H. A. KRAMERS

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PREFACE

The great loss caused by the premature death of Hans Kramers gave rise to the desire among his many friends and pupils to commemorate in a concrete way his exceptionally gifted personality. The most appropriate form appeared to be an edition of his collected scientific papers, although this can give only an incomplete idea of Kramers' influence on the scientific and the cultural life of his country. It is impossible to do full justice to his lectures, his philosophical and popular articles, and his contributions to the work of his many pupils. These, together with his monumental textbook on the foundations of quantum mechanics and its application to the electron and the radiation field, have left Kramers' mark on the great development of theoretical physics in this century. For an evaluation of the work of Kramers we may refer to the addresses delivered by N. Bohr and H. B. G. Casimir at the memorial meeting of the Netherlands Physical Society in May 1952 (see Ned. Tijdschr. Natuurk., vol. 18, p. 161 and p. 167). Only a few biographical facts will be mentioned here.

Hendrik Anthony Kramers was born on Dec. 17, 1894 at Rotterdam, where his father was a physician. He studied at the University of Leyden from 1912 to 1916. In 1916 he went to Copenhagen to work with Niels Bohr. It was there that he worked out his famous formula for the scattering of light by atoms. In 1926 Kramers was appointed to the chair of theoretical physics at Utrecht, and in 1933 he succeeded Ehrenfest at Leyden. From 1931 on he was also connected with the "Technische Hogeschool" at Delft. He was a member of many learned societies, and held several medals and honorary degrees.

It is our hope that the present work will be instructive and inspiring to the future generation of physicists, for this would certainly fulfil a deeply felt wish of Hans Kramers.

H. B. G. Casimir
A. D. Fokker
C. J. Gorter
S. R. de Groot
N. G. van Kampen
J. Korringa
G. E. Uhlenbeck

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H. A. Kramers in a discussion at Princeton in 1946 *(Physical Science and Human Values*, Princeton University Press, Princeton 1947)

INTENSITIES OF SPECTRAL LINES

ON THE APPLICATION OF THE QUANTUM THEORY TO THE PROBLEM OF THE RELATIVE INTENSITIES OF THE COMPONENTS OF THE FINE STRUCTURE AND OF THE STARK EFFECT OF THE LINES OF THE HYDROGEN SPECTRUM

BY

H. A. KRAMERS

WITH FOUR PLATES

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Components represented by small squares in the case of original components and by one dot in the case of new components have generally theoretical intensities which are far too small to be conveniently represented on the scale used.

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* See pages [105-108]

Introduction.

In the quantum theory of line spectra it is assumed that the laws of electrodynamics cannot be applied to atomic systems, and the assumption is made that an atomic system can exist without emitting radiation in a number of states, which are called the "stationary states" of the system, and that a process of emission or absorption of energy can only take place by a complete transition between two such states. Further it is assumed that the radiation emitted or absorbed during such a transition is unifrequentic, and that its frequency is given by

$$\nu = \frac{1}{h}(E' - E''), \tag{1}$$

where E' and E'' are the values of the energy in the two states, and where h is **Planck**'s constant. As well known **Bohr** was able, on the basis of these assumptions, to account in a convincing way for the frequencies of the lines of the series spectrum of hydrogen and for some main features of the series spectra of other elements. In the course of the last years the quantum theory of line spectra has been developed considerably, due to the work of **Sommerfeld**, **Epstein**, **Schwarzschild** and others, who, by extending **Bohr**'s original theory, were able to explain, as regards the frequencies of the components, the characteristic fine structure of the hydrogen lines and the effect which strong external electric or magnetic fields have on these lines. Now **Bohr**[1]) has shown in a recent paper, which contains a general exposure of the principles of the quantum theory of line spectra, that it is not only possible to get information as regards the frequencies of spectral lines, but that at the present state of the theory we are also able to draw some conclusions regarding the polarisation and intensities with which these lines appear, by considering the amplitudes of the harmonic vibrations in which the motion of the particles in an atomic system may be resolved. On professor **Bohr**'s proposal I have undertaken in the present paper to treat in detail the application of his ideas to the problem of the intensity of spectral lines in the special case of

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[1]) N. **Bohr**, On the Quantum Theory of Line Spectra. D. Kgl. Danske Vidensk. Selsk. Skr, naturvidensk. og mathem. Afd., 8. Række IV, 1, 1918. This paper will in the following be referred to as. N. **Bohr**, loc. cit.

the fine structure and in that of the Stark effect of the hydrogen lines, and to compare the result of the calculations with the observations.

The paper is divided in two Parts.

Part I deals with the problem of the determination of the values of the amplitudes of the harmonic vibrations in which the motion of certain mechanical systems may be resolved, and is divided in four chapters.

In § 1 a short account will be given of the theory of mechanical systems for which the Hamilton-Jacobi partial differential equation may be solved by means of separation of variables, and it will be shown how it is possible to reduce the calculation of the amplitudes of the harmonic vibrations, in which the motion of these systems may be resolved, to the evaluation of simple definite integrals.

In § 2 the method exposed in § 1 will be applied to the model of a hydrogen atom which is uninfluenced by external forces, assuming that the motion is governed by the laws of relativistic mechanics.

In § 3 the same method will be applied to the model of a hydrogen atom, which is subject to the influence of an external homogeneous electric field of force, the intensity of which is so large that it is possible with a high degree of approximation to determine the motion by means of ordinary Newtonian mechanics.

In § 4 the perturbing influence is considered which a very weak homogeneous electric field of force will have on the motion of the system considered in § 2.

Part II deals with the application of the calculations given in Part I to the problem of the intensities of spectral lines, and is divided in four chapters.

§ 5 contains, besides a brief exposure of the theory of stationary states of systems which allow of separation of variables, an account of Bohr's theory of the connection between the polarisation and intensities of spectral lines emitted by an atomic system and the amplitudes of the harmonic vibrations in which the motion of such a system may be resolved.

In § 6 a discussion is given of the application of the theory to the relative intensities of the components in which the hydrogen lines are split up in case of the Stark effect, on the basis of the formulae deduced in § 3.

§ 7 contains a discussion of the relative intensities with which the components of the fine structure of the hydrogen lines appear, based on the formulae deduced in § 2 and § 4.

In § 8 a brief discussion will be given of certain questions which stand in connection with the application of the theory to the problem of the Zeeman effect of the hydrogen lines.

Finally I wish to express my best thanks to professor N. Bohr, the creator of the beautiful theory underlying the present paper, for his kind interest and encouragement during the achievement of the work.

Part I.

Examination of the trigonometric series representing the motion of the electron in the hydrogen atom.

§ 1. General method applicable to conditionally periodic systems.

Consider a mechanical system of s degrees of freedom, the equations of motion of which are given by the set of canonical equations

$$\frac{dp_k}{dt} = -\frac{\partial E}{\partial q_k}, \qquad \frac{dq_k}{dt} = +\frac{\partial E}{\partial p_k}, \quad (k = 1, 2, \ldots s) \tag{2}$$

where $q_1, \ldots q_s$ is a set of generalised coordinates by means of which the positions in space of the particles of which the system consists are uniquely determined, while $p_1, \ldots p_s$ are the canonically conjugated momenta, and where E is the energy of the system, which is assumed to be a function of the p's and q's only. The so called Hamilton-Jacobi partial differential equation is then obtained by writing $p_i = \frac{\partial S}{\partial q_i}$ where S is a function of the q's, and by putting E, considered as a function of the q's and $\frac{\partial S}{\partial q}$'s, equal to a constant α_1;

$$E\left(q_1 \ldots q_s, \frac{\partial S}{\partial q_1} \ldots \frac{\partial S}{\partial q_s}\right) = \alpha_1. \tag{3}$$

A complete solution of this equation will contain, besides an additional constant C, $s - 1$ other integration constants $\alpha_2, \ldots \alpha_s$. Now it may happen that, for a suitable choice of orthogonal generalised positional coordinates $q_1, \ldots q_s$, it is possible to write a complete solution of equation (3) in the form

$$S = \Sigma S_k(q_k; \alpha_1, \ldots \alpha_s) + C, \tag{4}$$

where S_k depends on the α's and on q_k only. If this is the case it is said that the equation (3) allows of "separation of variables" for the special choice of coordinates under consideration, or briefly, that the system allows of separation of variables. For such a system $\frac{\partial S}{\partial q_k}$, as seen from (4), will depend on the corresponding q_k only; moreover remembering that in Newtonian, as well as in relativistic mechanics, E contains the p's in the form of a sum of squares, $\frac{\partial S}{\partial q_k}$ must necessarily be the square root of a one-valued function of q_k. Hence, denoting this one-valued function by F_k, we see that S may be written in the form

$$S = \sum_{1}^{s} \int^{q_k} \sqrt{F_k(q_k;\ a_1, \ldots a_s)}\, dq_k. \tag{5}$$

If the a's satisfy the condition that every function $F_k(q_k)$ possesses at least two successive finite real simple roots q_k' and q_k'', between which the value of the function is positive, the function S will, considered as a function of the q's, possess s moduli of periodicity, defined by

$$I_k = \int \sqrt{F_k(q_k;\ a_1, \ldots a_s)}\, dq_k, \quad (k = 1, \ldots s) \tag{6}$$

where the integration is taken once up and down between q_k' and q_k''. It is clear that the quantities I thus defined are continuous functions of the a's in the region where the a's satisfy the just mentioned condition, and that generally the a's may reversely be expressed as functions of the Is. Introducing these expressions for the a's in (5), we obtain an expression for S as a function of the q's and of its moduli of periodicity $I_1, \ldots I_s$;

$$S = \sum_{1}^{s} S_k(q_k;\ I_1, \ldots I_s) = \sum_{1}^{s} \int^{q_k} \sqrt{F_k(q_k; I_1, \ldots I_s)}\, dq_k. \tag{7}$$

Let us now define a transformation of variables

$$p_k = \frac{\partial S}{\partial q_k}, \quad w_k = \frac{\partial S}{\partial I_k}, \quad (k = 1, \ldots s) \tag{8}$$

which may be considered as transforming the variables $q_1, \ldots q_s, p_1, \ldots p_s$, which originally described the positions and velocities of all particles of the system at any moment, into the variables $I_1, \ldots I_s, w_1 \ldots w_s$. It is easily seen from the periodicity properties of S that w_k, considered as a function of the q's and I's, will increase by 1 if q_k continuously oscillates once up and down between its limits q_k' and q_k'' and returns to its original value; while if one of the other q's performs a similar oscillation between its limits, w_k will return to its original value. From this we see that the q's, and also the p's, considered as functions of the w's and the I's, are one-valued functions of these variables, which are periodic in every of the w's with period 1, *i. e.* they assume their original values if the w's increase by arbitrary integers. The q's may therefore be expanded in an s-double Fourier series of the form

$$q_k = \Sigma\, C^{(k)}_{\tau_1, \ldots \tau_s}\, e^{2\pi i(\tau_1 w_1 + \ldots \tau_s w_s)}, \tag{9}$$

where the summation is to be extended over all positive and negative entire values of the τ's, and where the C's depend on the I's only. Similar expansions will hold for the p's.

Now, according to a well known theorem of JACOBI, the transformation (8) leaves the canonical form of the equations of motion unaltered, *i. e.* expressing by means of (8) E as a function of the I's and w's, the variations of the latter quantities with the time are given by

$$\frac{dI_k}{dt} = -\frac{\partial E}{\partial w_k}, \quad \frac{dw_k}{dt} = \frac{\partial E}{\partial I_k}. \quad (k = 1, \dots s) \tag{10}$$

Now E is, according to (3), equal to a_1, and consequently a function of the I's only. The solution of the equations (10) is therefore immediately obtained by putting

$$I_k = \text{constant}, \quad w_k = \omega_k t + \delta_k, \quad \omega_k = \frac{\partial E}{\partial I_k}, \quad (k = 1, \dots s) \tag{11}$$

where the δ's are a set of arbitrary constants, while the ω's obviously depend on the constants I only. We thus see that there exists for the mechanical system under consideration a family of solutions in which each of the q's oscillates between two limiting values depending on the constants $I_1, \dots I_s$. It is easily seen that ω_k represents the mean number of oscillations which the coordinate q_k performs between its limits in unit time, taken over a time interval in which a very large number of such oscillations are performed. The variables w are called "angle variables"; the quantities I, defined as the moduli of periodicity of the function S, are canonically conjugated to the w's. Mechanical systems for which the motion may be described by a set of angle variables $w_1, \dots w_s$ and canonically conjugated I's, possessing the properties just considered, are called "conditionally periodic".

Since the q's describe the positions of the particles in space uniquely, the displacement x of any of these particles in any direction in space will be a one-valued function of the q's. Considered as a function of the I's and w's, the displacement x will therefore, just as each of the q's, be periodic in each of the w's with period 1, and may consequently also be expressed by a trigonometric series of the form

$$x = \Sigma C_{\tau_1, \dots \tau_s} e^{2\pi i (\tau_1 w_1 + \dots \tau_s w_s)},$$

where the coefficients C depend on the I's only and where the summation is to be extended over all positive and negative entire values of the τ's. Introducing in this expression the values of the w's given by (11), we obtain for x, considered as a function of the time, an expression of the type

$$x = \Sigma C_{\tau_1, \dots \tau_s} e^{2\pi i \{(\tau_1 \omega_1 + \dots \tau_s \omega_s) t + c_{\tau_1, \dots \tau_s}\}}, \tag{12}$$

where the C's and c's are constants, showing that the motion of the particles of a conditionally periodic system may be resolved in a number of harmonic vibrations of frequencies $|\tau_1 \omega_1 + \dots \tau_s \omega_s|$ the amplitudes of which depend on the quantities I_k only.

For the systems under consideration the number of the quantities ω, which may be denoted as the "fundamental frequencies" characterising the motion, is