THE NEW QUANTUM MECHANICS

CHAPTER I

THE ORIGIN AND DEVELOPMENT OF THE NEW QUANTUM MECHANICS

1. *The origin of the new quantum mechanics* was an epoch-making memoir by Werner Heisenberg[1] which contained the new concept which was to lead to the phenomenal developments of quantum mechanics of the past two years. Up to this time the quantum theory (the 'older' quantum theory) postulated the existence of stationary states of the atom calculated by the use of the classical mechanics and selected by the use of quantum conditions satisfied by the action variables of that theory. In the new mechanics the equations have the same form as in the classical theory, but the variables no longer satisfy the commutative law of multiplication, that is, xy is not in general equal to yx; the quantum conditions of the older theory are replaced by equations which enable the difference $xy - yx$ to be calculated; these equations involve Planck's constant h.

For some years before 1925, Sommerfeld, Heisenberg, Landé and Pauli[2] had been grappling with the complex problem of the multiplets and their Zeeman separations. By the use of a system of quantum numbers l, s, j connected with the respective angular momenta of the series electron, the core, and the whole atom, they had given a qualitative account of the multiplets of the alkalis,

[1] W. Heisenberg, Zs. f. Phys. **33**, p. 879, July **1925**.
[2] Various papers in the Zs. f. Phys. from **1922** to **1924**.

alkaline earths, etc., the work culminating in a very general empirical formula—the g-formula of Landé—which enabled the Zeeman separations of a multiplet to be worked out quantitatively in terms of the quantum numbers l, s, j. An essential part of the scheme was the use of *half odd integers* as well as integers as possible values of l, s, j and this formed no part of the older quantum theory. Heisenberg's new theory however at once led to the formula $\left(n + \frac{1}{2}\right) h\nu$ as the energy of a stationary state of Planck's oscillator, so that half odd integers came quite naturally into the new results.

A real difficulty too had been met with in the spectrum of neutral helium, where *two* electrons revolve round the nucleus (the simplest many electron problem), all the theoretical results found being at variance with experiment; again in the problem of the 'crossed' fields, where an atom is exposed to the combined action of electric and magnetic fields, fundamental difficulties arose.

But the work which directly led to the formulation of the new mechanics was that of Kramers and Heisenberg[1] on dispersion.

They worked out the absorption and scattering of radiation by an atom regarded as a multiply periodic system of the classical theory, perturbed by the incident radiation. They thus found a result in terms of the orbital frequencies and amplitudes. This result was then translated, by the use of the correspondence principle, into one containing the experimentally observable magnitudes, namely, the frequencies and amplitudes of the spectral lines emitted by the atom[2].

Heisenberg then sought to develop a scheme of quantum kinematics by which the quantum formulae would be ob-

[1] H. A. Kramers and W. Heisenberg, Zs. f. Phys. **31**, p. 681, **1925**.
[2] 'The Quantum Theory of the Atom,' by G. Birtwistle, Cambridge, **1926**, §§ 148 to 154; this book will be referred to as Q.T.A.

tained directly in terms of these experimentally observable magnitudes, the frequencies and intensities of the spectrum, without the intermediate use of orbital frequencies and amplitudes, which by their nature can never probably be observed.

This meant that instead of representing a dynamical quantity, as on the classical theory, by a one-dimensional *line* of terms (a Fourier series) of the type

$$C_1 e^{2\pi i(\omega t)},\ C_2 e^{2\pi i(2\omega t)},\ \ldots\ C_n e^{2\pi i(n\omega t)},\ \ldots$$

it should, on the quantum theory, be represented by a two-dimensional *table* of terms (a matrix) of the type

$$\begin{pmatrix} A(1,1)\,e^{2\pi i\nu(1,1)t}, & A(1,2)\,e^{2\pi i\nu(1,2)t}, & \ldots \\ A(2,1)\,e^{2\pi i\nu(2,1)t}, & A(2,2)\,e^{2\pi i\nu(2,2)t}, & \ldots \\ \ldots & \ldots & \ldots \end{pmatrix}$$

where $A(n, m)\,e^{2\pi i\nu(n,m)t}$ represents the spectral line of frequency $\nu(n, m)$ and intensity dependent upon $A(n, m)$ due to a Bohr transition from the stationary state n to the stationary state m.

Heisenberg, Born and Jordan then proceeded to develop the matrix mechanics, and in two papers[1] worked out the theory of the harmonic and anharmonic oscillators, gave a perturbation theory for non-degenerate and degenerate systems, and with it a direct deduction of the dispersion formula and of formulae required for the calculation of Zeeman intensities.

While this matrix theory was being developed, Dirac[2] was working out a theory on somewhat different lines; he discovered that the quantum conditions for a multiply periodic system could be expressed in terms of the 'Poisson brackets' of the classical mechanics. As in the classical mechanics the only differential coefficients essential to the theory can be put into Poisson bracket form, the diffi-

[1] M. Born and P. Jordan, Zs. f. Phys. **34**, p. 858, Sept. **1925**. M. Born, W. Heisenberg and P. Jordan, Zs. f. Phys. **35**, p. 557, Nov. **1925**. These papers will be referred to as Q.M. I and Q.M. II respectively.

[2] P. A. M. Dirac, Proc. Roy. Soc. A. **109**, p. 642, Nov. **1925**.

culties met with by Born, Heisenberg and Jordan in their efforts to preserve the Hamiltonian form of the equations of motion by a suitable form of matrix differentiation, are not encountered on Dirac's theory. Dirac goes further and shows that we can work in the new mechanics without using matrices; he calls functions of the dynamical variables q-numbers (which do not obey the commutative law of multiplication) and ordinary numbers (which do) c-numbers; though in the interpretation of q-number results in terms of experiment (where c-numbers must be used) the matrix of the q-number is necessary.

In this way Dirac[1] gave the theory of the hydrogen atom on the new mechanics, a crucial test of the new system, as the Bohr formula is the basis of the whole structure of quantum mechanics; he found that the term form $\frac{Rhc}{n^2}$, with n equal to an integer $1, 2, \ldots$ is preserved in the new mechanics, as had been simultaneously shown by Pauli[2] who used the Heisenberg matrices.

For some time before this, serious difficulties had existed in the interpretation of the multiplets, their Zeeman separations and the corresponding X-ray multiplets. The function assigned to the core in the Landé (l, s, j) model, Pauli[3] urged should be assigned to the series electron, so that every electron has four independent quantum numbers. He further laid down the axiom that no two electrons in the atom can have all four quantum numbers the same; this axiom, known as the 'exclusion' principle of Pauli[4] (or the Pauli 'verbot'), at once accounted for the maximum number of electrons 2, 8, 18, 32, ... in the K, L, M, N, ... 'shells' in accord with Bohr's theory of the atomic structure of the elements.

[1] P. A. M. Dirac, Proc. Roy. Soc. A. **110**, p. 561, Jan. **1926**.
[2] W. Pauli, Zs. f. Phys. **36**, p. 336, Jan. **1926**.
[3] W. Pauli, Zs. f. Phys. **31**, p. 373, Dec. **1924**.
[4] W. Pauli, Zs. f. Phys. **31**, p. 765, Jan. **1925**.

In October 1925, Uhlenbeck and Goudsmit[1] put forward their theory of the spinning electron which enabled the quantum number s previously associated with the angular momentum of the core electrons to be associated with the spin of the series electron, thus giving a mechanical interpretation to the transfer of the quantum number s from the core to the electron, of which Pauli had postulated the theoretical necessity. In March 1926, Heisenberg and Jordan[2], using the new mechanics and the spinning electron theory of Uhlenbeck and Goudsmit, calculated the fine structure of the doublets of the alkalis, their Zeeman separations and intensities, and completely cleared up the difficulties with which this problem had been beset for many years. They proved the Landé g-formula and also the Sommerfeld formula for the Paschen-Back changes.

Early in 1926 the complexity of the matrix procedure had made itself felt, with its infinite number of difference equations with an infinite number of unknowns, and several writers endeavoured to bring the new mechanics within the range of more highly developed analysis. Lanczos[3], with his 'field theory,' had brought it into contact with the theory of integral equations; Born and Wiener[4] had devised an 'operator calculus,' but just about this time a most remarkable development of the theory on lines totally different from those of Heisenberg and Dirac was put forward by Schrödinger[5]. Fired by the new ideas of Louis de Broglie[6] on material particles and their associated waves, he assumed that the dynamics of an atom cannot be represented by a point moving through

[1] G. E. Uhlenbeck and S. Goudsmit, Naturwissensch. **47**, p. 953, Nov. **1925**; Nature, **117**, p. 264, Feb. **1926**.
[2] W. Heisenberg and P. Jordan, Zs. f. Phys. **37**, p. 263, March **1926**.
[3] K. Lanczos, Zs. f. Phys. **35**, p. 812, Feb. **1926**.
[4] M. Born and N. Wiener, Zs. f. Phys. **36**, p. 174, Jan. **1926**.
[5] E. Schrödinger, Ann. der Phys. **79**, p. 361, Jan. **1926**; **79**, p. 489, Feb. **1926**; **79**, p. 734, March **1926**.
[6] L. de Broglie, Ann. de Phys. **10**, p. 22, **1925** (Thèses, Paris **1924**).

the coordinate space (the q-space) as in the classical theory, but must be represented by a wave in that space, and obtained a differential equation which the 'wave function' ψ must satisfy. This equation contains E, the total energy of the atom. In general, this equation only has solutions (which are continuous, unique and bounded in the q-space) for certain definite values of E, viz. $E_1, E_2, \ldots$ ('eigenwerte'), and the corresponding solutions $\psi_1, \psi_2, \ldots$ are the 'eigenfunctions.' The eigenwerte are the energy levels of the atom, and Schrödinger shows how the eigenfunctions may be used to determine the Heisenberg matrices by a process of quadratures. The strength of Schrödinger's 'wave mechanics' lies in the fact that it brings the new mechanics within the scope of the highly developed analysis of differential equation theory, and then reduces the calculation of the intensities of the lines to a series of integrations.

In March and April 1926 appeared two further papers by Dirac. In the former[1] he obtained the angular momentum relations of Heisenberg, Born, and Jordan[2] by his Poisson bracket methods, and using his angle and action variable theory developed for q-numbers, found the g-formula of Landé, and also Kronig's results for the relative intensities of a multiplet and their components in a weak magnetic field.

In the latter[3] he extended his theory to relativity mechanics and used it to give the theory of the Compton effect; he obtained a more consistent agreement with Compton's experimental results than did Compton by his theory of light quanta.

In May and June 1926 two further memoirs by Schrödinger[4] appeared. In the former he develops a theory of

[1] P. A. M. Dirac, Proc. Roy. Soc. A. **111**, p. 281, March **1926**.
[2] Q.M. II.
[3] P. A. M. Dirac, Proc. Roy. Soc. A. **111**, p. 405, April **1926**.
[4] E. Schrödinger, Ann. der Phys. **80**, p. 437, May 1926; **81**, p. 109, June **1926**.

perturbations and applies it to find the *intensities* of the lines in the Stark effect and so calculates the 'total intensities' of the lines H_α, H_β, H_γ, H_δ; in the latter he develops a dispersion theory and obtains the Kramers-Heisenberg formula.

By this time the computational value of the Schrödinger methods had been appreciated by earlier workers. In June and July 1926, Born[1] published two papers on collision phenomena; he finds a solution of the Schrödinger wave equation consisting of incident plane waves representing the approaching electron, and these waves are scattered by the atomic system. He assumes that the square of the amplitude of the wave scattered in any direction determines the probability of the electron being scattered in that direction, with an energy given by the frequency of the wave.

In June 1926 Heisenberg[2] wrote an outstanding paper on *resonance* in atoms with two electrons, which contained the key to the solution of the spectrum of neutral helium, with its mystery of the ortho and para helium terms. It is well known that the latter is a single term system containing the 'ground' term, and the former a doublet system; also that the terms of the one system do not combine with those of the other.

All these characteristics were accounted for, the difference between the ortho and para terms corresponding to the frequency of the energy pulsations from the one electron to the other within the atom. This work is carried out by the use of his matrix mechanics, but for the first time he uses Schrödinger's calculus to confirm his theory of the non-combination of the ortho and para helium terms.

In a second paper in July[3] he computed the ortho and para helium separations by the use of Schrödinger's calculus and found results of the right order of magnitude both for

[1] M. Born, Zs. f. Phys. **37**, p. 863, June **1926**; **38**, p. 803, July **1926**.
[2] W. Heisenberg, Zs. f. Phys. **38**, p. 411, June **1926**.
[3] W. Heisenberg, Zs. f. Phys. **39**, p. 499, July **1926**.

He and Li+, though it is evident that a more refined perturbation theory is required in quantum mechanics with elaborations on the lines used in astronomy.

In August 1926, Dirac[1] gave an illuminating account of the derivation of the Heisenberg matrices by the use of Schrödinger's eigenfunctions and considered the two electron problem for the atom by the Schrödinger method; he found that there were two solutions satisfying the equations, and that one led to the Pauli verbot and the other to the Bose-Einstein statistical mechanics. He also worked out a perturbation theory for the wave mechanics of Schrödinger in which the approximation is carried to the second order, and expressions for the Einstein B coefficients are found.

In December 1926, Dirac[2] obtained a general formal matrix theory using operational methods, and derived Schrödinger's equation as part of this matrix calculus; he also generalised it for cases where the Hamiltonian contains the time explicitly.

In the first of two later papers (1927) Dirac[3] gave a new theory of emission and absorption of radiation. He considers the interaction of an assembly of light quanta with an atom and finds expressions for both of the Einstein A and B coefficients; in the second he gives a theory of dispersion and deduces the Kramers-Heisenberg formula.

It is hardly possible to pass on without remarking upon the almost uncanny anticipation by Courant and Hilbert[4] of the pure mathematical theory required for the new mechanics, which has had so much to do with the rapidity of its development.

[1] P. A. M. Dirac, Proc. Roy. Soc. A. **112**, p. 661, August **1926**.
[2] P. A. M. Dirac, Proc. Roy. Soc. A. **113**, p. 621, Dec. **1926**.
[3] P. A. M. Dirac, Proc. Roy. Soc. A. **114**, p. 243, Feb. **1927**; A. **114**, p. 710, April **1927**.
[4] 'Methoden der mathematischen Physik,' **1**, by R. Courant and D. Hilbert, Berlin, **1924**.

CHAPTER II

THE MULTIPLETS OF SERIES SPECTRA AND THE *l-s-j* SCHEME OF LANDÉ

2. *Series spectra and their multiplets.*

The 'terms' of a series[1] are of the form $\frac{Rhc}{n^2} f(n,l)$, where $f(n,l) \to 1$ as $n \to \infty$, n being the principal quantum number and l a second quantum number associated with the series to which the term belongs. Writing the above expression as $\phi(n,l)$, the terms can be written as

$\phi(n,0),\ \phi(n+1,0),\ \phi(n+2,0),\ \ldots,$
where $l=0$ (s terms)
$\phi(n+1,1),\ \phi(n+2,1),\ \ldots,$
where $l=1$ (p terms)
$\phi(n+2,2),\ \ldots,$
where $l=2$ (d terms)
$\phi(n+3,3),\ \ldots,$
where $l=3$ (b terms)
$\ldots.$

[For sodium, for example, where in the normal state the series electron is in the M shell, $n=3$.]

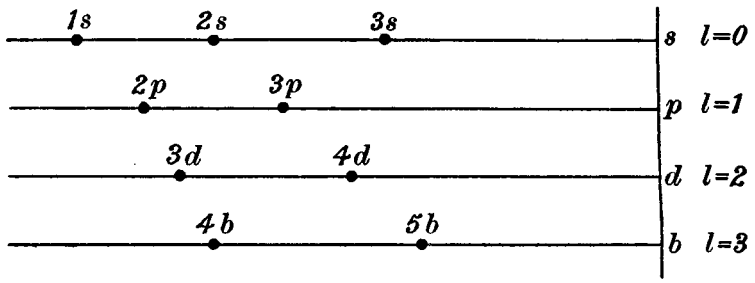
The above terms are usually written as

$$\left.\begin{array}{l} 1s,\ 2s,\ 3s,\ \ldots \\ 2p,\ 3p,\ \ldots \\ 3d,\ \ldots \\ 4b,\ \ldots \end{array}\right\} (Term \text{ series})$$

and the various series *lines* are given by the transitions

$$\left.\begin{array}{l} Np \to 1s,\ N=2,3,4,\ldots, \text{ the } \textit{principal} \text{ series} \\ Ns \to 2p,\ N=2,3,4,\ldots, \text{ the } \textit{sharp} \text{ series} \\ Nd \to 2p,\ N=3,4,5,\ldots, \text{ the } \textit{diffuse} \text{ series} \\ Nb \to 3d,\ N=4,5,6,\ldots, \text{ the } \textit{Bergmann} \text{ series} \end{array}\right\} (Line \text{ series})$$

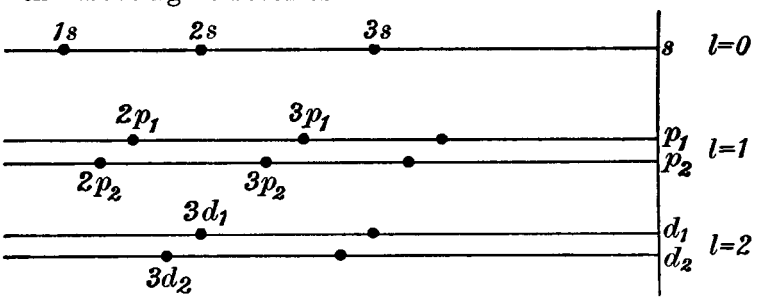
[1] Q.T.A. chap. XI.



The terms can be represented, after Bohr, by the above diagram where the horizontal distance of a term point from the vertical line measures its energy value.

3. *Multiplets.*

The series lines when examined with high power are found in general to be multiple in structure. Thus in the case of the alkalis, the s terms remain single, but the $p, d, b, \ldots$ terms each split up into two (a doublet) so that the above figure becomes



The separations become wide with increasing atomic number, the magnitude for the $p_1 p_2$ levels ranging from 6 Å for sodium to 422 Å for caesium.

Sommerfeld and Landé introduced a third quantum number j so that a pair of corresponding p_1, p_2 terms had $l = 1$, but different values of j.

4. *Earlier theory of the multiplets.*

In the earlier form of the theory the field acting on the