlenbeck and Goudsmit\(^7\) which led to the purely empirical but very complete descriptive scheme known as the vector model. Inasmuch as this body of principles ties together the spectra of all the elements and lends a particular significance to the quantum numbers in terms of which the energy levels are described, we shall briefly state its more important postulates and their consequences. It is to be regarded as a set of empirical rules the interpretation of which, in terms of the more physical conception of electrons in an atomic system, is to be arrived at only through a study of the quantum mechanical theory of complex spectra. Such a study is far beyond the scope of this treatment, though the elementary consideration of the simple hydrogen atom will be outlined in a subsequent section.

For the purposes of the vector model we require the following postulates and definitions:

1. Each electron has associated with it an integral quantity \( n \), known as the total quantum number by analogy with the similar quantity used by Bohr and Sommerfeld in the description of simple spectra.

2. Each electron has also a quantity \( l \), sometimes known as the orbital quantum number, associated with it which fulfills the condition \( l \leq n - 1 \). This is closely connected with the angular momentum of an electron in a Bohr orbit on the older conception. The actual value of the angular momentum is equal to \( \hbar / 2\pi \). \( l \) is a vector quantity, and its values of 0, 1, 2, 3, 4, etc., are represented by saying that the electron is of the type \( s, p, d, f, g, \) etc., respectively, in analogy with the nomenclature sharp, principal, and diffuse of the series which have been described previously.

3. Each electron has associated with it another vector quantity represented by \( s \). It is also of the nature of an angular momentum which for the purpose of concreteness may be thought of as a rotation or spin of the electron about its axis. It has, however, certain very remarkable properties, into which we shall not be able to go, that differentiate it from ordinary mechanical angular momenta. The value of \( s \) is \( \frac{1}{2} \) for all electrons and the actual value of the angular momentum associated with \( s \), which is \( \hbar / 4\pi \), is therefore \( \hbar / 4\pi \).

4. The total angular momentum quantum number of an electron, which is the vector sum of \( l \) and \( s \), is written as \( j \). It has half integral values only, these being \( l \pm \frac{1}{2} s \).

5. In an extremely large magnetic field these vector quantities would orient themselves in such a way that the projections of the \( Z \)'s and \( s \)'s along the field would be integers or half integers, respectively. Thus these projections, which are known as magnetic quantum numbers, are given by

\[
-m \leq m \leq l \quad \text{and} \quad -s \leq m \leq s
\]

\( m \) may have the \( 2l + 1 \) values from \(-l\) to \( l \), and \( m \) may have the two values of \( \pm \frac{1}{2} \).

The mechanism of interaction of the electrons in an atom, known as coupling, determines the characteristics of the configuration as a whole and of the spectrum terms or energy levels. If the principal influence is exerted between the separate \( Z \)'s and \( s \)'s of the individual electrons, we may consider that the vectors represented by these different letters add up vectorially to give \( L \) and \( S \) vectors of the configuration or of the atom as a whole.

\[
L = \sum m_i \quad \text{and} \quad S = \sum s_i
\]

We thus have a series of \( L \) values, depending on the orientation of the \( Z \)'s, designated by \( S, P, D, \) etc., respectively, characteristic of the different term series which in the Grotrian diagram are represented by the columns. The vector sum of \( L \) and \( S \), which is the total angular momentum vector of the atom \( J \), is also quantized; i.e., it has only half integral values if \( S \) is \( \frac{1}{2} \) half integer or integral values if \( S \) in an integer. Its value is generally written as \( \{ \text{subscript of the letter designating the} \ L \text{ value. These vectors} \}

\( L, S \), and \( J \) specify the terms due to the electron configuration. This type of electron interaction is known as Russell-Saunders or L-S coupling. All other types are possible, to the opposite extreme where the 1 and \( s \) vectors of each individual electron combine to yield \( j \) values whose sum is the atomic \( J \) value; we need only consider \( L-S \) coupling for the spectra to be described later.

To consider the possible structure or configuration for a given number of electrons surrounding a nucleus with a large positive charge we need the fundamental restriction principle, due to Pauli: that for no two electrons in any one atom may the corresponding four quantum numbers be the same. If we consider the atom in an extremely large magnetic field, we may choose as our four quantum numbers, say for the \( i \)th electron:

\[
\begin{align*}
\eta_i &= \text{total quantum number} \\
\ell_i &= \text{orbital angular momentum quantum number} \\
m_{\ell i} &= \text{component of} \ \ell_i \ \text{along the field} \\
m_{s_i} &= \text{component of} \ s_i \ \text{along the field}
\end{align*}
\]

Let us assume for the moment that the electrons occupy the lowest possible energy levels in the normal state and that these are the levels for which \( n \) is smallest. Then if we have but one electron in an atom its...
n value is 1. Of necessity its \( l \) and \( m_l \) values are zero and its \( m_s \) value may be \( \pm \frac{1}{2} \). There is thus room for one other electron of this \( n \) value for which \( m_s \) namely \( m_s = \pm \frac{1}{2} \); but in the latter case, as \( m_l \) may have the values \(-1, 0, \) and \( 1 \), for each of which we have the possibilities of \( \pm \frac{1}{2} \) for \( m_s \), we have six different combinations. This process can be continued for any number of electrons with increasing values of \( n \) to give us the largest number of electrons of a given \( n \) value are frequently said to compose or occupy a shell. These are known as \( K, L, M, \) etc., shells in X-ray nomenclature corresponding to the values of \( n = 1, 2, 3, \) etc., respectively. When all the possible combinations of the quantum numbers \( l, m_l \), and \( m_s \) for a given \( n \) represent electrons actually present, the shell is said to be closed. The total number of electrons of any particular type for a given \( n \) is evidently equal to the number of possibilities for \( m_s \) times the number of possibilities for \( m_s \). As the former is \( 2l + 1 \) and the latter is 2 the total number is \( 4l + 2 \). The following table may be constructed for the number of electrons of each type possible in the various closed shells.

<table>
<thead>
<tr>
<th>( n )</th>
<th>Type ( s )</th>
<th>Type ( p )</th>
<th>Type ( d )</th>
<th>Type ( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>6</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A closed shell has a very important property as may be seen from the following array representing six \( p \) electrons:

\[
\begin{align*}
&m_l = 1 \quad 1 \quad 0 \quad 0 \quad -1 \quad -1 \\
&m_s = \frac{1}{2} \quad -\frac{1}{2} \quad \frac{1}{2} \quad -\frac{1}{2} \quad 3 \quad -4
\end{align*}
\]

The sums of the quantities in each of these rows are equal to zero, therefore the resultant \( L, S, \) and \( J \) for the configuration as a whole are all zero. As a consequence, if another electron were added to the atom, the resultant \( L, S, \) and \( J \) values of the atom (the sums of the respective values for the closed shell and those of the new electron) would be simply those of this electron. As these are the quantum numbers which specify the spectroscopic terms, we see that they are determined only by the last electron and that the effect of the closed group may be neglected. Similarly if we took any one of the electrons out of the above array, the possible values of the resultant \( \Sigma m_l \) would be 1, 0, and \(-1 \) and those of \( \Sigma m_s \) would be \( \pm \frac{1}{2} \) and \( \mp \frac{1}{2} \), which corresponds to an \( L = 1 \) and an \( S = \frac{1}{2} \), characteristic of a single \( p \) electron. In general the presence of any number of electrons, say \( x \), in a closed group gives rise to the same terms as a number of electrons, \( y \), of the same type, where \( x + y \) is the total number possible in the group. The systematic development of these ideas yields a beautifully regular and complete skeleton framework of the types of terms to be expected for every possible electron configuration. For the details of these calculations reference should be made to the treatises on spectroscopy which have been cited. We shall consider briefly only those types of terms to be expected in the case of a one-electron spectrum, i.e., one electron besides a closed group, and in the case of a particularly simple type of two-electron spectrum as represented by mercury.

If we have one electron outside a closed group it can have any total quantum number \( n \) greater than that of the closed group of its type. It can have an \( s \) value of 0, 1, 2, 3, etc., corresponding to its being of an \( s, p, d, f, \) etc., type; as this determines the \( L \) of the atom, the spectral terms will be \( S, P, D, F, \) etc., respectively. As the \( s \) of an electron is \( \frac{1}{2} \), the \( S \) of the atom has also this value, and the \( J \) which is the vector sum of \( L \) and \( S \), can have the values \( L = 0, J = \frac{1}{2}; L = 1, J = \frac{3}{2} \) or \( \frac{1}{2}; L = 2, J = \frac{5}{2} \) or \( \frac{3}{2} \) etc. As there are two \( J \) values associated with each \( L \) (except \( L = 0 \)), the spectrum is known as a doublet spectrum, as is signified by writing an anterior superscript 2 before the letter designating the \( L \) value of the term. The terms to be expected are thus:

\[
^2S_1 \text{ or } ^2P_{1,1} \text{ and } ^2P_{3,0} \text{ or } ^2D_{1,1,0}
\]

There will be a level of each type (up to \( L = n - 1 \)) for each \( n \) value of the electron, and these series for increasing values of \( n \) represent the series of terms in the columns of the Grotrian diagram. Reference to the sodium spectrum later in the chapter will bring out clearly the application of this nomenclature to the diagram.

The other case we need consider is a simple two-electron spectrum for which one electron is of an \( s \) type, i.e., \( l_1 = 0 \). In this case the \( L \) of the atom is the 1 of the second electron, as \( L = l_1 + l_2 \) and \( l_1 = 0 \). The \( S \) value, which is the vector sum of \( s_1 \) and \( s_2 \), both of which are \( \frac{1}{2} \), can have the values 0 or 1. When \( S = 0, J = L \); and when \( S = 1, J = L + 1, L, \) or \( L - 1 \). For \( S = 0 \) we have single terms, i.e., only one \( J \) value; while for \( S = 1 \) we have triple terms, i.e., three \( J \) values per term (except when \( L = 0 \)). In general, as can be seen from the above example, the multiplicity of a spectrum is \( 2S + 1 \). The terms to be expected from such electron structures are thus

\[
^1S_0, ^3S_1 \text{ from } ns \text{ } n's; \text{ } ^1P_1, ^3P_{1,0} \text{ from } ns \text{ } n'p.
\]

*In this sentence \( s \) and \( S \) refer to the spin of the electron and atom respectively. The small \( s \) used here must not be confused with the symbol meaning \( n = 0 \).
LINE SPECTRA [7-4]

where the letters S, P, D, etc., correspond to the s, p, d, etc., of the second electron, and the series of terms of a similar type are due to increasing total quantum numbers of this electron. The application of this nomenclature to a Grotrian diagram can be seen from that of mercury later in the chapter.

Working backward in our description of the vector model we come to the final experimental test, namely the comparison of the combinations between these terms and the observed spectrum lines. For this purpose, since all possible intercombinations are not observed, we find that we need the following principles restricting the configuration changes:

The L Selection Rule.-Only those combinations occur for which the sum of the L vectors of the electrons forming the initial and final states of the atom changes from an even to an odd number, or vice versa. Even terms are often written as S, P', D, F', G', etc., and odd terms as S', P, D', F, G', etc. Recently a more logical notation has come into use: odd terms are denoted by S''P, P''D, etc. and even terms by S, P, D, etc. In simple spectra where no confusion can result, such indices are usually omitted. For atomic states that are due to a single electron outside a closed group or an s electron and one other, as in the last example, this rule degenerates practically into the statement that the L value of the atom may change only by 1 or -1.

The J Selection Rule.-Only those combinations occur for which the J value of the atom changes by 1, 0, or -1, the transition of J = 0 to J = 0 being further excluded.

With these rules we find that even the most complex spectra become comprehensible. The application of them to the explanation of the observed lines of sodium and mercury will be described later. The complete designation of a line is given as the difference between the two terms of the final and initial configurations. If in the case of one electron it was originally of type p with a total quantum number of 4, the J of the atom being 4 (term 4p^2P), and after the emission of radiation it became an s type of total quantum number 3 (term 3s^3S), the line would be completely represented by 3s^3S - 4p^2P. Similarly if, in the case of the simple two-electron configuration, the original state of the atom was 6s^2^1S and the final state 6s^6^1S, the line emitted would be written as 6s^6^1S - 6s^6^1P. When both electrons have the same n value a superscript is used, i.e., 6s^6s is written as 6s^6.

For these simple types of electron structure the identification of lines and assignment of terms are relatively easy, but for complex spectra it is very difficult and tedious. Spectrum analysis consists in discovering the numerical values of the energy levels, transitions between which give rise to the observed lines. The actual process is entirely one of trial and error, with certain rules for guides. If levels A and B both combine with C to give lines of wave numbers C - A and C - B, then the wave-number difference between these two lines is equal to (C - A) - (C - B) = B - A. If there is another level D that also combines with the levels A and B forming the lines D - A and D - B, the wave-number difference of these two lines is also B - A. Hence the list of wave numbers must be searched through for pairs of lines that have the same wave-number difference; the differences thus found determine the energies of the levels relative to an arbitrary zero taken at one of them. If a series of levels can be found that obey a Balmer, Rydberg, or Ritz formula, an absolute zero may be taken at the limit of the series of levels, i.e., at the ion formed by the removal of an electron. This, however, is not necessary; relative energy levels may be used just as well as absolute ones, since only differences are important.

The work is hampered by the fact that no wave-number measurements can ever be made exactly; a certain tolerance must be allowed when looking for constant differences. This leads to a large list of possibilities which can only be cut down to the true levels by cross differences and the aid of Zeeman patterns and certain empirical spectroscopic rules. Atomic radiations cover a vast range of wave lengths, and the experimental difficulties are very great except in the visible, near ultra-violet and near infra-red, so that in most cases only a portion of all the evidence for the construction of an energy-level diagram is at hand.

7-6. Quantum Mechanical Atom Model.-The highly empirical set of rules and principles embodied in the vector model has received a very complete and satisfactory theoretical justification through the application of quantum mechanics to the theory of complex spectra. These remarkable advances, which may be found in the work of Wigner,1 Weyl,2 Slater,3 and others, lie far beyond our scope, but we may briefly consider the application of wave mechanical conceptions to the simplest possible atomic system, namely that of the hydrogen atom. As we shall see, the results of this theory are the same as those of the original Bohr theory based on an orbital electron. The success of quantum mechanics, however, in accounting for the experimental facts extends throughout the cross-word puzzle backward; instead of being given the horizontal and vertical clues from which to derive the words, one is in effect given the words, which must first be set in their proper arrangement from which the clues are then to be deduced. Given the wave numbers of the observed radiation, the problem is to arrange sets of other numbers such that the differences between pairs of them correspond to the original data. The process is entirely one of trial and error, with certain rules for guides. If levels A and B both combine with C to give lines of wave numbers C - A and C - B, then the wave-number difference between these two lines is equal to (C - A) - (C - B) = B - A. If there is another level D that also combines with the levels A and B forming the lines D - A and D - B, the wave-number difference of these two lines is also B - A. Hence the list of wave numbers must be searched through for pairs of lines that have the same wave-number difference; the differences thus found determine the energies of the levels relative to an arbitrary zero taken at one of them. If a series of levels can be found that obey a Balmer, Rydberg, or Ritz formula, an absolute zero may be taken at the limit of the series of levels, i.e., at the ion formed by the removal of an electron. This, however, is not necessary; relative energy levels may be used just as well as absolute ones, since only differences are important. The work is hampered by the fact that no wave-number measurements can ever be made exactly; a certain tolerance must be allowed when looking for constant differences. This leads to a large list of possibilities which can only be cut down to the true levels by cross differences and the aid of Zeeman patterns and certain empirical spectroscopic rules. Atomic radiations cover a vast range of wave lengths, and the experimental difficulties are very great except in the visible, near ultra-violet and near infra-red, so that in most cases only a portion of all the evidence for the construction of an energy-level diagram is at hand.

1 WIGNER, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren," Vieweg, Braunschweig (1931).
The fundamental equation which is to describe the behavior of the electron is Eq. (5-9) with the reduced mass \(\mu\) replacing the mass of the electron in that equation:

\[
\nabla^2 \psi + \frac{8\pi^2 \mu}{\hbar^2} (E - U) \psi = 0 \tag{7-12}
\]

It will be recalled that \(E\) is the total energy, \(U\) the potential energy, and \(\psi\) is the Schrödinger function whose absolute magnitude in a small region is to be taken as giving the probability of the electron being observed in that region. The symbol \(\nabla^2\) stands for the Laplace operator \(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\). In this discussion we shall not be interested in the solutions of Eq. (7-12) themselves but only in the necessary conditions that must be imposed on \(E\) in order that these solutions shall be finite, continuous, and single valued throughout space, which are necessary conditions if the solutions are to be acceptable for the description of an electron. For a hydrogen-like atom the potential energy \(U\) is given by \(-Ze^2/r\), where \(Z\) is the nuclear charge. In the case of hydrogen itself \(Z\) is, of course, unity. As this term is spherically symmetrical; it is more convenient to write the Laplace operator in polar coordinates and Eq. (7-12) becomes

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 \mu}{\hbar^2} \left( E + \frac{Ze^2}{r} \right) \psi = 0 \tag{7-13}
\]

We shall now assume that a solution of this equation may be written as the product of two factors, one a function of \(r\) only and one a function of \(\theta\) and \(\phi\) only:

\[
\psi(r, \theta, \phi) = S(r) \times Y(\theta, \phi)
\]

Substituting this in Eq. (7-13) we find, that the equation groups itself into terms that depend only on \(r\) and terms that depend only on \(\theta\) and \(\phi\). As the variables \(r\), \(\theta\), and \(\phi\) are independent and as the equation is to be true for all values of these variables, each of these groups of terms must be equal to a constant; if the first group is equal to \(-C\), the second group must be equal to \(+C\). We thus have two equations:

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dS}{dr} \right) - \frac{C}{r^2} S + \frac{8\pi^2 \mu}{\hbar^2} \left( E + \frac{Ze^2}{r} \right) S = 0 \tag{7-14}
\]

\[
\frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + CY = 0 \tag{7-15}
\]

The second of these is familiar among mathematicians and the solution is well known. The point of extreme interest is that the solution is finite and continuous only if the quantity \(C\) has one of the series of values given by the relation

\[
c = l(l + 1)
\]

where \(l = 0, 1, 2, 3, 4, \text{ etc.}\).

We thus have an integral quantum number entering the picture quite naturally. It enters as the necessary consequence of the highly reasonable conditions which have been imposed on the solutions of the differential equation. This, of course, is much more satisfactory than the artificial introduction of this quantity in the older form of the quantum theory. The \(l\) defined above is the so-called orbital angular momentum of the vector model.

We may now put this value of \(C\) in Eq. (7-14) and make an attempt to solve it. The equation simplifies considerably if we define a new independent variable \(x\) and a new parameter \(n\) by means of the relations

\[
E = \frac{2\pi^2 \mu e^4 Z^2}{n^2 \hbar^2}
\]

and

\[
r = \frac{\hbar^2}{8\pi^2 \mu e^2 Z^2}
\]

Equation (7-14) then becomes

\[
\frac{d^2 S}{dx^2} + \frac{2dS}{x dx} + \left\{ \frac{1}{4} + \frac{n}{x} - \frac{l(l + 1)}{x^2} \right\} S = 0
\]

A satisfactory solution of this equation may be found in the form of a polynomial provided that when \(E\) is negative, the parameter \(n\) is an integer and satisfies the relationship

\[
n \geq l + 1
\]

Thus the total quantum number of the vector model has also appeared quite naturally in the endeavor to solve these differential equations. The above transformation involving \(E\) and \(n\) is recognized as Bohr's expression for the energy of an electron in a circular orbit so that the allowed energy states agree with those of the Bohr theory for hydrogen. This is very satisfactory as we have seen that the energy states on the Bohr theory agree with those found experimentally in the case of hydrogen. The negative value of \(E\) is consistent with the convention that the zero of energy is taken at ionization, the various excited states and the normal state having negative energies. A solution of Eq. (7-16) is possible for a continuous range of values of \(n\), if \(E\) is positive. This means that the energy content of the nucleus and electron can have any value when the atom is ionized; when the electron has sufficient energy to leave the atom it may fly off with any amount of kinetic energy.

This formulation of quantum mechanics not only supplies us with quantum numbers, but it also produces the selection rules governing the
allowed transitions between atomic energy levels in a quite analogous manner, i.e., as a result of the necessary properties of various mathematical expressions.

More complicated atoms than hydrogen do not admit of a simple solution of the Schrödinger equation (Eq. (7-12)) and so-called perturbation methods have to be used. The method is quite analogous in principle to that used in astronomy when the many-body problem is solved by successive approximations. Accounts of these methods are to be found in Ruark and Urey, and Condon and Morse.

As has been mentioned before, the solutions of even the simplest problems are often far from easy, involving the numerical evaluation of very formidable polynomials. It must be remembered, however, that these difficulties are probably only temporary, for when the useful expressions have been found they may be evaluated once and for all in tabular form. The infinite polynomial:

\[ x + \frac{x^3}{3} + \frac{2x^5}{15} + \frac{17x^7}{315} + \frac{62x^9}{2,835} + \cdots \quad \left( x^2 < \frac{\pi^2}{4} \right) \]

may give one pause until it is recognized by the abbreviation "tan \( z \)." It is to be hoped that analogous polynomials which occur in the solutions of problems in quantum mechanics will eventually become as familiar as the trigonometric functions.

7-6. The Normal Zeeman Effect. - Faraday, in 1862, endeavored to detect the effect of a magnetic field on light by placing a sodium flame between the poles of a magnet and looking for some change in the characteristic lines as seen through a spectroscope. He observed no alteration, but merely because of the relative crudity of his instruments. Zeeman, in 1897, with better apparatus, succeeded in detecting a splitting of each spectral line into several components which had both longer and shorter wave lengths than the original line. This Lorentz explained in terms of the classical electromagnetic theory by showing how the frequency of an oscillating electron should be affected by a magnetic field. We shall here give, first, a simple quantum-theory explanation of the normal or simple Zeeman effect wherein we have by Eqs. (4-1), (4-2) and (4-3):

\[
\begin{align*}
    m_0 \dot{z} - e \mathbf{H} &= F_z \\
    m_0 \dot{y} + e \dot{z} \mathbf{H} &= F_y \\
    m_0 \dot{z} &= F_z
\end{align*}
\]

We shall now make use of a device due to Larmor. Let us find the equation describing the acceleration of a particle in a fixed frame of reference OX'OY', from the point of view of a coordinate system OX'OY' that is revolving with a uniform angular velocity \( \dot{\psi} \) about the common OZ-axis of the two systems. The instantaneous \( y' \) coordinate, at the instant when the angular separation of the two systems is \( \psi \), of a particle at \( x, y \) in the rotating system is then given by:

\[ y' = y \cos \psi + z \sin \psi \]

Hence, differentiating this with respect to the time gives:

\[ y'' = \dot{y} \cos \psi - \dot{z} \sin \psi + z \cos \psi \]

and differentiating a second time, remembering that \( \dot{\psi} \) is a constant,

\[ y''' = \ddot{y} \cos \psi - 2 \dot{\psi} \sin \psi - \dot{\psi}^2 \cos \psi + 2 \dot{\psi} \sin \psi + 2 \dot{\psi}^2 \cos \psi - \dot{\psi}^2 \sin \psi \]

Now, since \( y'' \) is the true acceleration along the direction \( Y' \), we can find the true acceleration along OX and OY of the use of the above expression at the instants when \( OY' \) lies along OX and OY, respectively. Thus when \( \psi = \pi/2 \)

Acceleration along OX = \( x - \dot{z} \dot{\psi}^2 - 2 \dot{\psi} y \)

and when \( \psi = 0 \)

Acceleration along OY = \( \ddot{y} - \dot{z} \dot{\psi}^2 + 2 \dot{\psi} y \)

So if \( F_x, F_y \) and \( F_z \) are any external forces applied to a particle of mass \( m_0 \), the equations of motion in terms of the rotating axes are
Comparing these equations with those representing the motion in a magnetic field, Eq. (7-17), we see that they are the same if we omit terms in \( \psi \), which are small, and if we identify \( e qH \) with \( m_02q\psi \), and \( e\psi H \) with \( m_02q\psi \), both of which give the relations,

\[
\begin{align*}
\text{Angular velocity } \psi &= \frac{eH}{2m_0} \\
\text{Angular frequency } \omega &= \frac{eH}{4\pi m_0}
\end{align*}
\]

The fact that these two sets of equations have exactly the same form to this approximation shows that the actual complicated path of the electron may be described by saying that the original orbit maintains its shape, but that the whole coordinate system by which it is specified rotates uniformly about the direction of the magnetic field with the angular frequency \( \omega \), known as the Larmor precession frequency. The application of this to the Zeeman effect is quite simple. The kinetic energy of any system of electrons, each of mass \( m_0 \), is given in polar coordinates by

\[
E = \frac{1}{2}m_0(c^2 + r^2\dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2)
\]

When we apply a magnetic field \( H \) along the Z-axis, the energy is given by the same expression provided we consider that the entire system rotates about OZ with the angular velocity \( \dot{\psi} \). Hence in that case we have

\[
E_H = \frac{1}{2}m_0[c^2 + r^2\dot{\theta}^2 + r^2 \sin^2 \theta (\dot{\psi}^2 + \dot{\phi})^2]
\]

Expanding the bracket \((\dot{\phi} + \dot{\psi})^2\) and neglecting terms in \( \dot{\psi} \), as we have done before, we obtain on subtracting Eq. (7-18) from Eq. (7-19)

\[
\Delta E = E_H - E = \sum m_0 c^2 \sin^2 \theta \dot{\phi}
\]

\[
= \dot{\psi} \sum m_0 \sin \theta (r \sin \theta \dot{\phi})
\]

\[
= 2e\omega p \cos(pH)
\]

where \( p \) is the total angular momentum of the atom and \( \cos(pH) \) is the cosine of the angle between \( p \) and the field, so \( p \cos(pH) \) is the projection of the angular momentum vector in the direction of \( H \). Thus the increase in energy of an atom in a magnetic field is proportional to \( \omega \), which is itself proportional to the field, and to the projection of the angular momentum along the field.

Let us first consider the case of one electron with the restriction that the \( L-S \) coupling is much stronger than the couplings of either \( l \) or \( g \) with the field \( H \). The angular momentum vector \( J \) is the sum of \( L \) and \( S \), or expressed in the proper units it is \( Jh/2\pi = p \). We now recall that the projections of the vectors along the magnetic field are quantized, i.e., they have integral or half-integral values, hence the projection of \( J \) along the field, which is equal to \( p \cos(pH) \) of Eq. (7-20), and which we shall write as \( M \), can have only integral or half-integral values. Thus

\[
\Delta E = Moh \quad \text{or} \quad E_M = E_0 + Moh
\]

Any other electron level will undergo a similar increase in energy, so in a jump from one level to another an atom emits radiation of frequency \( v \) given by

\[
hv = (E_0 + Moh) - (E_0' + Moh) = (E_0 - E_0') + (M - M')oh
\]

or

\[
v = v_0 + o\Delta M
\]

where \( v_0 \) is the frequency of the light emitted by transitions between the undisturbed levels, and \( \Delta M \) is the change in the so-called magnetic quantum number \( M \). The selection rule governing the change is \( \Delta M = 1, 0, -1 \). Hence for such an atom in a magnetic field the frequencies emitted are either

\[
v_0, v_0 + 0 \quad \text{or} \quad v_0 - 0
\]

In any actual light source there are a large number of atoms each of which may emit any one of the above frequencies, so these three frequencies are observed from the source. In the expressions for these frequencies:

\[
\frac{\omega}{c} = \frac{4.674 \times 10^{-8}H}{c} \quad \text{wave-number units}
\]

where \( H \) and \( c \) are in electromagnetic units. Zeeman patterns are generally described in terms of the separation for a field of 1 gauss, i.e., \( 4.674 \times 10^{-8} \text{ cm}^{-1} \). This is called the Lorentz separation. We therefore see that the above analysis predicts the splitting of a spectral line into three components: one at the original frequency, and one on either side at a distance, in wave numbers, equal to one Lorentz unit for a unit field strength. Measurements of the Zeeman effect therefore give an accurate value of the ratio of the charge to the mass of an electron in an atomic system. References to such experiments have been given in Chap. IV.

7-7. The Anomalous Zeeman Effect—Although the above theory adequately describes the Zeeman effect for lines due to combinations between singlet terms, it is insufficient for the majority of other lines which are observed to split into more than three components when apparatus of sufficient resolving power is used. Such behavior was called “anomalous” when it was first observed, but as frequently happens the anomalous case turns out to be the general one, and the so-called normal case which we have just discussed is a very special instance. It has been found that the general
Zeeman effects can be described consistently if the increase in energy due to a magnetic field is written as

$$\Delta E = q \mu_H$$

instead of $AE = q \mu_H$ as in Eq. (7-21). The symbol $g$ is known as the Landé $g$ factor or splitting number. The special case which we have considered previously arises when $g = 1$. The significance of this factor may be most clearly brought out by the consideration of the energy of a small magnet of moment $\mu$, which represents the atom when it is in a magnetic field $H$ with the direction of its magnetic moment at an angle $\theta$ with the field. The potential energy is equal to $-\mu H \cos \theta$, as may be seen by integrating the torque $\mu H \sin \theta$ from $\theta = 0$ to $\theta$ (the zero energy state being taken when $\theta = 0$). Therefore, when a magnetic field of strength $H$ is applied, the increase in energy may be thought of as this increase in potential energy:

$$\Delta E = -\mu H \cos \theta$$

If we consider that the magnetic moment is in the same direction as the angular momentum (as the moving charges are negative the opposite sign is used), and equate these last two expressions, writing $p \cos \theta$ from $M$, and $eH/4\pi m_e$ for $a$, we obtain

$$g \approx \frac{a}{p}$$

if $\mu'$ is measured in units of $eH/4\pi m_e$. Thus the factor $g$ is the ratio of the magnetic moment to the angular momentum when the former is measured in unit $eH/4\pi m_e$, known as the Bohr magneton, and the latter in units of $h/2\pi$. Let us now consider what value of $g$ we should expect on the basis of classical electrodynamics for an electron, without any spin vector, traveling in a circular orbit.

By elementary electromagnetic theory, the magnetic moment associated with a current of strength $i$ flowing around the circumference of a circle of area $A$ is given by $\mu = iA$, where $i$ and $\mu$ are in electromagnetic units. Hence $\mu = e\pi r^2$, where $e$ is the electron's charge in electromagnetic units, $\pi$ the frequency in revolution in the orbit, and $r$ is the radius of the orbit. For the orbital angular momentum we have $p = m_e r \omega$ or $p = m_e r^2 \pi$. Hence we find that the ratio of the magnetic moment, due to the orbital motion, to the orbital angular momentum is

$$g_\ell = \frac{\mu}{p_\ell} = \frac{e\pi r^2}{m_e r^2 \pi} = \frac{e}{2m_e}$$

If we express $\mu$ and $p_\ell$ in their respective units, which we have previously adopted

$$g_\ell = 1$$

This means that the value of $g$ associated with the orbital motion of an electron is 1, and this may be shown to be true for much more general cases than the one we have chosen.

Unfortunately the effect of the spin vector cannot be calculated in this simple way. In the previous discussion we have made the assumption, which is necessary to account for the observed spectroscopic phenomena, that the angular momentum associated with the electron spin is $h/2\pi$, where $\pi$ is always equal to 1. In order to account for the general phenomena of the Zeeman effect, as well as certain allied phenomena such as the Stern-Gerlach effect and the so-called gyromagnetic anomaly, it is necessary to assume that the magnetic moment associated with the spin of an electron is $eH/4\pi m_e$, which is one unit of magnetic moment. This hypothesis, that in the case of this quantity, which we have called the electron spin, we have a whole

unit of magnetic moment associated with only half a unit of angular momentum, gives effectively

$$g_s = 2$$

This is as radical a departure from the classical quantities of electrodynamics as were Bohr's postulates when they were first enunciated, and it can be justified only by the results which it yields. It has, in fact, permitted the construction of an adequate theory of magnetic phenomena.

We shall not go through these calculations, however, which can be performed accurately only on the basis of quantum mechanics, but shall simply state the resulting value of $g$ for the atom as a whole, provided it exhibits Russell-Saunders coupling. This expression had previously been discovered empirically by Landé.¹

Tables of these $g$ numbers for different values of $L$, $S$, and $J$ are given by Back and Landé,²; Ruark and Urey,³; Pauling and Goudsmit,⁴ and Hund.⁵

In a magnetic field we have seen that $J$ is quantized; it can take only those orientations in the field such that its projection along the field, which we have called $M$, is integral or half integral according as $J$ is integral or half integral. We have further seen that the increase in the energy of the atom because of the field is $\Delta E = q \mu_H$, or taking $\mu_H$ as a unit, the increase in energy is $g g_H$. The magnetic quantum number $M$ may have any of the $2J + 1$ values $J, J - 1, J - 2, \ldots, -(J - 1), -J$, or, as there are actually many atoms present in the light source, all the $2J + 1$ values of $M$ may be considered to be present simultaneously. Now let us suppose that an atom changes from the state wherein $J = J_1$ and $g = g_1$ to the state $J = J_2$ and $g = g_2$. The effect of the magnetic field is to split each original $J$ level into $2J + 1$ so-called magnetic levels; transitions then occur between those levels obeying the selection rule $AM = 1, -1, 0$, with the restriction that if $\Delta J = 0$ the combination $M = 0$ to $M = 0$ is forbidden. This can be shown most conveniently by a diagram. Taking, for example, $J_1 = 3$ and $J_2 = 2$ we write the following two rows, the upper one the possible values of the product $M g_J$, and the lower the products $M g_J$:

$$\begin{align*}
M g_J (J_1 = 3) & \quad 3g_1, 2g_1, 1g_1, 0, -1g_1, -2g_1, -3g_1, \\
M g_J (J_2 = 2) & \quad 2g_2, 1g_2, 0, -1g_2, -2g_2.
\end{align*}$$

The vertical arrows, for which $\Delta M = 0$, indicate the so-called $\pi$ or parallel components of the Zeeman effect, for if the emitted light is examined at right angles to the field these components are found to be polarized with their electric vectors parallel to the magnetic field. The diagonal arrows, corresponding to $\Delta M = 1$ or -1, indicate the $\sigma$ (senkrecht or perpendicular) components, which are polarized with their electric vectors perpendicular to the field. The deviation in units of $a_0$ for a field of 1 gauss, of the emitted light from the original frequency is written symbolically

$$\pm (2g_1 - 2g_2, 1g_1 - 1g_2, 0, 3g_1 - 2g_2, 2g_1 - 1g_2, 1g_1, 2g_2 - 1g_2)$$

¹ Landé, Zeits. Physik, 16, 189 (1923).
where each difference corresponds to a single Zeeman component, the expressions in brackets indicating the \( \pi \) components and the others the \( \sigma \) components. The \( \pm \) sign shows that the pattern is symmetrical about the original line. The original frequency appears in the \( \pi \) group; it is completely lacking for those lines due to combinations between terms of even multiplicity (for then \( J \) has half-integral values, and so \( M \) cannot be zero), and also for terms of odd multiplicity if \( \Delta J = 0 \), because in this special case the transition \( M = 0 \rightarrow M = 0 \) is forbidden. The order of magnitude of the Zeeman pattern separation is a few Lorentz units per gauss, amounting to one or two wave numbers for a field of, say, 20,000 gauss.

It is of interest to observe how the above method of calculating Zeeman patterns always gives the original line plus two symmetrically placed companions for combinations between singlet terms. For these terms \( S = 0 \), hence always gives the original line plus two symmetrically placed companions for combinations between singlet terms.

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ments, only those corresponding to the allowed values of the quantity $\mu \cos(\mu H)$ will be observed. The experiment was first carried out by Stern and Gerlach in 1924 using silver atoms. The results showed definitely that the atomic beam was split into two components, one on either side of the original direction. The quantity $\mu \cos(\mu H)$ was shown to have the value of plus or minus one Bohr magneton, indicating that the normal silver atom possesses a magnetic moment of one Bohr magneton and that its orientation with respect to the field can be only parallel or antiparallel. This is in complete accord with the experimental and theoretical spectroscopic results which agree in assigning the normal level or antiparallel. This is in complete accord with the experimental and theoretical spectroscopic results which agree in assigning the normal level or antiparallel.

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For the $S_\uparrow$ state of silver, with $g = 2$, we have

\[
\mu \cos(\mu H) = Mg
\]

For the $S_\downarrow$ state of silver, with $g = 2$, we have

\[
\mu \cos(\mu H) = \frac{3}{2} \times 2 \quad \text{or} \quad -\frac{3}{2} \times 2 = 1 \quad \text{or} \quad -1
\]

which as we have seen agrees with the experimentally observed value of this quantity for silver.

A further point of interest in connection with the quantity $g$ is its bearing on the so-called gyromagnetic anomaly. This is a phenomenon connected with the mechanical and magnetic moments of matter in bulk. If by magnetization a magnetic moment $\mu$ is given to a sample of matter, and if the ratio of this magnetic moment to the associated mechanical moment $g$, an angular momentum equal to $\mu/g$ should appear on magnetization. On the straightforward classical theory it may be shown, as in the case of the orbital motion of an electron, that the value of $g$ should be 1. The experiments of Barnett,\textsuperscript{1} Chattock and Bates,\textsuperscript{2} and others, on those ferromagnetic elements such as iron, cobalt, and nickel, which are capable of acquiring large magnetic moments, have shown that this ratio is not 1 but 2 to within the limits of experimental error. This means that for these substances, at least, the quantity $g$ is equal to 2. This is the value of $g$ associated with an $S$ state or with a free electron whose only magnetic moment is that associated with its spin. The theory of ferromagnetism as developed by Heisenberg\textsuperscript{3} attributes the phenomenon to the action of free electrons in the crystal lattice. As 2 is the $g$ value for a free electron, the experiments which have been mentioned support this theory. Experiments have also been performed by Sucksmith\textsuperscript{4} on paramagnetic substances for which different values of $g$ would be expected since the orbital motion of the electrons contributes to the magnetic moment. The results are in good agreement with the theoretical predictions.

\[\text{(7-22)}\]

\[
n\lambda = D \left( \sin \theta_1 \pm \sin \theta_2 \right)
\]
where the integer n is called the order of the spectrum while \( \theta_r \) and \( \theta_i \) are the angles that the diffracted and incident beams make with the normal to the grating surface. The positive or negative sign is used depending on whether the incident and refracted beams lie on the same or different sides of the normal to the grating. A similar equation holds for a reflection grating. All these quantities except \( \lambda \) are directly measurable, in theory, so that \( \lambda \) may be determined. In practice absolute measurements are not easy to make, for the determination of the grating constant to the required degree of accuracy is difficult, even supposing for the moment that it really is a constant. However, making this assumption, it is evident that relative wave lengths can be determined to the accuracy with which the angles can be measured; the absolute values can be found subsequently by an exact determination of the grating space or by some independent absolute measurement of one wave length.

In photographic spectroscopy the angles are not measured directly, but rather the distances along the plate from one image to another; wave lengths may then be interpolated between lines of known wave length. It is obvious from Eq. (7-22) that a line of say 9000 \( \AA \) should fall on the plate in the first order at exactly the same place that a line of 4500 \( \AA \) will appear in the second order. Or putting it another way, if the wave length of a line is known very precisely to be 9000 \( \AA \), then is equivalent to knowing, with even greater precision, lines at 4500 \( \AA \), 3000 \( \AA \), 2250 \( \AA \), etc. Thus by the superposition of orders a single well-determined wave length may be used as a reference point in regions of shorter or longer wave length. This was the procedure adopted by Rowland in the eighteen-eighties when he measured the wave lengths of the absorption lines in the solar spectrum with a grating. One of the sodium yellow lines \((D_i)\) was used as the primary standard, with 5896.156 \( \times 10^{-8} \) cm. taken as the best average value of the wave length as previously determined by several observers who had directly measured their grating constants. As will be presently explained, Rowland's apparatus was such that, for relatively small wave-length ranges, the distance along the photographic plate was directly proportional to the wave-length change, so that interpolation between lines could be made very accurately. It was thus anticipated, in view of the principle of superposition and the fact that the spectrum was a so-called normal one, that any future redeterminations of the sodium line would merely involve correcting all of Rowland's wave lengths by one multiplicative factor.

This hope was blasted by the work of Michelson and Benoit,\(^1\) and of Fabry and Perot,\(^2\) who, about 1895, measured the wave length of the cadmium red line with an interferometer. In principle, though not in detail, the method consists in counting the number of wave lengths of this color that lie within 1 meter by observing the number of interference fringes that cross a fiducial mark when one plate of an interferometer is drawn away from the other through a measured distance. The primary standard was thus determined and it is taken to be

\[
\text{Cadmium red line} = 6438.4696 \text{ International Ångström units}
\]

in dry air at a pressure of 760 mm. Hg, 15° C., and with the gravitational constant equal to 980.67 cm. sec.\(^{-2}\). By choosing to call this an exact value, the International Ångström (Å) is thus defined. The previous Ångström unit had been defined as \(10^{-6}\) cm., so that no spectral line could be expected to be given exactly by a finite number of figures in that unit. For most work this fine distinction is unimportant, for the International Ångström equals \(10^{-4}\) cm. to within 1 part in \(10^7\). Further interferometer measurements on lines from an iron arc were made, using the cadmium red line as the primary standard, thus supplying secondary standards. Tertiary standards have been established by careful interpolation between the secondary standards from good grating spectrograms. The result of these interferometer measurements was to show that one factor was not sufficient to correct the Rowland wave lengths; the correction varied in magnitude throughout the spectrum. Tables of the corrections to reduce Rowland's values, which appear in all the older literature, to International Ångström units have been given by Baly\(^3\) and Fowler.\(^4\) An error may possibly have been introduced through Rowland's ignorance of the wave-length differences in solar and terrestrial lines, due to various causes. Furthermore, Kaysers\(^5\) experimentally demonstrated by careful measurements with two Rowland concave gratings that the principle of superposition did not hold to the high degree of accuracy desired. The discrepancy apparently lay in irregularities in the grating spacing. Parenthetically, it may be remarked that no gratings as good as Rowland's best have ever been made since.

All modern spectroscopic work is performed on the basis of these international primary, secondary, and tertiary standards by various methods of interpolation, both with gratings and with prisms. The combination of interferometric and spectroscopic methods in the hands of experienced workers has extended the list of accurate reference points

\(^{1}\) _Michelson_ and _Benoit_, *Mon. Sec. Int. Poids et Mfb.*, 2, 1 (1895).


\(^{3}\) _Baly_, “Spectroscopy,” Longmans (1929).


well down toward 2000 Å. Other standards may be inferred by the use of the combination principle; accurate term values are calculated from lines which he within the range of measured standards, and hence the wave lengths of lines due to different combinations of these same terms may be computed with equal exactness in spectral regions remote from the standards. In comparing an unknown spectrum with a standard one both are photographed on the same plate, recognition of the two spectra being facilitated by using shutters of different lengths over the slit.

The plane grating, whether of the transmission or reflection type, requires the use of a lens to collimate the light from the slit and a second lens to focus the diffracted rays on the photographic plate or eyepiece. This is a great disadvantage since it limits the use of gratings with glass lenses to wave lengths above about 3500 Å, for most glasses are highly absorbing for shorter wave lengths. Quartz lenses extend the range to about 1800 Å, and fluorite lenses several hundred Angstroms further, but large lenses of these materials are very rare and expensive. Rowland's introduction of the concave grating, in 1881, was a highly important advance. A concave mirror of glass or metal may be used to form an image of the slit directly on the photographic plate; if this mirror is ruled after the manner of a plane grating, the single "white" image of the slit is dispersed into a spectrum of its component colors. The rulings are not great circles but rather the projection of a plane grating on the spherical surface. This arrangement has one disadvantage for certain kinds of work and this is that it is not stigmatic; light from each point of the slit reaches a range of points on each image. This, however, is important only when it is desired to distinguish between the different regions of the illuminated slit, which is not generally the case.

As is shown in treatises on optics, if the slit and the grating are located on the circumference of a circle whose diameter is equal to the radius of curvature of the grating, all the lines of all orders are brought to a focus on this circle. It is this constancy of focus for all orders that permits their superposition; with a plane grating and lens this is not the case because complete achromatization cannot be obtained. In the Paschen type of mounting, the slit and grating are fixed in position and photographic plates are placed along the focal circle. Only those rays which leave the grating almost normally fall normally on a plate. For these rays the angle of diffraction, \( \theta_1 \), is almost zero, so that Eq. (7-22) becomes to a good approximation,

\[
\lambda = \frac{D}{n} \sin \theta_1 + \frac{DR}{n} L = \text{constant} + \text{constant} \times L
\]

Therefore the wave length is directly proportional to the distance along the photographic plate for those rays which lie almost along the normal to the grating. Interpolation between standard wave lengths is then very simple for this "normal" portion of the spectrum. For other regions of the spectrum the relationship is not linear, nor does the light fall perpendicularly on the plates. Any unevenness of the glass causes local compression or stretching of the dispersion. It is therefore necessary to plot a curve of position on the plate against the wave length for the known standards, or, better still, a curve may be drawn representing the difference between a strictly linear relation and the known standard wave lengths.
By giving up the somewhat doubtful advantage of being able to photograph simultaneously the entire spectrum in many orders, as is the case with the Paschen mounting, Rowland was able to devise an arrangement whereby the particular region being photographed is always normal to the grating and hence the wave length always proportional to the distance along the plate. In the Rowland mounting the slit is located at the junction of two mutually perpendicular tracks. On each of these is a track and these tracks carry on bearings the two ends of a beam of length equal to the diameter of the Paschen circle, i.e., the radius of curvature of the concave grating. The grating and plate are placed perpendicularly to the length of this beam at its two ends. The slit, grating, and plate thus always remain on the circumference of the Paschen circle. The device is obviously equivalent to having a movable slit capable of traveling around the Paschen mounting.

7-10. Wave-length Measurement with a Prism. - Due to the nature of the variation of the index of refraction with wave length, the spectrum produced by a prism does not give a linear variation of either wave length or wave number with position along the photographic plate. Direct linear interpolation between standards is therefore impossible except over extremely small ranges. We shall briefly review several indirect but accurate interpolation methods which have been developed. They all involve a considerable amount of multiplication or division so that a computing machine is almost a necessity. If one is not available, rough results, to 10 or 20 Å, may be obtained by plotting the wave lengths of as many standards as possible against position on the photographic plate and drawing a smooth curve through them. Wave numbers may be plotted instead of wave lengths and in this case the curve is more nearly linear, which facilitates interpolation. It is desirable to plot such a curve in any case, for it helps to avoid gross errors in identifying lines to be used as standards.

In the early days of the prism spectroscope, use was made of the Cauchy dispersion formula

\[ n = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} \]

where \( n \) is the refractive index of the prism, and \( a, b, \) and \( c \) are constants to be determined from known wave lengths. At minimum deviation, the index is connected with the angle of the prism \( A \) and the angle of deviation \( \phi \) by the relation [see Eq. (2-41)]

\[ n = \frac{\sin \left( \frac{A + \phi}{2} \right)}{\sin \frac{A}{2}} \]

Hence by measuring \( A \) and \( \phi \) the wave length can be computed over a range within which the different colors may all be taken as having passed through the prism at minimum deviation.

Hartmann Method. - The very laborious process indicated above was eliminated by Hartmann, in 1898, who showed that the expression

\[ n = C' + \frac{B'}{(\lambda - A')^p} \]

represents with sufficient accuracy the dependence of \( n \) on \( \lambda \) over a rather wide range. The quantities \( A', B', \) and \( C' \) are constants, while \( p \) has the value 1.2 for prisms made of crown or flint glass. Solving this equation for \( \lambda \) we obtain

\[ \lambda = A' + \frac{B'^{\frac{1}{p}}}{(n - C')^p} \]

A further simplification is possible if \( p \) is set equal to unity and the index of refraction is replaced by the linear distance \( L \) of a spectral line along the plate, measured from any arbitrary zero. We then have

\[ \lambda = A + \frac{B}{L - C} \]

This expression holds with remarkable accuracy; over a range of 1000 Å, the average error may be as small as 0.1 Å. The constants \( A, B, \) and \( C \) are found by solving simultaneously the three equations for three standard lines, located preferably at the two ends and the middle of the range. The solution is conveniently performed in the following manner:

\[ \lambda_1 = A + \frac{B}{L_1 - C} \]  \( (7-23) \)
\[ \lambda_2 = A + \frac{B}{L_2 - C} \]  \( (7-24) \)
\[ \lambda_3 = A + \frac{B}{L_3 - C} \]  \( (7-25) \)

Subtracting Eq. (7-23) from Eqs. (7-24) and (7-25) and rearranging, we obtain

\[ C' - (L_1 + L_2)C + L_1L_2 = \frac{L_1 - L_2B}{A^2} \]  \( (7-26) \)
\[ C' - (L_1 + L_3)C + L_1L_3 = \frac{L_1 - L_3B}{A^2} \]  \( (7-27) \)

Subtracting Eq. (7-27) from Eq. (7-26) and solving for \( B \), we have

\[ B = \frac{(L_2 - L_3)(L_1 - C)}{K} \]  \( (7-28) \)

\(^1\) Hartmann, Astrophys. J., 8, 218 (1898).
where

\[ K = \frac{(L_1 - L_2)}{\lambda_2 - \lambda_1} - \frac{(L_1 - L_3)}{\lambda_3 - \lambda_1} \]  

(7-29)

Eliminating B between Eqs. (7-23) and (7-28) and solving for A,

\[ A = \lambda_1 - \frac{(L_2 - L_3)}{K} \]  

(7-30)

Eliminating A and B between Eqs. (7-24), (7-28), and (7-29) and solving for C,

\[ C = L_2 + \frac{(L_2 - L_3)(L_1 - L_3)}{K \lambda_1 - \lambda_3} \]  

(7-31)

Equations (7-28) to (7-31), are perfectly general and may be used at once to determine the numerical values of A, B, and C in terms of the known wave lengths \( \lambda_1, \lambda_2, \lambda_3 \) and their corresponding traveling-microscope readings \( L_1, L_2, L_3 \). (Note that the quantity \( (L_2 - L_3)/K \) occurs three times and hence its separate evaluation is of advantage.) Care should be taken with the signs of the quantities evaluated; it is wise to check the final equation by calculating the three standard wave lengths before proceeding to the unknown lines.

The Hartmann formula is highly satisfactory and requires but three standard lines, yet it is a little cumbersome to use, since a new divisor of standard lines, but the advantages of rapidity and the ability to take work on certain instruments, but a few minutes spent in testing it is worth the time. It has the disadvantage of requiring a large number of lines to be measured, has been developed before proceeding to the unknown lines.

Russell-Shenstone Method.-A quick method of reducing prismatic spectra, which is superior to the Hartmann method when a spectrum containing a large number of lines is to be measured, has been developed by Russell and Shenstone. The process is purely empirical and will not work on certain instruments, but a few minutes spent in testing it is well worth the time. It has the disadvantage of requiring a large number of standard lines, but the advantages of rapidity and the ability to take care of fluctuations in the surface of the photographic plate. Furthermore it deals directly in wave numbers, which are the ultimate desiderata.

Essentially the method is one of successive approximations. A linear interpolation of the wave numbers of the standard lines is made:

\[ \tilde{\nu}_{\text{lin}} = \frac{\tilde{\nu}_2 - \tilde{\nu}_1}{L_2 - L_1} \times \Delta L + \tilde{\nu}_1 \]  

(7-32)

where \( \tilde{\nu}_1 \) and \( \tilde{\nu}_2 \) are the wave numbers of the standards at the two ends of the range, \( L_1 \) and \( L_2 \) are their corresponding traveling-microscope readings, and \( \Delta L \) is the difference between the scale reading for an intermediate standard line and \( L_1 \). (The scale reading \( L \) should increase with the wave number.) It is observed that \( \tilde{\nu}_{\text{lin}} \) is less than the true value \( \tilde{\nu} \) except at the ends of the range, and a curve is plotted of \( \tilde{\nu} - \tilde{\nu}_{\text{lin}} \).

\[ \tilde{\nu}_{\text{par}} = \tilde{\nu}_{\text{lin}} + M - y \]  

(7-34)

The value of \( \tilde{\nu} \) for each standard is next found by subtracting its \( L \) from the mid-point of the scale range; the appropriate \( y \) for each standard is then found from Eq. (7-33). This may be performed in one operation on a 20-in. slide rule to sufficient accuracy. The wave number calculated on the parabolic assumption \( \tilde{\nu}_{\text{par}} \), for each standard is determined from the equation

It will be found that \( \tilde{\nu}_{\text{par}} \) does not agree exactly with the known wave numbers, but the maximum departure should not be greater than about one wave number. A second correction curve is then drawn, plotting \( \tilde{\nu} - \tilde{\nu}_{\text{par}} \) against the scale reading \( L \) for all the standards. This curve is due to higher order terms, since \( \tilde{\nu} - \tilde{\nu}_{\text{par}} \) is not strictly parabolic. The form of the curve is quite sensitive to the chosen location of the origin 0. Sometimes the curve shows marked asymmetries, which indicate local depressions or humps in the photographic plate. In prism instruments with simple lenses, the light falls on the plate at a considerable angle with the normal, so that a slight surface irregularity causes a considerable shift in the position of the image. Since both the standards and the unknown lines in the same vicinity are affected by these variations, there is no error due to this cause in the Russell-Shenstone method, while the Hartmann formula is only correct for a perfectly smooth plate.

Having found that the standard lines give a consistent second-order correction curve, the calculation of the unknown lines may be accom-
plished rapidly. All that is required is the calculation first of $\tilde{v}_{\text{par.}}$ and then of $v_{\text{par.}}$, and the addition of a small correction read graphically from the second curve. The work is greatly simplified with a calculating machine capable of performing the operation

$$u = \alpha + \beta v$$

where $\alpha$ and $\beta$ are constants and $u$ and $v$ are variables. The quantity $\alpha$ has the value $M + \tilde{v}_1$, while $\beta$ is the linear dispersion constant $(\tilde{v}_2 - \tilde{v}_1)/(L_2 - L_1)$ which is set up once and for all as the multiplicant on the machine. With the multiplier keys set at the value $L_1$, the resultant is set equal to $\tilde{v}_1 + M$, so that as the multiplier is set successively at different values of $L$, the quantity

$$\tilde{v}_1 + M + \frac{\tilde{v}_2 - \tilde{v}_1}{L_2 - L_1} \times L$$

is determined. Subtracting the appropriate value of $y$ from this gives $\tilde{v}_{\text{par.}}$, and on adding the small correction read from the second curve, the final wave number is obtained. This avoids the necessity of finding $AL$ for each line. Aside from the original scale readings, all that is required is a table of the values of $x$, the distance of the line along the plate from the mid-point of the range.

General Technique.—In measuring a plate with a traveling microscope it is essential always to approach a line from the same side, in order to avoid back-lash in the screw. If the line is overrun the screw should be backed off several turns and another approach made. To guard against the very common personal error of consistently setting a little beyond or short of a line, as well as to average out the irregularities of the screw, it is worth while to measure each plate twice, in opposite directions, by turning the plate around and advancing the microscope in the same direction. This avoids the necessity of finding $AL$ for each line. Aside from the original scale readings, all that is required is a table of the values of $x$, the distance of the line along the plate from the mid-point of the range.

Aside from the original scale readings, all that is required is a table of the values of $x$, the distance of the line along the plate from the mid-point of the range. The change in path may be measured by observing a stage-micrometer scale, which is clamped to the moving system, through a microscope equipped with cross hairs. But as the accuracy of setting is, say, 0.001 mm., which corresponds to a displacement of four fringes, 20,000 fringes must be counted to obtain a value of the wave length correct to 1 A., i.e., 1 part in 5000. An accuracy of 0.5 per cent can be obtained by counting 800 to 1000 fringes, which can be done in about half an hour without undue fatigue.

Since precise measurements with an interferometer are difficult and tedious, it is more satisfactory for our purposes to obtain absolute measurements with a grating where an accuracy of a few hundredths of a per cent can readily be achieved. The simplest arrangement to use is a plane transmission grating mounted on an ordinary spectrometer table with the light incident normally upon its surface. The equation for the grating then becomes:

$$nA = D \sin \theta,$$

Hence

$$\lambda_{\text{vac.}} - \lambda_{\text{air}} = n\lambda_{\text{air}} - \lambda_{\text{air}} = (n - 1)\lambda_{\text{air}}$$

Since

$$\lambda_{\text{vac.}} = \frac{\lambda_{\text{air}}}{n}$$

Therefore

$$\lambda_{\text{vac.}} = \lambda_{\text{air}}$$

Therefore

$$\lambda_{\text{vac.}} - \lambda_{\text{air}} = n\lambda_{\text{air}} - \lambda_{\text{air}} = (n - 1)\lambda_{\text{air}}.$$

Hence to find $\lambda_{\text{vac.}}$ we add to $\lambda_{\text{air}}$ the product $(n - 1)\lambda_{\text{air}}$. The values of $n$ for air have been accurately measured by Meggers and Peters.1 A very convenient set of tables has been published by Kayser2 in which $\lambda_{\text{air}}$ is directly changed to wave numbers in vacuum $(\tilde{v}_{\text{vac.}} = 1/\lambda_{\text{vac.}})$ through the above mentioned values of the index of refraction for the range from 10,000 A. to 2000 A. The magnitude of the error involved in merely taking $1/\lambda_{\text{air}}$ as the wave number is 1.5 A. or 4.2 wave numbers at 6000 A. and 0.9 A. or 10 wave numbers at 3000 A. Hence the correction to vacuum is trivial for measurements made on a small prism instrument.

7-11. Experiment on Wave-length Measurement.—With the proper technique the most accurate absolute value of a wave length can be obtained with an interferometer. In the Michelson form, a single wave length, such as the cadmium red line, enters the instrument, and the fringes passing a fiducial mark are counted as one plate is moved perpendicularly to its surface through a known distance. A shift of one fringe corresponds to a motion of this plate of half a wave length. The details for the absolute determination of a wave length by this method are given by Fabry and Perot.3 In practice with an ordinary interferometer it is very difficult to obtain really accurate values of wave length by any simple procedure. As an example, the mercury green line, $\lambda = 5460$, may be isolated by the Wratten filter 77-A and its fringes counted as one plate of the interferometer is moved relatively to the other. The change in path may be measured by observing a stage-micrometer scale, which is clamped to the moving system, through a microscope equipped with cross hairs. But as the accuracy of setting is, say, 0.001 mm., which corresponds to a displacement of four fringes, 20,000 fringes must be counted to obtain a value of the wave length correct to 1 A., i.e., 1 part in 5000. An accuracy of 0.5 per cent can be obtained by counting 800 to 1000 fringes, which can be done in about half an hour without undue fatigue.

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$$nA = D \sin \theta,$$


2 KAYSER, "Tabelle der Schwingungszahlen," Hirzel (1925).

The grating constant $D$ is ideally determined by observing the diffraction angle for the same wave length as was used in the interferometer measurement and applying the grating equation. Since for practical reasons only moderate accuracy can be expected by this method, it is preferable to measure the grating constant directly by the use of a good microscope equipped with a micrometer eyepiece. The grating is placed, rulings uppermost, on the microscope stage and illuminated in the usual way. Care must be taken that the objective of the microscope does not come in contact with the surface of the grating when the focusing adjustments are being made, as this would injure the rulings, particularly of a replica grating. Several hundred lines should be measured in groups of ten to prevent a miscount. The eyepiece-micrometer screw may be calibrated by measuring a standard stage-micrometer scale.

The necessary adjustments of the telescope, grating, and collimator in setting up a plane transmission eating spectrometer may be briefly summarized as follows. The Gauss eyepiece of the telescope is first set up for parallel light by focusing the telescope on some distant object through an open window. No parallax, i.e., relative motion of the images of the cross hairs and distant object, should be observed as the head is moved from side to side. The telescope is then replaced in the instrument and the collimator focused until a sharp image of the slit is seen when the telescope and collimator are in line. The grating is then mounted with the ruled side away from the collimator, directly over the axis of the turntable and parallel to the line joining two of the three leveling screws. The Gauss eyepiece is then illuminated and the tilt of the grating and telescope adjusted until the image of the cross hairs, seen by reflection from the grating, coincide with the cross hairs themselves. The grating is then rotated through 180° and this coincidence again brought about, making half the adjustment by tilting the grating and half by tilting the telescope. This procedure is repeated till the images stay in coincidence. The telescope is then perpendicular to the axis of the turntable and the grating parallel to it. The collimator is made parallel to the telescope by adjusting its tilt until the image of a fine wire stretched across the middle of the slit coincides with the intersection of the cross hairs. The angular position, $\theta_0$, of the telescope circle is read when the image of the slit is on the cross hairs, and the telescope is then turned through 90°. The grating table is rotated till the directly reflected image of the slit is seen at the intersection of the cross hairs; turning the grating table back through 45° then puts the grating normal to the incident light. If there is no scale on the grating table, this adjustment can be made by illuminating the Gauss eyepiece again with the telescope in the $\theta_0$ position and rotating the grating till coincidence between the cross hairs and their reflected image from the surface of the grating is obtained. The rulings are made parallel to the table axis by adjusting the leveling feet under the grating, until the image of the wire across the slit, as seen in the various diffracted orders to the right and left of the central image, remains at the level of the cross-hair intersection. After this adjustment the alignment of the grating on the axis of rotation should be rechecked. Finally, the slit, which should be made very narrow, is adjusted to be parallel to the grating rulings by observing one of the diffracted images and rotating the slit until the image appears sharpest.

A convenient source to use with the grating is a quartz or glass mercury arc; it has many strong lines widely dispersed throughout the visible spectrum and these arcs, which are readily obtained, are very constant and reliable. These sources may be placed directly in front of the slit, or an image of them may be cast on it by means of a condensing lens. The angular settings of the telescope are then measured as accurately as possible when the cross hairs are brought into coincidence with the diffracted images of the slit for 10 or 12 of the strongest mercury lines. As many orders as possible should be used on both sides of the central image. To reduce the percentage error in reading the scale, the diffraction angle $\theta_0$ for any wave length, in a given order, should be taken as half the difference between the scale readings when set on the images in the right and left orders. As the accuracy of measurement increases with the order, the highest order in which the line can be accurately set upon should be used in the calculation of its wave length. Results accurate to within 2 Å or 3 Å can be obtained even with an inexpensive replica grating when used in the second order.

These mercury lines whose wave lengths have been measured with a grating can be used as standards for determining the wave lengths of the weaker mercury lines and also of lines in other spectra if a mercury comparison spectrum is photographed over the unknown spectrum. The photographs are most conveniently made with a prism instrument, for, as all the light contributes to the formation of a single spectrum, the intensity is greater than with a grating. Small instruments, such as the quartz Hilger E31 or Gaertner L-250 for the ultra-violet or the constant-deviation Hilger D-77 or Gaertner L-230 for the visible, are satisfactory for the analysis of the following sections. The slit should be made as fine as possible and a series of focusing exposures taken varying the two adjustments, collimator focus and plate angle, separately. The plates are then examined for the best focus and the pertinent data recorded. Rapid panchromatic plates such as the Eastman Wratten and Wainwright plates, or the Ilford special rapid panchromatic plates, are suitable for general spectroscopic work throughout the visible and near ultra-violet. The positions of the lines in the spectrum photographs may be measured with a traveling microscope or comparator.
be photographed quite easily with a small quartz prism spectroscope. An ordinary glass instrument is not satisfactory for this purpose as the lenses and prism absorb a great deal of the light of the higher series members, which are quite feeble to begin with. Quartz has the disadvantage, however, of having very small dispersion in the red so that the long-wavelength region is crowded together, thus reducing the accuracy of measurement. Exposures of from $\frac{1}{2}$ to 2 mm. are generally quite adequate. The slit length is then reduced a trifle in order to identify the spectra, and a mercury arc is photographed for 2 or 3 sec. These lines are used as standards for calculating the wave numbers of the Balmer series.

The Balmer series may be represented by the equation

$$\varphi = \frac{R_H}{n^2} - \frac{R_H}{n^2}$$

where $n = 3, 4, 5, 6, \text{etc.}$ Hence a plot of $\varphi$ against $1/n^2$ should give a series of points through which a straight line may be drawn; the slope of this line is $R_H$ and the intercept $R_H/4$. This experimental value of $R_H$ may be compared with the theoretical value

$$R_H = \frac{2\pi^2 \mu e^4}{\hbar c}$$

where $\mu = mM/(m + M)$, $m$ and $M$ being the masses of the electron and proton, respectively, using the values of the constants that have been determined previously.

It is interesting to examine the completely calculable case of hydrogen from the viewpoint of the vector model. The single electron may be an $s$ type so that there is the possible series of levels $1s^1 2s^1$, $2s^1 3s^1$, $3s^1 4s^1$, etc., or it may be a $p$ or $d$ type giving the series $2p^1 3p^1$, $3p^1 4p^1$, $4p^1 5p^1$, etc., and $3d^1 4d^1$, $4d^1 5d^1$, etc., respectively. But for the two-body problem, the analysis shows that the energy of a level depends to a first approximation only on the total quantum number of the electron; hence the lowest state is $1s^1 2s^1$; the next higher is $2s^1 3s^1$, $2p^1 3p^1$ (all three coincident); the second level is a mixture of $3s^1 3p^1$, $3p^1 3p^1$, $3d^1 3d^1$, etc. Of course, for any one atom only one of these possibilities exists at one time, but as there are always many atoms present all the possibilities may be considered at once. The series of transitions from the levels $n = 2, 3, 4, \text{etc.}$, to the lowest one where $n = 1$ gives the Lyman series in the ultra-violet; the Balmer series arises from the transitions to the second level, $n = 2$, from those still higher, while the infra-red
series are due to inward transitions to the third, fourth, and fifth levels, respectively. Apparatus of very high resolving power shows, however, that the hydrogen lines are really very close multiplets, indicating that the coalescence of the terms is not as exact as has been stated above.

FIG. 7-11.—Hydrogen energy levels. The ordinates are the wave numbers, which are proportional to the energies of the levels, plotted on a logarithmic scale for convenience. The zero is taken at the ion. Transitions are indicated by vertical lines; the corresponding wave lengths in Angstroms are given beside them. Electron structures are shown on the right.

Relativity in conjunction with the electron spin suffices to explain the slight separation of the levels.

**LOW HYDROGEN TERMS**

<table>
<thead>
<tr>
<th>Level</th>
<th>Energy (in wave-number units)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s 7p 7d etc.</td>
<td>2,238.33</td>
<td></td>
</tr>
<tr>
<td>3s 3p 3d etc.</td>
<td>12,186.46</td>
<td></td>
</tr>
<tr>
<td>4s 4p 4d 4f etc.</td>
<td>27,419.51</td>
<td></td>
</tr>
<tr>
<td>5s 5p 5d etc.</td>
<td>4,387.13</td>
<td></td>
</tr>
<tr>
<td>6s 6p 6d etc.</td>
<td>3,046.62</td>
<td></td>
</tr>
</tbody>
</table>


7-13. **Experiment on the Sodium Spectrum**—The simplest source for the sodium yellow lines is a piece of asbestos washed in a sodium chloride solution and held in a Bunsen flame. This produces only the yellow lines with any appreciable intensity; a more violent source of excitation is required to bring out the rest of the spectrum. A very simple and adequate method is a carbon arc inoculated with sodium chloride or metallic sodium. The carbon electrodes, about the diameter of a lead pencil, are ground down to a rough point and a small hole is drilled in the end of each. Salt is put into these cavities, or better still a small pellet of metallic sodium is pushed into each. The arc should be run in a vertical position, with the positive pole below if direct current is available. A series rheostat limits the current to 2 or 3 amp. Carbon is particularly suitable as a holder since the line spectrum consists of but one line at 2478 Å in the whole range from the extreme red to 2000 Å. There is, however, an intense continuous spectrum given off by the incandescent solid and, to lesser extent, by the hot particles of carbon which fly off the electrodes into the arc. Hence it is desirable to make the spectroscope slit quite short and cast on it an image of the arc between the electrodes. The lens used for this purpose must be of quartz if it is desired to photograph the principal series. If such a lens is not available, the source is simply mounted a few inches in front of the slit. An exposure of about 1 sec. is sufficient to bring up the principal, sharp, and diffuse doublets in the yellow region with a small prism instrument and a panchromatic plate, but several seconds more are required to photograph the lines of shorter wave length. To prevent overexposure of the yellow lines a didymium filter, such as the Corning 512, may be placed in front of the slit during this part of the exposure. The spectrum photographed in this manner gives excellent reason for the historical phraseology "diffuse series"; the lines of this group are extremely fuzzy. Beautifully sharp lines in all the series may be obtained by using as a source a vacuum sodium arc. Strutt has given a description of an arc which can be made very simply and which is easily demountable for cleaning and repair. As ordinary glass is attacked by hot sodium vapor, a sodium-resistant glass should be used if possible. Pyrex is not attacked so rapidly as some other glasses and may be rendered still more resistant by coating it with a layer of borax. This may be done by pouring a hot saturated solution of borax into the bulb, coating the walls thoroughly and decanting the excess liquid. The bulb may then be connected to a vacuum system to promote evaporation. When the borax is dry, the glass is heated nearly to its melting point, until the borax fuses and leaves a clear, smooth coating. Vacuum sodium arcs may be obtained commercially. For these arcs the didymium filter should be used for about 2 mm. and a blue filter added for about 2 hr. to bring up the higher series
LINE SPECTRA

members. Argon in the tube gives a strong set of lines below 4980 Å, so that the resultant picture exhibits the sodium series rather less strikingly.

The sharp and diffuse series may be photographed with a glass instrument, but to obtain more than the first member of the principal series a quartz spectroscope must be used. For a few seconds a comparison spectrum of mercury is put on the plate with the slit a different length, and the wave numbers of the lines in the sodium series calculated by means of the Hartmann formula.

Sodium gives a typical example of a one-electron spectrum. The electron structure of the normal state is:

\[
\begin{align*}
1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^1 \\
\text{He} \quad \text{Be} \quad \text{Ne}
\end{align*}
\]

in which we see the completed shells of helium, beryllium and neon underlying the single 3s electron characteristic of sodium. By the vector-model theory we see that the closed shells may be neglected and that the 3s electron gives rise to a \( ^2S^1 \) term. As the electron is raised to greater total quantum numbers but remaining of an s type, i.e., through the series 4s, 5s, 6s, 7s, etc., we obtain a series of \( ^2S^1 \) terms, until for \( \infty \) the electron is completely removed leaving the sodium ion behind. For other than the normal state the electron may be of the p type, so that the various excited conditions 3p, 4p, 5p, etc., form a series of pairs of levels, \( ^2P^1, ^2P^3 \). If the electron is of the d type we have the 3d, 4d, 5d, etc., configurations yielding the series of level pairs \( ^2D^3, ^2D^1 \). These multiple levels are "regular," i.e., the smaller \( J \) value goes with the lower term. We anticipate transitions from the \( ^2P \) terms to the \( ^2S \) and \( ^2D \) terms, but none between the latter two because of the \( L \) selection rule.

The sharp line series is composed of pairs of lines with a constant wave-number difference, for they are given by \( 3p^2P^1 - ns^2S^1 \) and \( 3p^2P^3 - ns^2S^1 \), where \( n \) increases by unit steps from the lowest value \( n = 4 \). In the Rydberg form this is written as

\[
\tilde{\nu} = \frac{R}{(n' + \mu)^2} - \frac{R}{(n + \mu)^2}
\]

where \( n' \) and \( \mu \) are each constant, \( n \) increases by unit steps, and \( \mu \) can have either of two constant values: the fixed term is double.

The principal line series is made up of pairs of lines with a decreasing wave-number difference since they are given by \( 3s^2S^1 - np^2P^1 \) and \( 3s^2S^1 - np^2P^3 \), with \( n \) increasing through integral values, beginning at 3. The Rydberg expression is

\[
\tilde{\nu} = \frac{R}{(n' + \mu)^2} - \frac{R}{(n + \mu)^2}
\]

FIG. 7-12. - The spectrum of sodium in the visible region, photographed with a small glass-prism instrument. The source was a carbon arc inoculated with metallic sodium. A didymium filter was used during part of the exposure. Several members of the sharp and diffuse and one member of the principal series are indicated.

The diffuse series is composed in a similar manner of triplet sets of lines. The fixed term has two components \( 3p^2P^1 \) and \( 3p^2P^3 \) while the running term is also double, \( nd^2D^3 \) and \( nd^2D^1 \), but only three out of the four possible combinations occur because of the \( J \) selection rule, i.e., the combination \( ^2P^1 - ^2D^3 \) is forbidden since \( J \) may not change by 2.

Two of the lines maintain a constant wave number difference throughout the series due to the doubleness of the fixed term, while the third line
line spectra

Closes in on the others as the separation of the two components of the running term becomes less. When the d electron is completely removed, the two 2D levels coincide. (As a matter of fact the separation of the two levels of the 2D term of sodium is so small that it has never been directly observed. The 2P - 2D combinations are apparently pairs of lines with a constant wave-number difference.)

It is worth while noting why one would expect the pair of 2P levels and the pair of 2D levels, each to fuse together as the ionizing limit is reached. Whether the ion is formed by the removal of an electron characterized by the symbol s, p, or d the resulting electron configuration is the same, namely, the closed shell of neon. As we have seen, closed shells give rise only to a 1S0 term. Hence the result of ionization must always be this single level, which condition the 2P and 2D levels approach in the limit. It should also be noted that we might expect to observe the “second” principal, sharp, and diffuse series which are the results of combinations with the fixed lower terms 4s2S0, 4p2P1/2, and 4d2D5/2, respectively. These lines are, however, quite faint.

The Grotrian diagram of the low energy levels of sodium is shown in Fig. 7-14; the zero energy is taken at the ion so all the levels have negative energies, the lowest level being the normal state of the atom. It is observed that the smallest energies that can be absorbed by the sodium atom in the normal state, 3s 2S1/2, raise it to the states 3p 2P1/2. These upward transitions correspond to the absorption of energy equal to that emitted in the two yellow lines 5889 Å and 5895 Å. These lines are called the resonance lines of the atom by analogy with an oscillating mechanical system which is easily set into motion by a periodic force in resonance with the natural period of the system. These lines and the other members of the principal series are the only lines that can be absorbed by a sodium atom in the normal state. We shall refer again to this point in the following chapter.

The sodium terms obey a Ritz formula more accurately than a Rydberg one, but we may consider that the simpler Rydberg expression is adequate for the accuracy which can be attained with a small prism.
LINE SPECTRA

Any two successive lines of a series to which a Rydberg expression is applicable may be represented by

\[ \tilde{\nu}_1 = L - T_1 \]
\[ \tilde{\nu}_2 = L - T_2 \]

where \( n \) is an integer and \( \mu \) is a constant characteristic of the series. \( L \) is the unknown energy, expressed in wave numbers, of the lower fixed term measured from the ion as zero. \( T_1 \) and \( T_2 \) are the energies of two successive running terms, also measured from the ion. The difference of the wave numbers of the two lines is then the difference between the values of two successive terms

\[ \tilde{\nu}_2 - \tilde{\nu}_1 = T_2 - T_1 = \frac{R}{(n + \mu)^2} - \frac{R}{(n + 1 + \mu)^2} \]

Theoretical Rydberg values of the succeeding terms in the series may be found from the tables by taking the numbers given under successive values of \( n \) and the same value of \( \mu \) as found before. These theoretical terms, \( T_3, T_4, T_5, \) etc., when subtracted from the limit \( L \) (just determined) give the theoretical values of the successive lines in the series, \( \tilde{\nu}_3, \tilde{\nu}_4, \tilde{\nu}_5, \) etc. The order of agreement of these values with those found from the plate measurement shows how accurately the particular series obeys a Rydberg formula. In general, a more accurate fit is obtained if the limit \( L \) is determined by applying the Rydberg equation to two of the higher members of the line series.

7-14. Experiment on the Mercury Spectrum.-The source of mercury radiation is most conveniently one of the commercially obtainable glass or quartz arcs. The latter type is necessary if the ultra-violet spectrum is to be obtained. Alternatively one of the home-made mercury discharges or arcs, as described in Sects. 7-16 and 8-5 may be used. As the dispersion of a glass spectrograph is better in the visible region, it is advisable to use one of this type for the lines down as far as 4000 Å. The arc is focused on the slit of the spectroscope with a glass lens. Exposures of a few seconds suffice for most of the lines if a rapid panchromatic plate is used. The red lines may be brought up by an additional exposure of a few minutes with either of the Wratten filters A-25 or F-29. In the ultra-violet region the discharge tube, lens, and spectroscope train must all be of quartz. Again exposures of a few seconds suffice. The strong visible lines which were measured with a grating are used as standards, and the wave numbers of the weaker lines in the visible and the lines in the ultra-violet are calculated with a Hartmann formula.

Mercury gives an interesting example of a simple two-electron spectrum. The electron structure in the normal state consists of:

\[ 1S^2 2S^2 2p^6 3S^2 3P^6 3d^10 \]

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\[ 1S^2 2S^2 2p^6 3S^2 3P^6 3d^10 \]

higher or excited levels are occupied when one of the 6s electrons is raised to a more energetic state. In this case all but these two electrons are in closed shells, so that the expression “two-electron spectrum” is under-
standable. The configuration 6s 6p according to the vector model forms the levels $^1P_{1/2}$, $^3P_{1/2}$, and $^3P_{3/2}$; further excitation of the p electron to the 7p, 8p, 9p, etc., states gives rise to the series of higher $^1P$ and $^3P$ levels. The structures 6s6s, 6s8s, 6s9s, etc., form the series of levels $^2S_1$ and $^2S_0$, while 6s6d, 6s7d, 6s8d, etc., give the series of $^2D_{3/2}$ and $^2D_{5/2}$ terms. The Z-sum rule permits combinations between the even (S and D) and odd (P) terms. We see from the Grotrian diagram that combinations occur not only within the singlet and triplet systems, from $^1S$ to $^1D$, $^3P$ to $^3D$, and $^3D$ to $^3F$, but also that intersystem jumps occur from $^3S$ to $^2P$ and from $^3P$ to $^1P$; these are sometimes called intercombination lines. The multiplets are said to be regular as the small J's go with the low levels.

Whereas in sodium the several lines due to combinations between the various levels of two multiplets are very close together, in mercury they are often quite far apart. The close pairs of lines from the combinations $^1P_1 - ^3P_1$ and $^3P_1 - ^3P_0$ can be seen for two members of the series in the accompanying photograph; the three lines due to $^3S_1 - ^3P_0$, $^3S_1 - ^3P_1$, and $^3S_1 - ^3P_2$, showing wider separations are also visible in Fig. 7-15.

Examples of multiplets for which the relationship is not visible at first sight but comes only from a detailed analysis of the spectrum are given by the combinations $^3P_{2,1,0} - ^3S_1$ and $^3P_{2,1,0} - ^3D_{2,1,1}$. In the first case not only are the three lines of each multiplet widely separated, but several members of the series overlap; in the second case the multiplets are each composed of six lines in close groups of three, two, and one; here again the successive members of the series overlap.

It is often convenient to express energies given in wave numbers in terms of equivalent electron volts, or the potential through which an electron would have to fall in order to acquire the given energy. This may be done through the relation

$$h\nu = \frac{h\nu}{c} = eV$$

$$\bar{\nu} = \frac{300hc}{\nu}$$

where the potential is in volts and the wave number in cm$^{-1}$.

The resonance line, 6s$^3$S$_0 - 6s6p$^3P$_1$, has a wave length of 2536 Å, corresponding to 4.86 electron volts. The J selection principle (AJ = ± 1 or 0 with the change J = 0 to J = 0 excluded) forbids the absorption transitions from the low $^3S_0$ state to either of the companion levels 6s6p $^3P_2$ or $^3P_0$. The second resonance line, 6s$^3$S$_0 - 6s6p$^3P$_1$, is at 1849 Å, which corresponds to 6.67 electron volts. Hence if the normal atom be supplied with energy ranging from zero to something less than 6.67 volts, only that part of it equal to 4.86 volts can be absorbed and only the 2536 line will be subsequently emitted. It should also be noted that if the atoms are left at the end of some process in the $^3P_{2,1,0}$ energy states only those atoms in the $^3P_1$ state can return to the normal level with the emission of radiation. There are no possible ways for the $^3P_{2,0}$ levels to become emptied by radiation from the atoms because

*FIG. 7-17. - The Grotrian diagram of mercury. The $^3P$ and $^3D$ levels are all triple: the dots represent the center of gravity. In a set of multiple levels the J value decreases downward. For a more detailed diagram of the lower levels see Fig. 8-3.*

of the J selection rule. These two levels are therefore called metastable because they remain occupied until their energy is drained away as kinetic energy or energy of excitation upon collision with the walls of the tube or with other atoms or molecules. As a consequence these levels are occu-
Experiment on the Zeeman Effect.—A brief calculation shows that the Zeeman effect cannot be observed except with spectroscopic apparatus of high resolving power, at least with magnetic fields that can be produced readily. As \( \lambda = l / G \), \( \Delta \lambda = -AC/P = -\lambda^2 \Delta \delta \), and since the Lorentz separation for unit field is \( \Delta \delta = 4.674 \times 10^{-6} \text{ cm.}^{-1} \) per gauss, we have \( AX = 1.7 \times 10^{-4} \AA \) per gauss at 6000 \AA, and \( AX = 0.4 \times 10^{-6} \AA \) per gauss at 3000 \AA. The large electromagnets used in spectroscopic research give about 40,000 gauss, so that \( AX \) is about 0.17 and 0.04 at these limits for a Zeeman pattern of one Lorentz unit, which is the order of magnitude generally found. The resolving power of a grating is equal to the product of the total number of lines and the order used. Good original gratings are expensive and replicas cannot be used with much success beyond the second order, so that a Z-in. replica grating containing, say, 30,000 lines could theoretically resolve lines separated by 0.1 \AA at 6000 \AA in the second order. A Zeeman separation of one Lorentz unit, with 10,000 gauss in the red end of the spectrum, might possibly just be detectable with such a grating, but it would scarcely be subject to quantitative measurement. It must be recalled that resolving powers are calculated on Rayleigh's definition of the term: Two lines of equal intensity are said to be resolved if the first diffraction minimum of one line lies

This gives, to a first approximation, the resolving power to be expected from any optical arrangement. Lines have been observed as separate which are not resolvable in accordance with this definition, but it gives the order of magnitude of the resolution to be expected.

The simple Zeeman effect can, however, be easily measured with a small prism instrument in conjunction with a Fabry-Perot interferometer. Fixed-separation types of this instrument are relatively inexpensive and quite adequate for the purpose. We shall content ourselves with only as much of the theory as is necessary for the present discussion.

This type of interferometer consists of two accurately plane parallel plates of glass separated by a distance \( L \) and coated with a deposit of silver or other highly reflecting substance on their inner surfaces. If parallel monochromatic light strikes these plates at a small incidence angle \( \theta \), as in Fig. 7-18, part of the beam emerges at \( C \) and part is reflected at \( B \) back to \( D \). Further partial reflection and transmission at each semi-silvered surface results in a group of beams emerging from the right-hand plate, apparently originating from the line of sources, \( A, D, G, \) etc. The path difference between adjacent beams, \( \delta \), is given by the following considerations:

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**Low Mercury Terms**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Term</th>
<th>Term</th>
<th>Configuration</th>
<th>Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>6s 7s</td>
<td>6s  6p</td>
<td>46,536.2</td>
<td>6s 6d</td>
<td>12,845.1</td>
</tr>
<tr>
<td>6s 8s</td>
<td>6s  7p</td>
<td>14,664.6</td>
<td>6s 7d</td>
<td>7,096.5</td>
</tr>
<tr>
<td>6s 9s</td>
<td>6s  8p</td>
<td>7,734.6</td>
<td>6s 8d</td>
<td>4,502.7</td>
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<tr>
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<td>6s  9p</td>
<td>7,174.4</td>
<td></td>
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<td>6s  10p</td>
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<td>6s 11p</td>
<td>6s  11p</td>
<td>31,122.8</td>
<td>6s 9d</td>
<td>3,110.2</td>
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<tr>
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<td>6s  12p</td>
<td>13,866.1</td>
<td>6s 10d</td>
<td>3,104.5</td>
</tr>
<tr>
<td>6s 13p</td>
<td>6s  13p</td>
<td>13,006.1</td>
<td>6s 11d</td>
<td>3,096.3</td>
</tr>
</tbody>
</table>

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The interferometer is most conveniently mounted between the collimating lens and the prism of a photographic spectroscope. The plates are pressed together by three springs, controlled by screws, against three quartz separators of equal length; three carefully selected ball bearings may be used satisfactorily. The approximate separation is given by the manufacturers, or it can be measured with a good pair of calipers. Tightening the screws against the elasticity of the separators permits adjustment to exact parallelism; two other screws allow motion of the interferometer as a whole about vertical and horizontal axes perpendicular to the axis of the collimator. Adjustment is accomplished by trial and error until the dots appear as sharp as possible when viewed with a lens held behind the opening for the plate holder. A rather wide slit should be used, and it is desirable that the dots representing the intersections of the slit images with the interference circles lie along a diameter of these circles rather than along a chord. Due to the lower reflecting power of the silver coatings for the violet end of the spectrum, the number of contributing reflections, and hence the resolving power, falls off with decreasing wave length. Also, for a given setting of the plates, there are more orders visible in the short wave-length region so that the dispersion of the orders is less there, hence it is desirable to work in the long wave-length region if possible. The apparent sharpness of the spots increases away from the center of the pattern, but their separation also becomes less. It is most convenient, therefore, to effect a compromise by working with the rings, say between the fifth and the tenth, from the center of the pattern.

A source of mercury radiation which has been used satisfactorily for this experiment will be briefly described. To obtain as large a magnetic field as possible it is necessary to have the pole pieces of the magnet close together; hence a capillary discharge tube should be used. The electrodes, nickel cylinders welded to tungsten rods, are in bulbs outside the region of the pole pieces. Pyrex glass is essential, as soft glass is likely to break under the heat developed. The tube should be baked for several hours at about 400° C. and the electrodes heated with an induction furnace, if one is available, while the tube is on the pumping system. Alternatively, neon may be admitted at a pressure of a few millimeters and a discharge run for about an hour to remove, at least partially, undesirable impurities from the electrodes and the walls of the tube; this gas is then pumped out. A small amount of mercury is introduced and a few centimeters of neon; the tube is then sealed off. The neon greatly facilitates the running of the tube in a strong magnetic field, and practically no spectrum but that of mercury is observed at high current densities. The tube may also be used for measuring the Zeeman separations for the strong neon lines in the red if it is run with smaller currents. A small 10,000-volt transformer is an adequate power supply. A rheostat in the primary permits adjustment of the current; trial will show at what currents the discharge is most satisfactory. Occasional shaking to drive the mercury into the upper bulb is often helpful if the neon spectrum begins to appear. A lens is used to focus an image of the capillary between the pole pieces on the slit of the spectrograph.

Although the magnetic field may be increased by using wedge-shaped pole pieces to concentrate the lines of force near the capillary tube, the procedure is undesirable for the present purpose where an absolute determination of the field is to be made. Flat pole pieces produce a more uniform field into which a small search coil connected to a fluxmeter or ballistic galvanometer may be introduced. The coil should have an area small enough so that it can completely enter the region between the pole pieces when the discharge tube is in place, and it should have as large a number of turns as possible in order to obtain large throws. The number of maxwells, or total number of lines of force, indicated by the calibrated fluxmeter, is divided by the product of the area and the number of turns of the search coil to give the number of lines per square centimeter or the strength of the field in gauss. The theory of the fluxmeter
or ballistic galvanometer may be found in many books on electrical instruments, such as those of Terry or Smythe and Michels. The magnet is quite likely to retain several hundred gauss of residual magnetism after the energizing circuit has been opened. Hence before taking the zero-field picture a rather weak current should be sent through the coils in the reverse direction until the fluxmeter indicates a vanishingly small residual field. A series of pictures are then taken with increasing field strengths up to the maximum of which the magnet is capable; care being taken to see that the plate holder is moved an adequate amount between each exposure.

Due to the closeness on the photographic plate of the different orders, it is not easy to distinguish the several additional spots produced by the anomalous Zeeman effect, so it is feasible to examine quantitatively only the simple type of pattern such as is produced by the combination between two singlet terms. We have seen that for such a line the pattern should consist of the original wave length accompanied by a satellite on either side, distant one Lorentz unit from the parent line for a field of 1 gauss. The singlet lines of the mercury spectrum are well suited for this experiment, and for the reasons given above those at the long wave-length end of the spectrum are the most convenient to use. The line 6,234.35 (6s7s 1S0 - 6s9p 1P1) would be excellent except that long exposures with red-sensitive plates are required, and the presence of neon lines might confuse the picture. The yellow line 5,790.66 (6s6p 1P1 - 6s6d 1D2) is well suited; it is almost coincident with 5,789.69 (6s6p 1P1 - 6s6d 1D1), but this line is very faint and does not appear with any appreciable intensity in the short exposures required.

Figure 7-19 shows the pictures obtained with a series of 20-sec. exposures at varying field strengths. At zero field the pattern is a series of dots given by the various orders. As the field increases, "wings" grow out from each order and finally become separated as distinct dots, thus showing that high- and low-frequency companion lines are developed. It is possible to compute the accurate wave lengths corresponding to every dot shown, provided the accurate wave lengths of three lines in the vicinity are known, but the process is rather laborious. We shall use an approximate method which is, however, capable of sufficient accuracy to determine the Zeeman separations to within a few per cent.

The positions of each dot on each pattern of the line 5790 are measured with a traveling microscope to 0.001 mm. if possible, and the results plotted against the measured field strength as shown in Fig. 7-20. Straight lines are drawn through the points representing the Zeeman components, and these are used to determine the field strength at which the Zeeman component of λ in the order n + 1 has been shifted to the position of the nth order of λ. Extrapolation of the lines may be resorted to if the largest available field is not sufficient to make the Zeeman component shift by one order. An average value of this field, \( H_f \), is found from the behavior of each order visible. It should be observed that this field is just twice that at which the long and short wave-length components of two adjacent orders intersect.

We have in general that \( n\lambda = 2L \cos \theta \) as the criterion for constructive interference, or, since \( \theta \) is very small, \( n\lambda = 2L \) approximately. Hence

\[ \text{FIG. 7-19. - The interferometer patterns of the singlet mercury line } \lambda = 5790.66 \AA \text{ for a series of values of the magnetic field at the source.} \]

\[ \text{FIG. 7-20. - A plot of the interferometer patterns against the magnetic field strength, in the determination of the Zeeman separation of the mercury line 5790.66 \AA.} \]
for the field $H_1$ at which the Zeeman component $\lambda'$ of order $n + 1$ has moved into coincidence with the $n$th order of the original line $A$, we have

$$n\lambda = (n + 1)\lambda'$$

hence

$$\lambda' - \lambda = \frac{n}{n + 1} \lambda - \lambda$$

or

$$\Delta\lambda = -\frac{\lambda}{n + 1}$$

We do not know the exact value of the order $n$, but we know that it is given approximately as $n = \frac{2L}{\lambda}$. Hence for a plate separation of 1 or 2 cm. and $\lambda = 5790 \AA$, $n$ is of the order of $10^4$. We certainly may neglect unity in comparison with this and write

$$\Delta\lambda = -\frac{\lambda}{n}$$

As $\tilde{\nu} = 1/X$, where $\tilde{\nu}$ is the wave number, we have

$$\Delta\tilde{\nu} = -\frac{\Delta\lambda}{\lambda^3} = \frac{1}{n\lambda} = \frac{1}{2L}$$

This is the expression for the wave-number change due to the field $H_1$, and therefore the Zeeman separation for unit field is

$$\frac{\Delta\tilde{\nu}}{H_1} = \frac{1}{2LH_1}$$

where $L$ is the separation of the interferometer plates, and $H_1$ is the field required to give a Zeeman separation equivalent to a shift of one order for the parent line. This quantity $\frac{1}{2LH_1}$ should theoretically be equal to the Lorentz unit. $e/4\pi m = 4.674 \times 10^{-10} \text{ cm}^{-1}$. An accuracy of a few per cent may be expected. From this standpoint the experiment verifies the theory of the Zeeman effect and identifies the line 5,790 as being a singlet-singlet combination. Or, if the theory is assumed to be correct, the result may be taken as a measurement of the quantity $e/m$, the ratio of the charge to the mass of an electron in an atomic system.

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**CHARTER VIII**

**ATOMIC ENERGY STATES**

8-1. **Introduction.** When considered as a whole the preceding chapter may be regarded as an exposition of how the multitude of spectroscopic lines emitted by an element may be described systematically by the introduction of the concept of stationary energy states. Though these states, represented by spectroscopic terms, are called stationary, the great majority of them are far from stable, and an atomic system remains in an ordinary excited state only a very small fraction of a second. When the atom changes from one of these characteristic configurations to another of lower energy content the excess energy is radiated in accordance with the expression

$$h\nu = E_2 - E_1$$

The *ad hoc* characteristic of the assumptions made in the development of the preceding theory is greatly diminished by the completeness and consistency of the final scheme, and by its theoretical derivation, either on the old quantum theory with its highly arbitrary rules or on the more satisfactory and consistent methods of modern quantum mechanics. Nevertheless a great deal more confidence will be felt in the theory if further experimental evidence can be found to substantiate the predictions and consequences of the stationary state concept when applied to the explanation of phenomena other than those for which it was originally developed.

A large number of corroborative experiments suggest themselves. Under the ordinary conditions of exciting the spectrum of an element, such as in flames, arcs, or sparks, the atoms are subjected to a very heterogeneous supply of energy, e.g., collisions with neutral atoms and molecules, ions, electrons, excited atoms, and photons. All these sources are often present and contribute in varying degrees to the phenomena observed, namely, the spectrum emitted and the positively and negatively charged particles which appear. More information as to the individual atomic processes may be gained by simplifying the mechanism of excitation and studying the effects of these different processes separately. In the subsequent sections we shall confine ourselves to a consideration of the simpler phenomena connected with the transfer of energy to atomic systems from radiation and from rapidly moving electrons, i.e., by photon or electron bombardment.