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THE QUANTUM THEORY*

ONE of the most surprising and interesting developments of the quantum theory is that which shows that quantum numbers determine not only the size and form of the electronic Keplerian orbits in atoms, but also the orientation of these orbits in space with regard to a favored direction such as that provided by an intra-atomic or by an external magnetic or electric field of force. For any arbitrary value of the azimuthal quantum number k, the simple theory shows that there are exactly $k+1$ quantum positions of the orbital plane characterized by whole numbers. For example, if $k=1$ the normal to the orbit may be either parallel to the direction of the controlling field or at right angles to it. If $k=2$ the normal to the orbit may take up in addition to these two positions a third one, in which the normal to the orbit makes an angle of 60° with the field. For higher values of the quantum number k, the possible orientations of the corresponding orbits become regularly more numerous.

A striking confirmation of this theory is afforded by the very beautiful experiments of Gerlach and Stern.[1] In these a stream of atoms of vaporized silver was allowed to flow past a wedge-shaped pole of an electromagnet which provided a radial non-uniform magnetic field. The atoms were caught on a glass plate placed immediately behind the pole, and it was found that they were deposited in two distinct sharply defined layers, indicating that the atoms were sorted out into two distinct and separate beams. The positions of the bands on the plate showed that one of the beams was attracted by the pole and the other repelled by it, the attraction being slightly the greater in intensity. No evidence was obtained of an undeflected beam. From these results it was concluded that all the silver atoms in the stream of vapor possessed a definite magnetic moment, and that while the atoms were passing through the magnetic field their magnetic axes had two distinct orientations in space.

By assuming the correctness of this interpretation, Gerlach and Stern found from measurements on the

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* Concluding part of the address of the president of the Section of Mathematics and Physics, British Association for the Advancement of Science, Liverpool, September, 1923.

[1] Gerlach and Stern, *Zeit. für Phys.*, vol. 7, p. 249, 1921; vol. 8, p. 110, 1921; vol. 9, p. 349 and p. 353, 1922.

various magnitudes involved in the phenomenon that within the limits of error of their experiments the magnetic moment of the normal atom of silver in the gaseous state was that of one Bohr magneton.

Bohr, also, has drawn attention to another possible illustration of the principle of the quantization of orbits in space. It is known that all the rare gases do not exhibit the property of paramagnetism. From this fact the conclusion has been drawn that the atoms of these gases in their normal condition do not possess any angular momentum. According to the quantum theory, however, this conclusion may not be warranted, for we have seen that for an atom which has a finite angular momentum and, consequently, possesses a magnetic moment, the theory prescribes certain definite directions for the axis of momentum relative to a magnetic field in which the atom may be situated. If we assume that the atoms of the rare gases in a magnetic field can place themselves with their momentum axes perpendicular to the magnetic field, it follows that they could appear to be diamagnetic, and all indication of paramagnetism on their part would be absent. In this connection I may point out that Bohr has made the suggestion that evidence in support of the validity of this view is derivable from the results of an analysis, on the basis of the quantum theory, of the anomalous Zeeman effect shown by the rare gases.

One point that may be worthy of notice in dealing with phenomena associated with the principle of space quantization is that the permitted orientations depend only on the values of the quantum number involved, and not on the magnitude of the magnetic field applied.

Orbits characterized by certain definite values of the quantum number should take up their permitted orientations in weak magnetic fields as well as in strong ones, provided the time allowed for the process to take place was ample, and provided suitable pressures were used and disturbances arising from the presence of contaminating gases were eliminated. Such conditions as these have recently been realized by Gerlach and Schutz,[2] and they have been able to obtain with sodium vapor at low pressures in the absence of foreign gases remarkably striking manifestations of the magnetic rotation of the plane of polarization of the light passing through the vapor with magnetic fields as low as a few tenths of a gauss.

This idea of space quantization may perhaps throw some light on the interesting and suggestive experiments of R. W. Wood and A. Ellett[3] on the polarization of the resonance light emitted by mercury and sodium vapors. In their experiments, it will be recalled, strong polarization of the resonance light from mercury or sodium vapors could be produced by weak magnetic fields properly orientated. Moreover, they found that the polarization of the resonance light emitted by these vapors in the presence of the earth's magnetic field could be destroyed by applying a magnetic field of less than one gauss provided it was suitably orientated. It is highly desirable that the experiments of Wood and Ellett should be followed up in order that sufficient information may be gained to enable us to elucidate the principles underlying the modifications in the polarization of the resonance light observed by them.

It seems clear that atoms of sodium, for example, when excited by the absorption of resonance radiation would tend during the period of excitation to take up definite and characteristic orientations even in weak magnetic fields that would result in the polarization of the resonance radiation emitted being different from that of the radiation emitted from atoms of the vapor situated in space in which absolutely no magnetic field existed. It should be remembered, too, that in the normal atom of sodium the orbit in which the valency electron is bound has the value 1 for its characteristic azimuthal quantum number k. When the atom is excited by the absorption of resonance radiation the azimuthal quantum number of the orbit, in which the valency electron becomes bound for a time, takes on the value 2. It seems clear then that the electronic orbit of the valency electron may be subject to different orientations relative to the rest of the atom when the atom is in the excited state from what it would be with the atom in its normal state. These relative orientations, moreover, would again be different in the presence of even a weak external magnetic field from what they would be in the complete absence of such a field. It is, therefore, quite conceivable that changes in orientation of electron orbits may be able to account for the phenomena observed by Wood and Ellett, but at present the whole matter appears to be rather involved and rather difficult to clear up with the information as yet available.

Among the most fruitful of the principles utilized by Bohr in the development of his theory of radiation is the Adiabatic Hypothesis enunciated by Ehrenfest.[4] To this hypothesis Bohr has given the name the Principle of Mechanical Transformability. Numerous examples of the application of this principle might be cited, but the one that concerns us most here is that which deals with the effect of the establishment of a magnetic field on the electronic orbits in atoms. It is well known that Larmor has shown that one result of the establishment of such a field is to endow an

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[2] Gerlach and Schutz, *Die Naturwissenschaften*, vol. 11, Heft 28, p. 638, 1923.

[3] Wood and Ellett, *Proc. Roy. Soc.*, A, June, 1923, p. 396.

[4] Ehrenfest, *Die Naturwissenschaften*, vol. 11, Heft 27, July 6, 1923, p. 543.

electronic orbit with a uniform rotation about the direction of the magnetic field, the angular velocity being given by

$$\omega = \frac{1}{2} \frac{e}{m} \frac{H}{c}.$$

Langevin has also pointed out that the size and form of the electronic orbit remain unaffected by the magnetic field. Ehrenfest's hypothesis asserts that if the magnetic field be established slowly the energy of the electron in its orbital motion and the frequency of its revolution in the orbit may be changed, but the *number* of quanta defining its energy undergoes no modification. With the adoption of these principles it is an easy matter to show that when we quantize the angular momentum about the direction of the magnetic field the normal Zeeman components are exactly the same as those provided by the older classical theory of Lorentz. The singular beauty and simplicity of this method of explaining the normal Zeeman effect constitute one of the finest achievements placed to the credit of the quantum theory.

Efforts to explain the abnormal Zeeman effect have not as yet met with the same success. Among the contributions made to this subject perhaps that of Heisenberg[5] is the most stimulating and suggestive. In addition to offering an explanation of the abnormal Zeeman effect it constitutes an attempt to account for the doublet and triplet structure of series spectra.

Taking for example the case of an alkali element, Heisenberg postulates that through magnetic coupling a movement of rotation within an atom of these elements involves simultaneously the valency electron and the core of the atom as well. According to the theory it is supposed that in the various stationary states there is a partition of the angular momentum between the two, one half an azimuthal quantum being assigned to the core and $k - \frac{1}{2}$ azimuthal quanta to the electron. The author supposes further that through space quantization the two axes of rotation are in the same direction, and that the rotation of the core and that of the electron may take place either in the same sense or in opposite senses. As far as the radial quanta for the electronic orbits are concerned, it is assumed that they are given by $n' + \frac{1}{2}$ where n' has integral values. This device leads to the result that the total quantum number characterizing the orbit of the electron is an integer n that is equal to the sum $k + n'$. In this way the author is enabled, at the same time, to characterize the spectral terms in the Rydberg series formulae by integral quantum numbers.

This scheme, it will be noted, provides for the binding of the valency electron in one or other of two energy levels and reduces the frequency difference characterizing the members of the doublet series of the spectra of the alkali elements to a manifestation of what is practically a Zeeman effect produced by an internal atomic magnetic field. To account for the triplet structure of series spectra such as we obtain with the alkaline earth elements, Heisenberg supposes the magnetic coupling to involve not only the core of the atom but the two outer valency electrons as well. It is shown when the theory is extended to take account of an external magnetic field in addition to the internal one, that the Zeeman separations of the magnetic components of doublet and triplet lines are in exact agreement with the laws formulated by Preston and Runge.

When the external magnetic field is high compared with the internal one, the theory shows that for doublets and triplets the final result is a normal Zeeman triplet in complete accordance with the observations of Paschen and Back.[6]

To illustrate the validity of the theory Heisenberg used his formulae to evaluate the magnitude of the internal magnetic field of the atoms of lithium, and found that it led to a value of 0.32 cm^{-1} for the frequency difference characterizing the doublets of the second subordinate series in the spectrum of this element. As the experimental value found by Kent[7] is 0.34 cm^{-1}, it will be seen that the agreement is good.

Again, in connection with the matter of triplet series the theory shows that in the case of the p terms the ratio of the triplet frequency differences should be as 2 : 1, for the d terms it should be as 3 : 2, and for the f terms as 4 : 3. These deductions find ample verification in the measurements made on the frequency differences of triplet series in the spectra of such elements, as magnesium, calcium, strontium, barium, zinc and cadmium.

To say the least, the theory outlined above is extremely suggestive. It leads, however, to rather surprising results. If we are to account for doublet separations generally as being due to Zeeman separations produced by intra-atomic magnetic fields, it follows that with some atoms these must be exceedingly high. Taking the doublet separations of the second subordinate series in the spectra of the alkali elements, we find the following values for the internal magnetic fields of the different atoms:

Element	$\Delta\nu_p$	H_i
Lithium	0.34 cm^{-1}	7,173 Gauss
Sodium	17.18 “	366,744 “
Potassium	57.71 “	1,231,945 “
Rubidium	237.6 “	5,072,090 “
Caesium	554.0 “	11,826,330 “

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[5] Heisenberg, *Zeit. für Phys.*, No. 8, p. 257 and p. 273, 1922.

[6] Paschen and Back, *Ann. der Phys.*, vol. 39, p. 897, 1912; vol. 40, p. 960, 1913.

[7] Kent, *Ast. Phys. Jl.*, vol. 40, p. 343, 1914.

If it should turn out that magnetic fields so high as those given above are present in atoms of elements such as those in the alkali group, the results obtained by Wood and Ellett would be easily explained.

Whether the existence of a magnetic coupling between the valency electron and the atomic core justifies Heisenberg in adopting the artifice of partitioning the quanta of rotation between the electron and the atomic core is a debatable point.

It does not appear to be permissible to adopt the value ½ for the azimuthal quantum number in defining the stationary orbits of a heavy atom such as that of uranium. In a recent paper by Rosseland,[8] in which a suggestion is put forward that the phenomenon of radioactivity exhibited by the heavier atoms may be due to some interaction between the nuclear and the external electrons in these atoms, he finds that the nearest approach of an electron to the nucleus in the atom of uranium according to Bohr's scheme of orbits is 16×10^{-12} cm. If the electronic orbit closest to the nucleus in the atom of uranium had ½ for the value of its azimuthal quantum number, it would mean that the shortest distance of approach to the nucleus would be equal to 4×10^{-12} cm. As the radius of the nucleus of the atom of uranium has been shown to be 6.5×10^{-12} cm. it is evident that such an orbit could not exist. For reasons of this character we are practically precluded from assigning to k, the azimuthal quantum number, a value less than 1 in defining the electronic orbits in atoms.

In this paper an attempt has been made to outline some of the leading features of the quantum theory as it is being used to solve the problems of atomic structure as well as of those connected with the origin of radiations emitted by atoms. Other illustrations of special interest might have been drawn from the treatment of problems that have arisen in a study of band spectra[9] and of fluorescence phenomena.[10] The recent work of Cabrera,[11] Epstein[12] and Dauvillier,[13] on paramagnetism, too, has a most interesting connection with the development of inner systems of electronic orbits in atoms in Bohr's scheme of the genesis of atoms.

I venture to think, however, that the few illustrations presented may serve, in a measure, to indicate the power and also the beauty of the methods being put forward to elucidate the problem of the origin of radiation.

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[8] Rosseland, *Nature*, March 17, p. 357, 1923.

[9] Kratzer, *Die Naturwissenschaften*, vol. 11, Heft 27, p. 577, 1923.

[10] Franck and Pringsheim, *Die Naturwissenschaften*, Heft 27, vol. 11, July 6, p. 559, 1923.

[11] Cabrera, *Jl. de Phys.*, t. 6, p. 443, 1922.

[12] Epstein, Science, vol. lvii, No. 1479, p. 532, 1923.

[13] Dauvillier, *C.R.*, June 18, p. 1802, 1923.

BY-PRODUCT VALUES IN THE STUDY OF QUANTITATIVE ANALYSIS[1]

Many of the friends of chemistry as well as some of chemistry's devotees, chemists in the making, do not completely appreciate the value of the study of quantitative analysis because they do not realize the tremendously important rôle which quantitative analysis plays in an industrious world and because some of the worth of its study is in the form of intangible values difficult to analyze and evaluate. Quantitative analysis may be regarded by the student as a meat and potatoes course. After his appetite has been whetted for it by preliminary general and qualitative courses, it forms the "pièce de résistance" of a college chemical education, but leaves room for such hearty side dishes as organic chemistry, physical chemistry, etc., and a light chemical research dessert. But it is meat and potatoes to a young graduate in a very literal sense, for the first position of a large majority of young chemists is in analytical work. Many an ambitious man has used his routine analytical position as a stepping stone to a larger salary in his industry.

The rôle of quantitative analysis in the world's work is truly tremendous. It is absolutely essential to the appraisal of basic raw materials—the different ores and minerals, coal, water, limestone and a host of others. It furnishes the means whereby factory processes are controlled in iron and steel, sulfuric acid, corn products, fertilizer, dye and explosives industries, for example. By it the finished products are analyzed. It is necessary to the enforcement of the federal pure food laws and the state fertilizer and feed laws and it is the backbone of pure and applied chemical research.

Once the student has had the importance of quantitative chemistry pointed out to him and the undoubted help that it will be to him in earning his living some day, he quickly understands part of the benefits of its study. There are, however, other values which the instructor and student both should keep in mind, if full benefit for the latter is to be derived from the analytical courses.

Chief among these are:

(1) Stimulation of the logical mental processes required in thinking through the reasons for the steps necessary in each new method, for figuring out results

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[1] These undoubtedly also apply to many other laboratory courses as well.