The Ehrenfest Adiabatic Hypothesis and the Old Quantum Theory, before Bohr

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Paul Ehrenfest at University of Leiden, c.1919

Outline

1. Antecedents of the Ehrenfest's adiabatic hypothesis (1905-1914).
2. "On the adiabatic changes of a system in connection with the quantum theory" (1916).
3. First reactions, before Bohr's irruption (1916-1918).
4. Adiabatic hypothesis in 1918 Bohr's work.

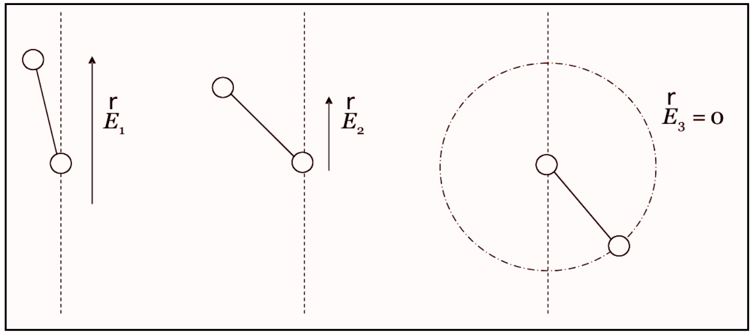
Ehrenfest towards the adiabatic hypothesis, I (1905-1911).

- **1905-1906**: **Criticism of the Planck's theory of black-body radiation.**
  - **1905**: "Über die physikalischen Voraussetzungen der Planck'schen Theorie der irreversiblen Strahlungsvorgänge". *Ak. Wiss., Vienna. Sitz.,* 1301-1314.
  - **1906**: "Zur Planckschen Strahlungstheorie". *Physikalische Zeits.*, *7*, 528-532**.**

- **1907-1911**: **Statistical analysis of radiation.**
  - **1911:** "Welche Züge der Lichtquantenhypothese spielen in der Theorie der Wärmestrahlung eine wesentliche Rolle?". *Annalen der Physik*, *36,* 91-118*.*
  - **By imposing** $S = k \log W$ **, he obtains Wien's displacement law.**
  - **He uses the adiabatic invariant:** $\frac{E}{\nu}$
  - **He proves that the quantization must be applied to adiabatic invariants, and justifies Planck's quantum:** $\frac{E}{\nu} = 0, h, 2h, \ldots$

Ehrenfest towards the adiabatic hypothesis, II (1912-1914).

- **1912-1913**: **Extension of the results to any periodic motion.**
  - **1913:** "Bemerkung betreffs der spezifischen Wärme zweiatomiger Gase". *Verhandlungen der Deutschen Physikalischen Gesellsachft*, *12*, 451-457.
  - **1913:** "A mechanical theorem of Boltzmann and its relation to the theory of energy quanta". *Proceedings of the Amsterdam Academy*, *16*, 591-597.
- **Connection between allowed motions of different systems.**



- **1914**: **Inquiries on the validity of Boltzmann principle:** $S = k \log W$
  - **1914:** "Zum Boltzmannschen Entropie-Wahrscheinlichkeits-Theorem". *Physikalische Zeitschrift*, *15*, 347-352.

Baptism of the adiabatic hypothesis (1914)

"Beiträge zur Quantentheorie". *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 16, 820-828.

Beiträge zur Quantentheorie;

von A. Einstein.

(Vorgetragen in der Sitzung vom 24. Juli 1914.)
(Vgl. oben S. 735.)

Im nachfolgenden sind zwei Betrachtungen wiedergegeben, die insofern zusammengehören, als sie zeigen, inwieweit die wichtigsten neueren Ergebnisse der Wärmelehre, nämlich die PLANCKsche Strahlungsformel und das NERNSTsche Theorem ohne Zuhilfenahme des BOLTZMANNschen Prinzips auf rein thermodynamischem Wege mit Benutzung des Grundgedankens der Quantentheorie abgeleitet werden können. Insoweit die im folgenden gegebenen Überlegungen der Wirklichkeit entsprechen, gilt das NERNSTsche Theorem für chemisch reine, kristallisierte Stoffe, nicht aber für Mischkristalle. Auf amorphe Stoffe läßt sich wegen der über das Wesen des amorphen Zustandes herrschenden Unklarheit nichts aussagen.

Zur Rechtfertigung des hier vorliegenden Versuches, das NERNSTsche Theorem theoretisch zu erfassen, muß ich einleitend bemerken, daß alle Bemühungen, das NERNSTsche Theorem auf thermodynamischem Wege unter Benutzung des Erfahrungssatzes vom Verschwinden der Wärmekapazität bei $T = 0$ theoretisch abzuleiten, als mißglückt anzusehen sind. Ich bin gerne bereit, diese Behauptung den einzelnen versuchten Beweisen gegenüber zu begründen, falls dies von Kollegen gewünscht wird.

§ 1. Thermodynamische Ableitung der PLANCKschen Strahlungsformel. Wir betrachten ein chemisch einheitliches Gas, dessen Moleküle je einen Resonator[1]) tragen. Die Energie dieses Resonators soll nicht jeden beliebigen Wert annehmen können, sondern nur gewisse diskrete Werte ε_σ (auf das Mol bezogen). Ich will mir nun erlauben, zwei Moleküle als chemisch verschieden, d. h. als prinzipiell durch semipermeable Wände

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[1]) Unter „Resonator" sei hier allgemein ein Träger innerer Molekularenergie von vorläufig nicht näher präzisierter Beschaffenheit verstanden.

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“On the adiabatic changes of a system in connection with the quantum theory” (1916)

Proceedings of the Amsterdam Academy
19 (1916), 576–597

Annalen der Physik
51 (1916), 327-352

Philosophical Magazine
33 (1917), 500-513.

“On the adiabatic changes of a system in connection with the quantum theory” (1916)

Contents:

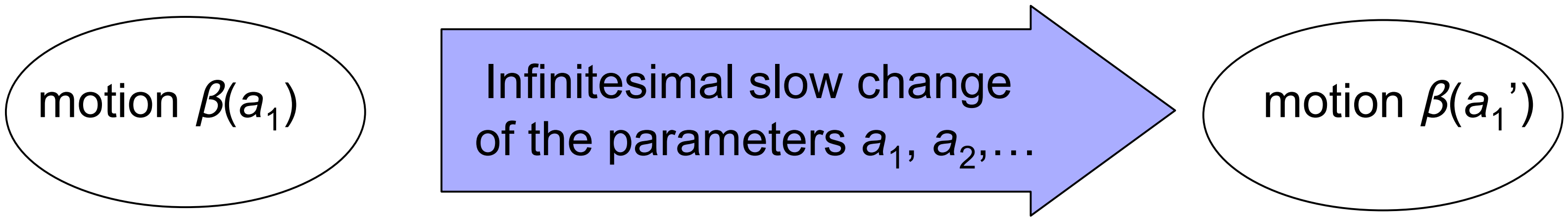
1. Formulation of the hypothesis.
2. Relation with quantum rules.
3. Difficulties: singular motions.
4. Compatibility with the statistical interpretation of the second law of thermodynamics.

Formulation of the hypothesis

Reversible adiabatic influence on a system:

•Potential energy depends on the coordinates q_1, q_2,.. and "slowly changing parameters" a_1, a_2,…

•Kinetic energy T is an homogeneous quadratic function of the velocities.



Given the admissible motions for the parameters a_{1o}, a_{2o},… ***"For a general set of parameter values** a_1, a_2,… **only those motions are possible that are adiabatically related with motions possible for the special values** a_{1o}, a_{2o},…"*

Adiabatic invariants

If we assume that for certain admissible motions a ***definite adiabatic invariant*** Ω *has the discrete numerical values* Ω_1, Ω_2 *for the special values* a_{1o}, a_{2o},..., *then it has exactly the same values for the admissible motions belonging to the arbitrary values of the parameters* a_1, a_2,...

An adiabatic invariant for periodic motions:

$$\delta' \int_0^P dt\, 2T = 0 \quad \Rightarrow \quad \frac{2\overline{T}}{\nu} \quad \xrightarrow{\text{Harmonic vibration}} \quad \frac{\varepsilon}{\nu}$$

One-dimensional systems

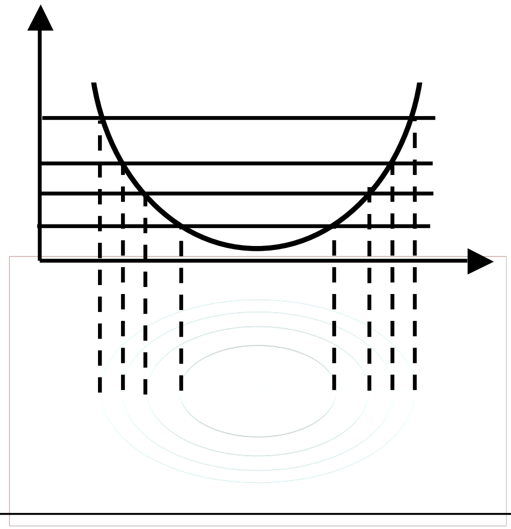
Resonator with a non-linear equation of motion:

$$\ddot{q} - (\nu_o^2 q + a_1^2 q^2 + a_2^2 q^3 + \dots)$$

If, $a_1 = a_2 = \ldots = 0$:

$$\frac{\varepsilon}{\nu_o} = \frac{\overline{2T}}{\nu_o} = \iint dq\,dp = 0, h, 2h, \ldots$$

Planck resonator

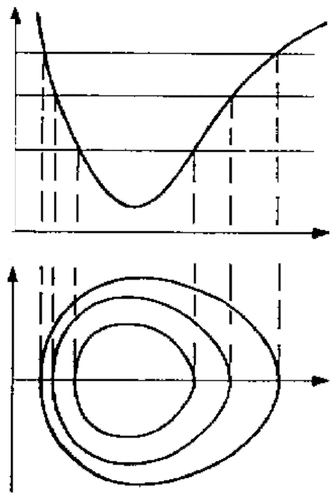


Adiabatic transformation

If, $a_1 \neq a_2 \neq \ldots \neq 0$:

$$\frac{\varepsilon}{\nu} = \frac{\overline{2T}}{\nu} = \iint dq\,dp = 0, h, 2h, \ldots$$

Debye's anharmonic oscilator



More than one degree of freedom

Potential $\chi(r, a_1, a_2, \ldots)$ of central attracting force in polar coordinates:

$$\left.\begin{aligned} m\ddot{r} - mr\dot{\varphi}^2 + \frac{d\chi}{dr} = 0 \\ \frac{d}{dt}(mr^2\dot{\varphi}) = 0 \end{aligned}\right\} \quad \text{As } mr^2\dot{\varphi} = p_2 = const., \quad \left\{\begin{aligned} m\ddot{r} + \frac{d\Phi}{dr} = 0 \\ \Phi = \frac{p_2^2}{2mr^2} + \chi(r, a_1, a_2) \end{aligned}\right.$$

By the Ehrenfest's adiabatic hypothesis:

$$\frac{\overline{2T}}{\nu_1} = \iint dq_1\, dp_1 = ad.\ inv.$$

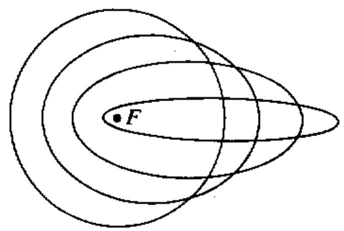
$$\frac{\overline{2T}}{\nu_2} = \iint dq_2\, dp_2 = ad.\ inv.$$

where q_1 is the radial variable, and q_2 the angular variable

Sommerfeld quantization:

$$\iint dq_1 dp_1 = 0, h, \ldots, n_1 h, \ldots$$

$$\iint dq_2 dp_2 = 0, h, \ldots, n_2 h, \ldots$$

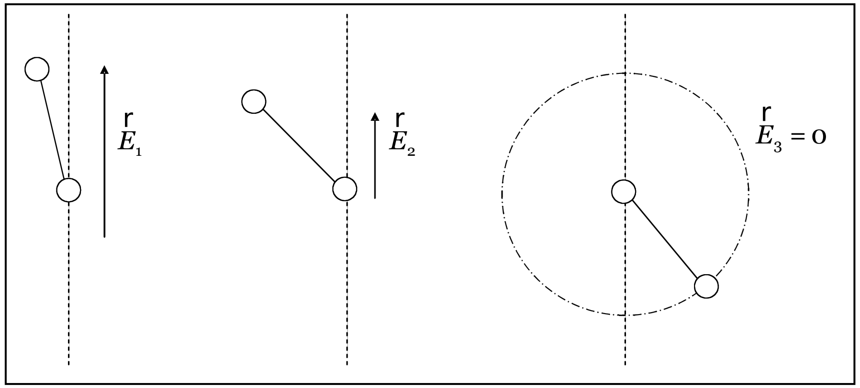


This procedure is valid for all central forces

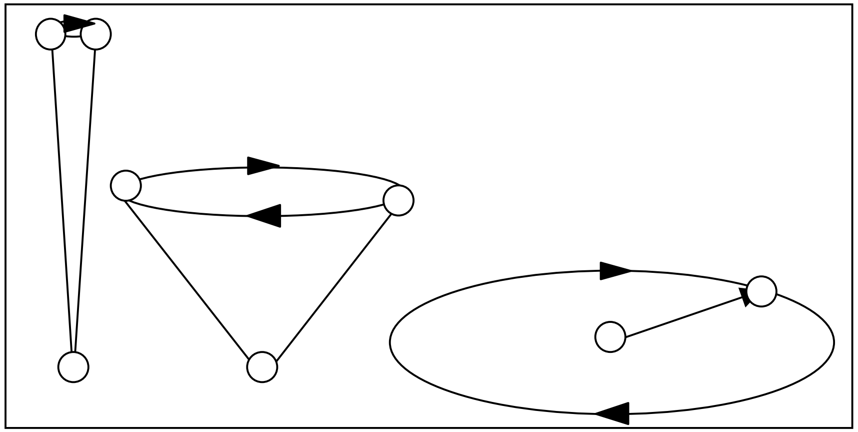
Difficulties: singular motions

Electric dipole

Path 1: Indetermination in the final motion, as the dipole passes through a singular motion during the adiabatic transformation:

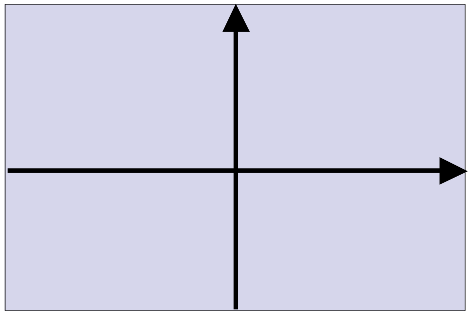


Path 2: No indetermination in the final motion, as the dipole doesn't pass through a singular motion during the adiabatic transformation



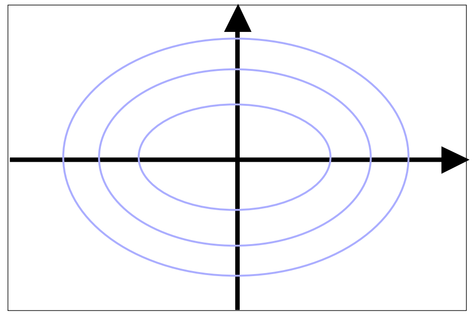
Connection to the statistical basis of the second law of thermodynamics

Boltzmann statistics



• All initial conditions –compatible with constraints- are possible.
• Regions with equal area in the phase - space are equally probable.

Planck statistics



• Not all initial conditions compatible with constraints are possible.
• Possible motions are equally probable

Does the Boltzmann principle remain valid in the quantum theory?

¿$S = k \log W$?

•One degree of freedom: if $\frac{\overline{2T}}{\nu} = \iint dq\,dp =$ fixed values.

•More than one degree of freedom: it's still doubtful

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Multiperiodic systems

•$\iint dp_i dq_i = 0, h, \ldots, n_i h, \ldots$ in certain cases depends on the coordenate system.

•**Epstein and Schwarzschild** use H-J theory $H\left(q_1,\ldots,q_n;\frac{\partial S}{\partial q_1},\ldots,\frac{\partial S}{\partial q_n}\right)+\frac{\partial S}{\partial t}=0$

If the system is separable,

$$H_i\left(q_i;\frac{\partial S_i}{\partial q_i};\alpha_1,\ldots,\alpha_n\right)+\frac{\partial S_i}{\partial t}=0$$

$S=\sum_i S_i(q_i;\alpha_1,\ldots,\alpha_n:t)$, where

$\alpha_1,\ldots,\alpha_n$ are motion constants.

⇒

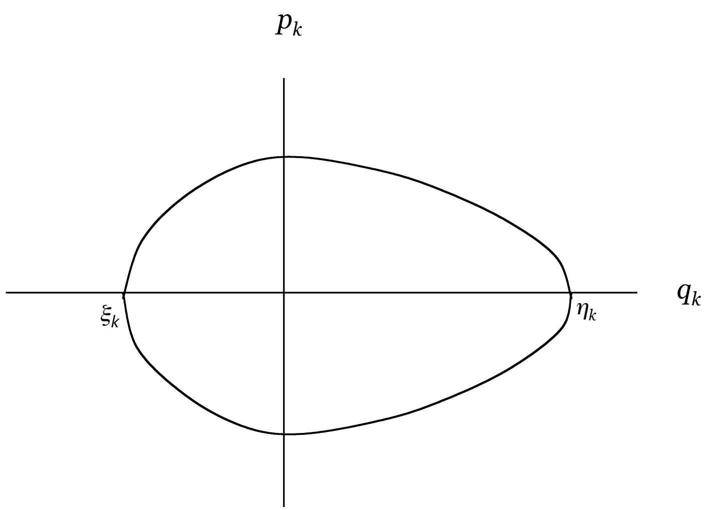
$$I_i=\oint p_i dq_i = n_i h$$

Are the phase integrals adiabatically invariant?

Burgers (1916-1917)

Are $I_k = \oint p_k dq_k$ adiabatically invariant?

For separable systems, there are *p* independent motions, with characteristic frequencies ν_i:



•<u>Non degenerate motion</u>: $\sum_{i=1}^{p} m_i \nu_i \neq 0$

H-J equation is separable only in one coordinate system

•<u>Degenerate motion</u>: $\sum_{i=1}^{p} m_i \nu_i = 0$

H-J equation is separable in more than one coordinate system

•In the case of non degenerate motions, $\delta I_k = \delta \oint dq_k dp_k = 0$ **always.**

•In the case of degenerate motions, $\delta Y_s = \delta \sum_k r_s^k I_k = 0$ **only in certain cases.**

Contributions to adiabatic hypothesis, before Bohr

•**Burgers** (1916-1917; *Proceedings of the Amsterdam Academy, **20***, 149-157, 158-162, 163-169): He proves the adiabatic invariance of phase integrals for non degenerate multiperiodic motions.

•**Kramers** (1917; *Unpublished manuscript*): He studies the non degenerate motions more depthly and he considers also the relativistic case.

•**Krutkow** (1919; *Proceedings of the Amsterdam Academy, **21***, 1112-1123): He proposes a way to find adiabatic invariants.

Uses of the adiabatic hypothesis (1917-1918)

- Related to statistical implications of the adiabatic hypothesis:
  - **Smekal** (1918; *Physikalische Zeitschrift, **19**,* 7-10*,* 137-142).
- Applications:
  - **Planck** (1918**;** *Preussische Akademie der Wissenschaften,* 1166-1174). Quantization of the asymmetric spinning top.
  - **Sommerfeld** (1917**;** *Annalen der Physik, **53**,* 497-550). On light's dispersion.

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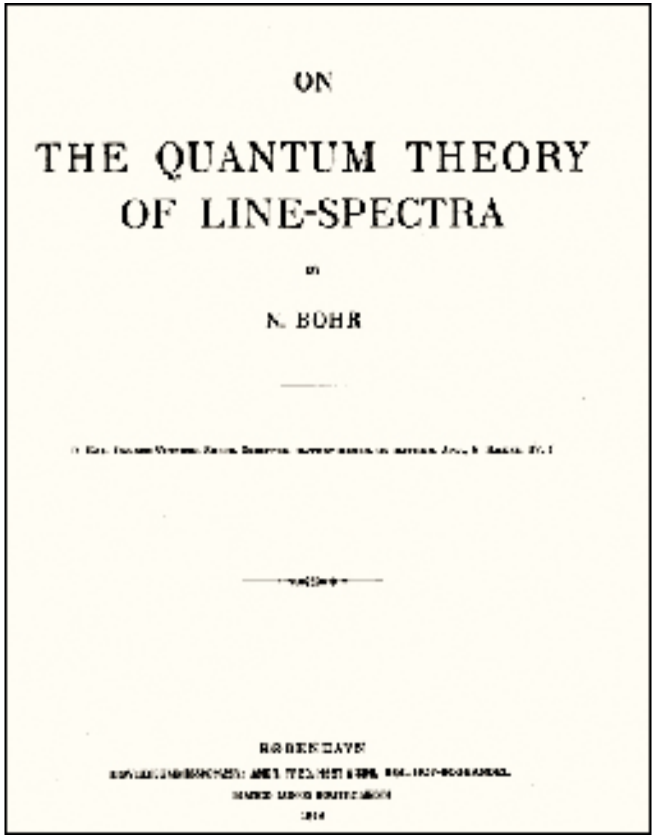
The adiabatic hypothesis in Bohr’s paper of 1918


ON

THE QUANTUM THEORY
OF LINE-SPECTRA

N. BOHR

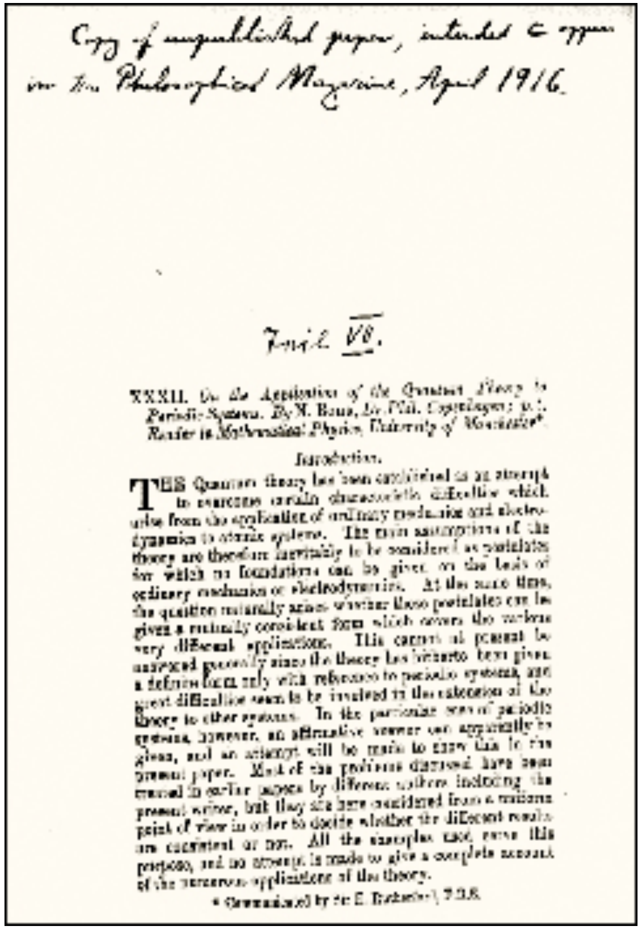
KØBENHAVN

“On the Quantum Theory of Line Spectra.

Part I”.

Det Kongelige Danske Videnskabernes Selskab. Matematisk-Fysiske Meddelser*, 4(1), 1-36*

Bohr's unpublished theory of 1916



Copy of unpublished paper, intended to appear in the Philosophical Magazine, April 1916.

XXXII. *On the Application of the Quantum Theory to Periodic Systems.* By N. Bohr, *Dr. Phil. Copenhagen;* [illegible] *Reader in Mathematical Physics, University of Manchester**.

Introduction.

The Quantum theory has been [illegible] as an attempt to overcome certain characteristic difficulties which arise from the application of ordinary mechanics and electrodynamics to atomic systems. The main assumptions of the theory are therefore inevitably to be considered as postulates for which no foundations can be given on the basis of ordinary mechanics or electrodynamics. At the same time, the question naturally arises whether these postulates can be given a mutually consistent form which covers the various very different applications. This cannot at present be answered generally since the theory has hitherto been given a definite form only with reference to periodic systems, and great difficulties seem to be involved in the extension of the theory to other systems. In the particular case of periodic systems, however, an affirmative answer can apparently be given, and an attempt will be made to show this in the present paper. Most of the problems discussed have been treated in earlier papers by different authors including the present writer, but they are here considered from a uniform point of view in order to decide whether the different results are consistent or not. All the examples [illegible] this purpose, and no attempt is made to give a complete account of the numerous applications of the theory.

* Communicated by Sir E. Rutherford, F.R.S.

"On the Application of the Quantum Theory to Periodic Systems"

…intended to appear in the Philosophical Magazine*, April 1916.*

Bohr uses Ehrenfest's adiabatic invariant to characterize stationary states:

$$\frac{\overline{T}}{\omega} = \oint T dt = \frac{1}{2} nh$$

Principle of the "mechanical transformability" (1918)

- **Stability of orbits:**

> *... the motion of an atomic system in the stationary states can be calculated by direct application of ordinary mechanics, not only under constant external conditions, but in general also during a slow and uniform variation of these conditions ...*

- **A priori probabilities:**

> *If the* ***a-priori probabilities*** *are known for the states of a given atomic system, however, they may be deduced for any other system which can be formed from this by a continuous transformation without passing through one of the singular systems referred below.*

Bohr’s contribution to the adiabatic hypothesis

- Boltzmann principle is valid also for systems of more than one degree of freedom.
- Extension to the relativistic case.
- Transformations between states of the same system.
- Calculation of a-priori probabilities in degenerate systems.

Final remarks

- The Ehrenfest's hypothesis has no considerable impact before the publication of Bohr's paper of 1918.
- Despite his own developments, Bohr's use of the adiabatic hypothesis is very close to the original formulation.
- Since 1918, the references to the adiabatic hypothesis increase.
- After the paper of 1916, Ehrenfest didn't work anymore on the adiabatic hypothesis.