

H. A. KRAMERS

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SCIENTIFIC
PAPERS**



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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.

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TABLE OF CONTENTS

H. A. Kramers, <i>Intensities of spectral lines</i> . (Doctoral Thesis) D. Kgl. Danske Vidensk. Selsk. Skrifter, naturvidensk. og mathem. Afd., (8) 3, 284–386 (1919)	3
H. A. K., <i>Über den Einfluss eines elektrischen Feldes auf die Feinstruktur der Wasserstofflinien</i> . Z. Phys. 3, 199–223 (1920)	109
H. A. K., <i>On the application of Einstein's theory of gravitation to a stationary field of gravitation</i> . Proc. Acad. Amst. 23, 1052–1073 (1921)	134
H. A. K., <i>On the theory of X-ray absorption and of the continuous X-ray spectrum</i> . Phil. Mag. 46, 836–871 (1923)	156
H. A. K., <i>Über das Modell des Heliumatoms</i> . Z. Phys. 13, 312–341 (1923)	192
H. A. K., <i>Über die Quantelung rotierender Moleküle</i> . Z. Phys. 13, 343–350 (1923)	223
H. A. K. und W. Pauli jr., <i>Zur Theorie der Bandenspektren</i> . Z. Phys. 13, 351–367 (1923)	231
J. A. Christiansen and H. A. K., <i>Über die Geschwindigkeit chemischer Reaktionen</i> . Z. Phys. Chem. 104, 451–471 (1923)	249
N. Bohr, H. A. K. und J. C. Slater, <i>Über die Quantentheorie der Strahlung</i> . Z. Phys. 24, 69–87 (1924)	271
H. A. K., <i>The law of dispersion and Bohr's theory of spectra</i> . Nature 113, 673–674 (1924)	290
H. A. K., <i>The quantum theory of dispersion</i> . Nature 114, 310–311 (1924)	292
H.A.K. und W. Heisenberg, <i>Über die Streuung von Strahlung durch Atome</i> . Z. Phys. 31, 681–708 (1925)	293
H. A. K., <i>On the behaviour of atoms in an electromagnetic wave field</i> . Skand. Mat. Kongress 143–153 (1925)	321
H. A. K., <i>La diffusion de la lumière par les atomes</i> . Atti Congr. Intern. Fisici, Como, 2, 545–557 (1927)	333
H. A. K., <i>Die Dispersion und Absorption von Röntgenstrahlen</i> . Phys. Z. 30, 522–523 (1929)	347
H. A. K., <i>Wellenmechanik und halbzahlige Quantisierung</i> . Z. Phys. 39, 828–840 (1926)	348
H. A.K., <i>Investigations on the free energy of a mixture of ions</i> . Proc. Acad. Amst. 30, 145–158 (1927)	361
L. S. Ornstein und H. A. K., <i>Zur kinetischen Herleitung des Fermischen Verteilungsgesetzes</i> . Z. Phys. 42, 481–486 (1927)	375
R. de L. Kronig und H. A.K., <i>Zur Theorie der Absorption und Dispersion in den Röntgen-spektren</i> . Z. Phys. 48, 174–179 (1928)	382
H. A. K., <i>Zur Struktur der Multipllett-S-Zustände in zweiatomigen Molekülen. I</i> . Z. Phys. 53, 422–428 (1929)	388
H. A. K., <i>Zur Aufspaltung von Multipllett-S-Termen in zweiatomigen Molekülen. II</i> . Z. Phys. 53, 429–438 (1929)	395
H. A. K., <i>Zur Ableitung der quantenmechanischen Intensitätsformeln</i> . Proc. Acad. Amst. 33, 953–958 (1930)	405
H. A. K., <i>Die Multiplettaufspaltung bei Koppelung zweier Vektoren</i> . Proc. Acad. Amst. 34, 965–976 (1931)	411
H. A. K. und G. P. Ittmann, <i>Zur Quantelung des asymmetrischen Kreisels. I</i> . Z. Phys. 53, 553–565 (1929)	423
H. A. K. und G. P. Ittmann, <i>Zur Quantelung des asymmetrischen Kreisels. II</i> . Z. Phys. 58, 217–231 (1929)	437

H. A. K. und G. P. Ittmann, <i>Zur Quantung des asymmetrischen Kreisels. III.</i> Z. Phys. 60, 663–681 (1930)	453
H. C. Brinkman und H. A. K., <i>Zur Theorie der Einfangung von Elektronen durch α-Teilchen.</i> Proc. Acad. Amst. 33, 973–984 (1930)	472
H. A. K., <i>La rotation paramagnétique du plan de polarisation dans les cristaux uniaxes de terres rares.</i> Proc. Acad. Amst. 32, 1176–1189 [Commun. K. O. Lab. 18 Suppl. 68b, 19–36] (1929)	485
H. A. K. et J. Becquerel, <i>La rotation paramagnétique du plan de polarisation dans les cristaux de tysonite et de xénotime.</i> Proc. Acad. Amst. 32, 1190–1198 [Commun. K. O. Lab. 18 Suppl. 68c, 39–50] (1929)	503
J. Becquerel, W. J. de Haas and H. A. K., <i>Experimental verification of the theory of the paramagnetic rotatory polarisation in the crystals of xenotime.</i> Proc. Acad. Amst. 32, 1206–1211 [Commun. K. O. Lab. 18, No. 204b, 15–21] (1929)	515
H. A. K., <i>Théorie générale de la rotation paramagnétique dans les cristaux.</i> Proc. Acad. Amst. 33, 959–972 (1930)	522
H. A. K., <i>Propriétés paramagnétiques de cristaux de terres rares, I–II.</i> Proc. Acad. Amst. 35, 1272–1281 (1932); Proc. Acad. Amst. 36, 17–26 (1933)	536
H. A. K., <i>Paramagnetische Eigenschaften der Kristalle seltener Erden.</i> Leipziger Vorträge, Magnetismus 43–58. (Hirzel, Leipzig 1933)	557
H. A. K., <i>L'interaction entre les atomes magnétogènes dans un cristal paramagnétique.</i> Physica 1, 182–192 (1934)	574
W. J. de Haas, E. C. Wiersma and H. A. K., <i>Experiments on adiabatic cooling of paramagnetic salts in magnetic fields.</i> Physica 1, 1–13 [Commun. K. O. Lab. 21, No. 229a, 1–13] (1934)	585
G. Heller und H. A. K., <i>Ein klassisches Modell des Ferromagnetikums und seine nachträgliche Quantisierung im Gebiete tiefer Temperaturen.</i> Proc. Acad. Amst. 37, 378–385 (1934)	598
H. A. K., <i>Zur Theorie des Ferromagnetismus.</i> Rapp. et Comm. 7e Congr. intern. du froid, La Haye-A'dam, no. 29; [Commun. K. O. Lab. 22, Suppl. 83, 1–22] (1936)	607
Jean Becquerel, J. van den Handel et H. A. K., <i>Sur l'aimantation et le pouvoir rotatoire paramagnétique du sulfate de nickel hexahydraté α.</i> Physica 17, 717–736 [Commun. K. O. Lab. 286b, 1–20] (1951)	629
A. R. Olson and H. A. K., <i>The normal vibrations of acetylene.</i> J. Amer. Chem. Soc. 54, 136–138 (1932)	650
E. M. van Engers und H. A. K., <i>Zur Anwendung der Methode der Phasenintegrale auf das Wasserstoffmolekülion.</i> Z. Phys. 82, 328–336 (1933)	654
H. A. K., C. C. Jonker und T. Koopmans, <i>Wigners Erweiterung des Thomas-Kuhnschen Summensatzes für ein Elektron in einem Zentralfeld.</i> Z. Phys. 80, 178–182 (1933)	664
H. A. K., <i>Das Eigenwertproblem im eindimensionalen periodischen Kraftfeld.</i> Physica 2, 483–490 (1935)	669
P. A. Coenen und H. A. K., <i>Zum Intensitätsverlauf in der diffusen Serie des Kaliums.</i> Physica 3, 341–345 (1936)	677
H. A. K., <i>On the classical theory of the spinning electron.</i> Physica 1, 825–828 (1934)	683
H. A. K., <i>Classical relativistic spin theory and its quantization.</i> Verh. Zeeman jubil. 403–412 (1935)	687
H. A. K., <i>The use of charge-conjugated wave-functions in the hole-theory of the electron.</i> Proc. Acad. Amst. 40, 814–823 (1937)	697

TABLE OF CONTENTS

H. A. K., F. J. Belinfante und J. K. Lubański, <i>Über freie Teilchen mit nichtverschwindender Masse und beliebiger Spinquantenzahl.</i> Physica 8, 597–626 (1941)	707
H. A. K., <i>Didaktisches zur Verwendung der grand Ensembles in der Statistik.</i> Proc. Acad. Amst. 41, 10–24 (1938)	738
H. A. K., <i>Brownian motion in a field of force and the diffusion model of chemical reactions.</i> Physica 7, 284–304 (1940)	754
H. A. K., <i>The behavior of macromolecules in inhomogeneous flow.</i> [<i>Het gedrag van macromoleculen in een stroomende vloeistof.</i> Physica 11, 1–19 (1944)]. J. Chem. Phys. 14, 415–424 (1946)	775
H. A. K. and C. H. Wannier, <i>Statistics of the twodimensional ferromagnet. Part. I.</i> Phys. Rev. (2) 60, 252–262 (1941)	786
H. A. K. and C. H. Wannier, <i>Statistics of the twodimensional ferromagnet. Part. II.</i> Phys. Rev. (2) 60, 263–276 (1941)	797
H. A. K. et D. ter Haar, <i>Sur les tensions dans la cornée.</i> Physica 9, 234–240 (1942)	812
H. A. K., <i>On multipole radiation.</i> Physica 10, 261–272 (1943)	819
H. A. K., <i>Die Wechselwirkung zwischen geladenen Teilchen und Strahlungsfeld.</i> Nuovo Cimento, 15, 108–114 (1938)	831
H. A. K., <i>Fundamental difficulties of a theory of particles.</i> [<i>Principieele moeilijkheden van een theorie der deeltjes.</i>] Ned. T. Natuurk. 11, 134–147 (1944)	838
H. A. K., <i>Non-relativistic quantum-electrodynamics and correspondence principle.</i> Solvay Congress 1948 (Rapport et Discussions, Bruxelles 1950)	845
H. A. K. and J. Kistemaker, <i>On the slip of a diffusing gas mixture along a wall.</i> Physica 10, 699–713 (1943)	871
H. A. K., <i>On the behaviour of a gas near a wall.</i> Nuovo Cim. Suppl. 6, 297–304 (1949)	887
H. A. K. and D. ter Haar, <i>Condensation in interstellar space.</i> Bull. Astron. Inst. Netherl., 10, 137–146 (1946)	895
H. A. K., <i>The stopping power of a metal for alpha-particles.</i> Physica 13, 401–412 (1947)	905
H. A. K., <i>On a modification of Jaffé's theory of columnionization.</i> Physica 18, 665–675 (1952)	917
H. A. K., <i>Remarks on the perturbation formulae of Brillouin and Wigner.</i> Courant Anniversary Volume, 205–210 (1948)	929
H. A. K., <i>Vibrations of a gas column.</i> Physica 15, 971–984 (1949)	935
H. A. K., <i>On the quantum theory of antiferromagnetism.</i> Physica 18, 101–103 (1952)	949
H. A. K., <i>Some reflections on phonons and rotons.</i> Physica 18, 653–664 (1952)	953

My own pet notion is that in the world of human thought generally, and in physical science particularly, the most important and most fruitful concepts are those to which it is impossible to attach a well-defined meaning

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 COMPO-
NENTS OF THE FINE STRUCTURE AND OF THE STARK EFFECT
OF THE LINES OF THE HYDROGEN SPECTRUM

BY

H. A. KRAMERS

WITH FOUR PLATES

D. KGL. DANSKE VIDENSK. SÆLSK. SKRIFTER. NATURVIDENSK. OG MATH. AFD., 8. RÆKKE, III. 3



KØBENHAVN

HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL

BIANCO LUNOS BOGTRYKKERI

1919

CONTENT

Introduction	Page 3 (287)
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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	5 (289)
§ 2. Hydrogen atom undisturbed by external influences	10 (294)
§ 3. Hydrogen atom under the influence of a strong homogeneous electric field of force	16 (300)
§ 4. Hydrogen atom under the influence of a weak homogeneous electric field of force	26 (310)

Part II.

Discussion of the intensities of the components of the hydrogen lines.

§ 5. Application of the quantum theory to the problem of the intensity of spectral lines	38 (322)
§ 6. The Stark effect of the hydrogen lines	49 (333)
§ 7. The fine structure of the hydrogen lines	68 (352)
I. The relative intensities of the components of the fine structure of the lines of the spectrum of the undisturbed hydrogen atom	71 (355)
II. Effect of a weak electric field on the fine structure	75 (359)
III. Comparison of the theory with the observations on the fine structure	84 (368)
§ 8. The effect of a magnetic field on the fine structure of the hydrogen lines	94 (378)

DESCRIPTION OF PLATES*

Plate I and Plate II. Stark effect of hydrogen lines. Fig. 1, 2, 3 and 4. Comparison for H_α , H_β , H_γ and H_δ of theoretical estimate of relative intensities of components with STARK's observations (see page 55).

Fig. 5. Reproduction of STARK's photographs of effect of electric field on H_β , H_γ and H_δ (see page 54).

Fig. 6. Theoretical estimate of effect of electric field on hydrogen line H_ϵ (see page 63).

Plate III. Stark effect of helium lines. Fig. 7, 8, 9. Theoretical aspect of electric resolution of 4686 Å, 3203 Å, 2733 Å, compared with the rough analysis of this resolution observed by NYQUIST and by STARK, the observed components being indicated by arrows (see page 64).

In all figures of theoretical estimate of intensities of Stark effect components, components represented by dots mean that the theoretical estimate for the intensity of these components is too small to be conveniently represented on the same scale as other components.

Plate IV. Fine structure of hydrogen and helium lines. Fig. 10, 11, 13. Theoretical fine structure of helium lines 4686 Å and 3203 Å, and of hydrogen line H_α , compared with PASCHEN's observations. Lengths of drawn components proportional to estimate of intensities of components of fine structure for undisturbed atom. For the sake of convenience, however, component (04 → 03) in fig. 10 and component (03 → 02) in fig. 13 are represented by lines 2.5 times shorter than that corresponding to scale of other components. Dotted lines represent estimates of intensities of new components corresponding to electric field of 600 Volt/cm in fig. 10, of 90 Volt/cm in fig. 11 and of 100 Volt/cm in fig. 13 (see pages 85, 90 and 93).

Fig. 12. Theoretical estimate of intensities of original components of fine structure of helium line 5411 Å, compared with PASCHEN's observations (see page 91).

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.

* 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 unifrequent, and that its frequency is given by

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

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 BOHR¹⁾ 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

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

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

where q_1, \dots, 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, \dots, 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 a_1 ;

$$E\left(q_1, \dots, q_s, \frac{\partial S}{\partial q_1}, \dots, \frac{\partial S}{\partial q_s}\right) = a_1. \quad (3)$$

A complete solution of this equation will contain, besides an additional constant C , $s - 1$ other integration constants a_2, \dots, a_s . Now it may happen that, for a suitable choice of orthogonal generalised positional coordinates q_1, \dots, q_s , it is possible to write a complete solution of equation (3) in the form

$$S = \sum S_k(q_k; a_1, \dots, a_s) + C, \quad (4)$$

where S_k depends on the a '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

$$S = \sum_1^s \int^{q_k} \sqrt{F_k(q_k; a_1, \dots, a_s)} dq_k. \quad (5)$$

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

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

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 I s. 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, \dots, I_s ;

$$S = \sum_1^s S_k(q_k; I_1, \dots, I_s) = \sum_1^s \int^{q_k} \sqrt{F_k(q_k; I_1, \dots, I_s)} dq_k. \quad (7)$$

Let us now define a transformation of variables

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

which may be considered as transforming the variables $q_1, \dots, q_s, p_1, \dots, p_s$, which originally described the positions and velocities of all particles of the system at any moment, into the variables $I_1, \dots, I_s, w_1, \dots, w_s$. 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

$$q_k = \sum C_{\tau_1, \dots, \tau_s}^{(k)} e^{2\pi i(\tau_1 w_1 + \dots + \tau_s w_s)}, \quad (9)$$

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

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

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

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

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

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

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

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

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