

the extension of the Pauli Principle, which has been shown to be the guiding principle in the formation of atoms out of protons and electrons, to the case of an ensemble of N independent particles possessing only translatory motion (e. g., Hall, Proc. Nat. Acad. Sci. 1928). The deduction given here follows exactly the same lines as the deduction of the van der Waals's correction for finite volumes, and is therefore physically more comprehensible.

Of greater difficulty is the comprehension of the Bose-Einstein statistics. Here " ω ", the phase-volume of any particle, has to be put negative ($-h^3$). These statistics have therefore to be definitely ruled out in the case of material particles. But as it is found to be correct in the statistics of light-particles, we have to assume that when a photon enters a phase-space, the space expands, since the total

phase-volume is increased by the phase-volume of the photon. A discussion will be found in Brillouin's paper above referred to.

References

- (1) Bose, *Zeits. f. phys.* xxvii. p. 384 (1924). Einstein, *Sitz. Preuss. Akad.* p. 261 (1924); p. 3 (1925).
- (2) Fermi, *Zeits. f. phys.* xxxvi. p. 902 (1926). Dirac, *Proc. Roy. Soc. A*, cxii. p. 66, (1926).
- (3) Boltzmann, "Über die Eigenschaften Monozyklischer System" *Wien. Ber.* xc. (1884); *Wiss. Abhandl.* iji. Nr. 73, S. 132ff.
- (4) Gibbs, 'Statistical Mechanics.'
- (5) Ehrenfest and Trkal, *Proc. Amst. Acad.* xxiii. (1920).
- (6) Planck, *Zeits. f. phys.* xxxv. p. 155 (1925).
- (7) Saha and Sur, *Phil. Mag.* i. p. 280 (1926).
- (8) Jeans, 'Dynamical Theory of Gases,' 2nd ed. chap. iv. pp. 58-62. Wassmuth, *Statistische Mechanik.*

48. COLOURS OF INORGANIC SALT

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No satisfactory explanation of the colours of inorganic salts in the vapour state, in solution, or in crystalline form has yet been put forward, excepting certain suggestions by Fajans ("Handbuch der Physik", Bd. 24, p. 564), that the colours are due to the deformation of the cation produced by surrounding anions and molecular complexes. The ideas of Fajans were rather vague, but the time has now come to put forward a more precise hypothesis. It is well known that salts like NaCl, CaCl₂, AlCl₃ in which the electrons of the cation form closed shells (p^6), are colourless or white. Herzfeld found from a study of dispersion of NaCl that there are three ultra-violet absorption bands, one at $\lambda 340$ which was ascribed to Na⁺, another at about $\lambda 1500$, which was ascribed to Cl⁻-ion. This last one has been experimentally obtained by Pfund (*Phys. Rev.*, vol. 32) by the *Reststrahlen* method. The wave-length $\lambda 340$ ascribed to Na⁺ agrees remarkably well with the resonance line of Na⁺ identified by K. Majumdar (*Ind. Jour. Phys.*, 1927) and Bowen, though definite assignment of values of the absorption wave-length from dispersion data in this region is subject to certain uncertainties.

Colours are almost entirely shown by the compounds of the transitional group of elements (the first group consisting of elements from scandium to copper). Let us fix our attention on the first group alone, as the same arguments will apply to other groups. The colours are somewhat modified by the anion, or the state of aggregation (solution or crystal), but intrinsically it is due to the cation. Taking a compound like CrCl₃, we can say that it consists of a Cr⁺⁺⁺-ion, surrounded by three Cl⁻-ions. The absorption of light in the visible region is due entirely to the outer

electrons of the Cr⁺⁺⁺-ion. Let us see how this absorption takes place.

The outermost shell of the Cr⁺⁺⁺-ion (and generally of all ions of transitional elements) consists of a number of electrons in the d -shell. In Cr⁺⁺⁺, the number is 3. The multiplicity of the most stable combination state is obtained by adding up the multiplicity vector $r = \frac{1}{2}$ for all the electrons, and the next metastable states are obtained by reversing the vector r for one of the electrons. In d^3 , the states are respectively 4X and 2Y , where X and Y are further to be formulated. This is obtained by considering the l -coupling according to Pauli's principle, and in the case of Cr⁺⁺⁺, $X = F$ and P in 4X , and $Y = H, G, D$ in 2Y . The average difference in energy between the terms obtained in this way, that is, by having the rotating quantum number all in one direction, and then reversing only one, is about $C_{av} = 20,000$, the value increasing with the number of net charges in the nucleus, as shown by the spectroscopic data of Russell, Gibbs and White, Lang, Shenstone, etc. (see various papers in the *Physical Review*).

It is therefore evident that the absorption of light in the visible region is due to some of the κ -electrons changing their r -vector from $\frac{1}{2}$ to $-\frac{1}{2}$. This type of transition is possible only in transitional groups, and though usually forbidden they become very prominent in all molecular formations. We cannot, of course, expect that the values of energy difference which we obtain from spectroscopic studies will continue to hold good in molecules or complex formation, but they will remain of the same order of magnitude. An indefiniteness will be introduced by the modification of the rules of l -coupling (*vide* Stoner's

suggestive paper in the *Phil. Mag.*, September 1929, which explains D. M. Bose's hypothesis that it is only the rotating vector r which is responsible for the magnetism of the ions of transitional elements in a similar way).

There seems to be no experimental evidence in existence which can be utilised in support of the above hypothesis. The absorption spectra of none of these compounds have been studied in the vapour state (the work of Franck and his school being confined mostly to the study of alkali

halogenides). The emission spectra of some of these salts have been studied, but it is difficult to draw any conclusion from them. Other interesting experiments may also be devised to test the above hypothesis. Some of them are in progress.

Department of Physics,
Allahabad University,
Dec. 27, 1929.

49. ÜBER DIE VERTEILUNG DER INTENSITÄT UNTER DIE FEINSTRUKTURKOMPONENTEN DER SERIENLINIEN DES WASSERSTOFFS UND DES IONISIERTEN HELIUMS NACH DER DIRACSCHEN ELEKTRONENTHEORIE.

VON M. SAHA UND A. C. BANERJI

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Mit 4 Abbildungen. (Eingegangen am 5 Oktober 1930)

1. *Eingleitung.* Die Feinstruktur der Linien des Wasserstoffs und ionisierten Heliums sowie die Intensitätsverteilung unter die Feinstrukturkomponenten sind in älterer und neuester Zeit Gegenstand der Untersuchungen vieler hervorragender Forscher gewesen¹. Auch heute ist das Interesse daran noch nicht erloschen, da L. Goldstein in einer vor kurzem im *Journal de Physique* (Dezember 1929) erschienenen Arbeit die Intensitätsverteilung unter die Feinstrukturkomponenten von $H\alpha$ und $\lambda=4686$ des He^+ nach der relativistischen Wellenmechanik von Dirac untersuchte und recht auffallende Abweichungen gegenüber den Beobachtungen fand. Das Ergebnis schien aus zwei Gründen einigermaßen überraschend: 1. ist die Diracsche Elektronentheorie so erfolgreich in der Deutung der Dublizität und der Feinstruktur der H-Linien gewesen, dass an ihr Versagen in der Intensitätsberechnung nur schwer zu glauben ist, und 2. haben Sommerfeld und Unsöld in der oben genannten Arbeit eine Theorie der Intensitätsverteilung auf Grund von Schrödingermechanik und statistischen Überlegungen ausgearbeitet, mit deren Hilfe sie in sehr befriedigender Form viele der voneinander abweichenden Beobachtungen der Intensitätsverteilung auf die Feinstrukturkomponenten der $H\alpha$ -Linie und von $\lambda=4686$ des He^+ erklären konnten. Die Verfasser der vorliegenden Arbeit sind mit dieser selben Frage schon vor der Veröffentlichung der Goldsteinschen Arbeit beschäftigt gewesen, aber ihre Ergebnisse stehen mit den

Versuchsergebnissen in ausgezeichneter Übereinstimmung, ebenso wie mit den Ergebnissen von Sommerfeld und Unsöld. Wir haben die Diracsche Theorie in der von Weyl und Darwin² gegebenen Form benutzt. Die vorliegende Arbeit enthält nur die Endergebnisse, da die Wiedergabe aller mathematischen Schritte zu umfangreich und langweilig werden dürfte.

2. *Historische Skizze der Frage.* Die Theorie für die Feinstruktur der H-Linien ist bekanntlich zuerst von Sommerfeld auf Grund der Elektronenniveautheorie ausgearbeitet worden. Ist ein Elektronenniveau durch die Gesamtquantenzahl n und die azimutale Quantenzahl k gegeben, so ist seine Energie durch

$$\nu_{nk} = -Rz^2 \left[\frac{1}{n^2} + \frac{\alpha^2}{n^4} \left(\frac{n}{k} - \frac{3}{4} \right) \dots \right] \quad (1)$$

ausgedrückt. (Die Energie des Niveaus ist gleich $h\nu_{nk}$. α ist die Sommerfeldsche Feinstrukturkonstante $\left(\frac{2\pi e^2}{ch} \right)$. Die Frequenz einer Emissionslinie ist durch

$$\nu = Rz^2 \left[\frac{1}{n^2} - \frac{1}{n'^2} \right] + R\alpha^2 z^2 \left[\frac{1}{n^4} \left(\frac{n}{k} - \frac{3}{4} \right) - \frac{1}{n'^4} \left(\frac{n'}{k'} - \frac{3}{4} \right) \right] = \nu_0 + \Delta\nu \quad (2)$$

gegeben, wo

$$\left. \begin{aligned} \nu_0 &= Rz^2 \left[\frac{1}{n^2} - \frac{1}{n'^2} \right] \\ \Delta\nu &= R\alpha^2 z^2 \left[\frac{1}{n^4} \left(\frac{n}{k} - \frac{3}{4} \right) - \frac{1}{n'^4} \left(\frac{n'}{k'} - \frac{3}{4} \right) \right] \end{aligned} \right\} (2')$$

¹Für einen zusammenfassenden Bericht vgl. A. Sommerfeld, *Atombau und Spektrallinien*, 4. Aufl., S. 439 ff. Die dort vertretenen Ansichten sind inzwischen abgeändert worden; vgl. A. Sommerfeld u. A. Unsöld, *Zeit. f. Phys.* **36**, 259, 1926; **38**, 237, 1926.

²H. Weyl, *Gruppentheorie und Quantenmechanik*, Kap. 4, S. 1
C. G. Darwin, *Proc. Roy. Soc. (A)* **118**, 654, 1928.