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

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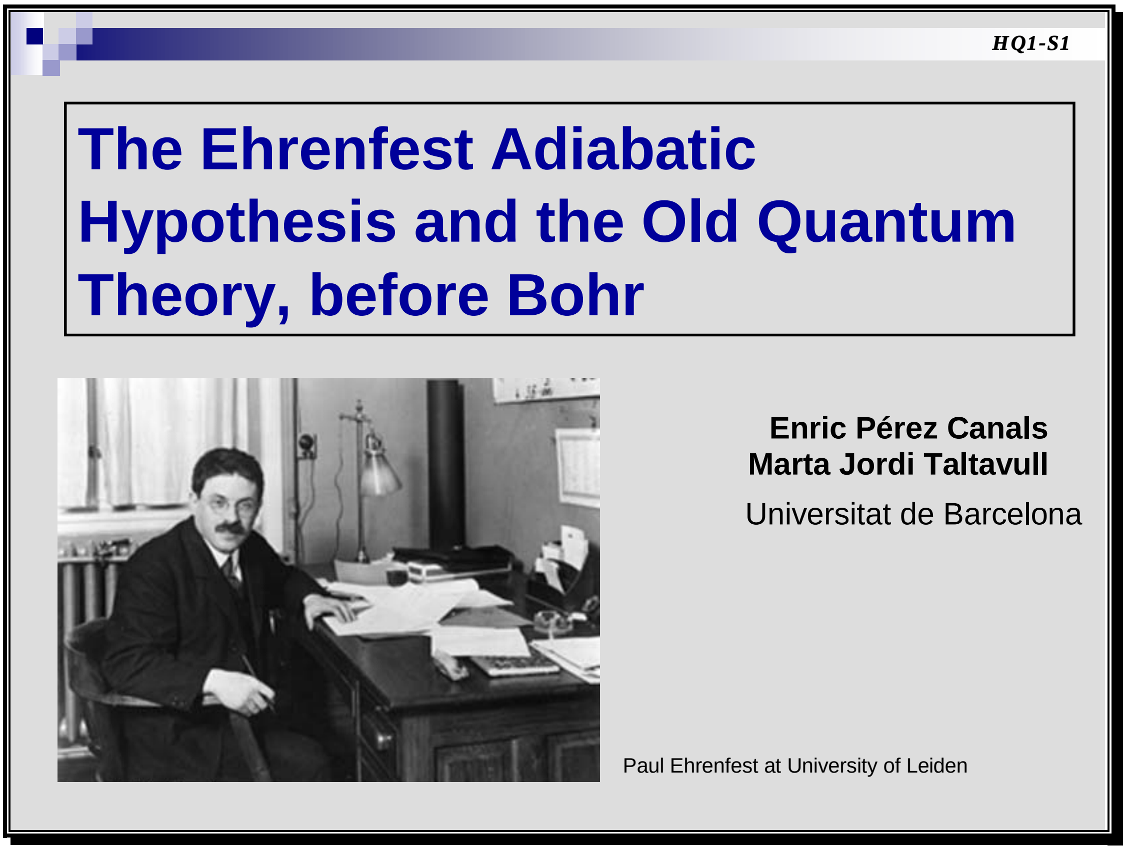
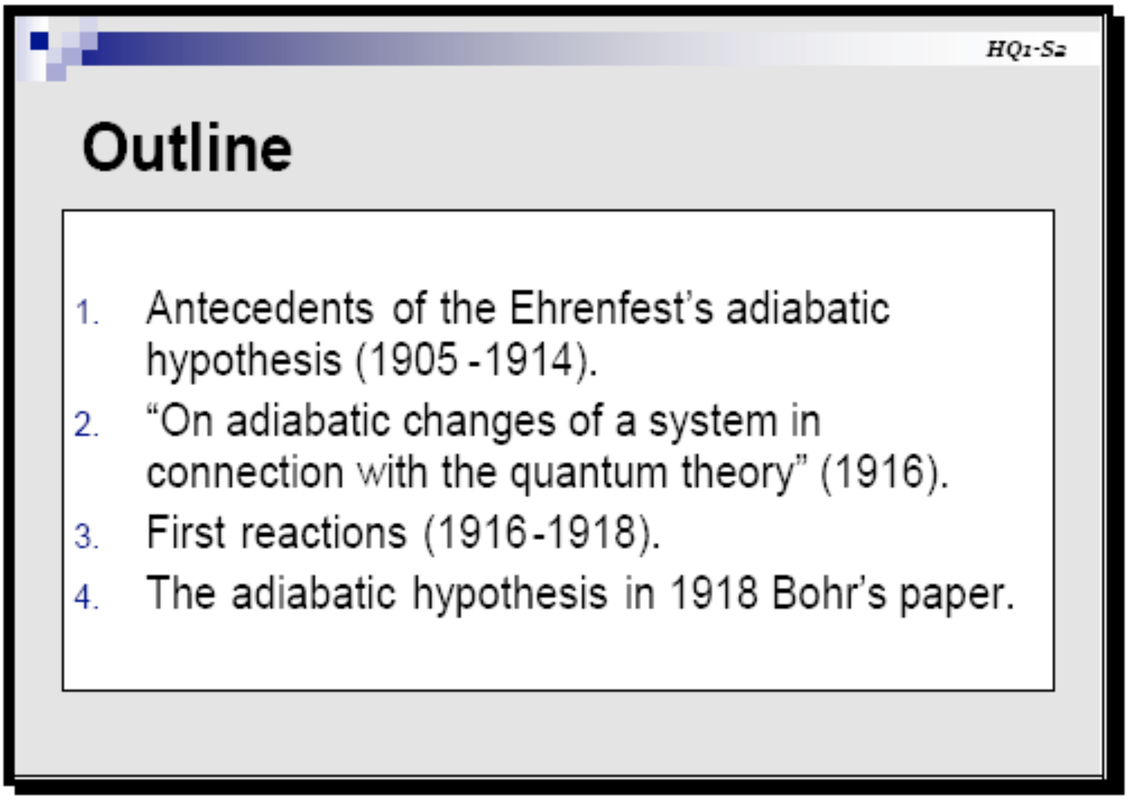


This talk deals with the role of the adiabatic hypothesis in the development of the old quantum theory. This hypothesis was formulated by Ehrenfest in a paper published in 1916, but practically all the results that appeared there had been published by him during the previous ten years. What Ehrenfest did in 1916, was to collect all those earlier results on the adiabatic transformations and their relations to the quantum theory, with the idea that they should become widely known. Far from that, the Ehrenfest's 1916 paper had little impact during the next few years. It was only after Bohr in 1918 published an essential work about the quantum theory, where he used the adiabatic hypothesis, that its importance began increasing.

To sum up the role that the adiabatic hypothesis played in the development of the old quantum theory up to 1918, what follows is centred in these four axes:

1. Summary of the antecedents of the Ehrenfest's adiabatic hypothesis (1905–1914).
2. Description of the main contents of the Ehrenfest's 1916 paper.
3. Analysis of the first responses, before the publication of the Bohr's work in 1918.
4. Commentaries on the role of the adiabatic hypothesis in the Bohr's work.



Antecedents of Ehrenfest's Adiabatic Hypothesis (1905–1914)

Paul Ehrenfest was born in 1880 in Vienna, where he carried out his studies in Physics and Chemistry, and became a doctor in 1904 under the guidance of Boltzmann. That is why it is not strange that one of his principal interests was statistical mechanics.

In 1905, Ehrenfest published his first paper on quantum theory (see slide $S_3/1$). However, it would not be until the paper published one year later that he clearly adopted a statistical approach to the quantum theory. In both papers, he criticized Planck's theory of black-body radiation.

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

- **1905-1906**: **Criticism of Planck's theory of black-body radiation.**
  - **1905**: "Über die physikalischen Voraussetzungen der Planck'schen Theorie der irreversiblen Strahlungsvorgänge". *Akademie der Wissenschaften, Vienna. Sitzungberichte. Abteilung II,* 1301-1314.
  - **1906**: "Zur Planckschen Strahlungstheorie". *Physikalische Zeitschrift 7*, 528-532.

Anyway, at that time, Ehrenfest's statistical tools were only insinuated. It was in the ensuing years that he would develop them in his notebooks. With the paper of 1911 being the cornerstone of his work, for there he carries out a statistical analysis of the radiation (see slide $S_3/2$). It is important to highlight some points of this crucial publication that specially concern our purposes in this brief exposition:

- Ehrenfest proved that by imposing the validity of Boltzmann's principle,

$$S = k \log W$$

  (S is the entropy, k Boltzmann's constant, and W the probability of a macrostate), Wien's displacement law could be obtained.

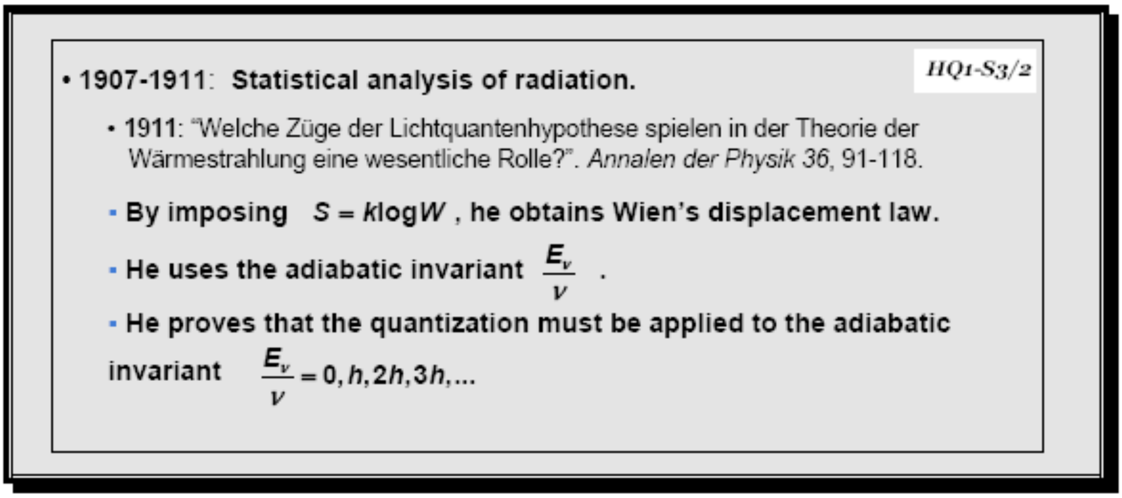
- In the corresponding proof, Ehrenfest imposed that the variation of the entropy was zero during an adiabatic compression of the cavity that contained the radiation (in an adiabatic compression the work done completely turns into energy of the system). Here Ehrenfest took advantage, for the first time, of an adiabatic invariant, which is a quantity that remains constant during this type of transformations. In the case of the radiation in a cavity, the invariant quantity is:

$$\frac{E_\nu}{\nu},$$

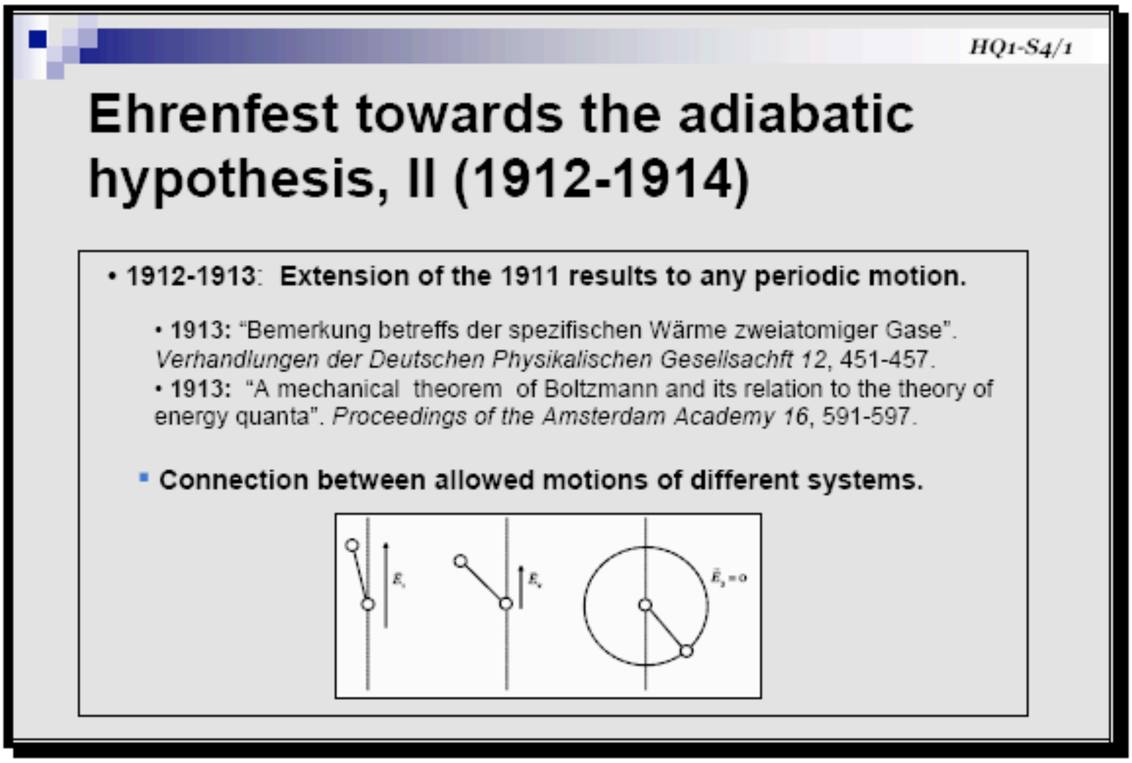
  where E_ν is the energy of a mode of vibration, and ν its frequency.

- By following this procedure, he also discovered that, in order to account for some indisputable features of the spectral distribution law, the quantization might be applied precisely to the adiabatic invariants, so justifying the form of the Planck's quantum of energy, as any other quantization would have contradicted Boltzmann's law (h is Planck's constant):

$$\frac{E_\nu}{\nu} = 0, h, 2h, 3h, \ldots$$



In 1912, Ehrenfest tried to extend these results to more general mechanical systems. This research gave rise to two papers in 1913.



In the first one, Ehrenfest deduced the quantization of the energy of a system of rotating molecules, by using an adiabatic transformation. To analyze it, Ehrenfest:

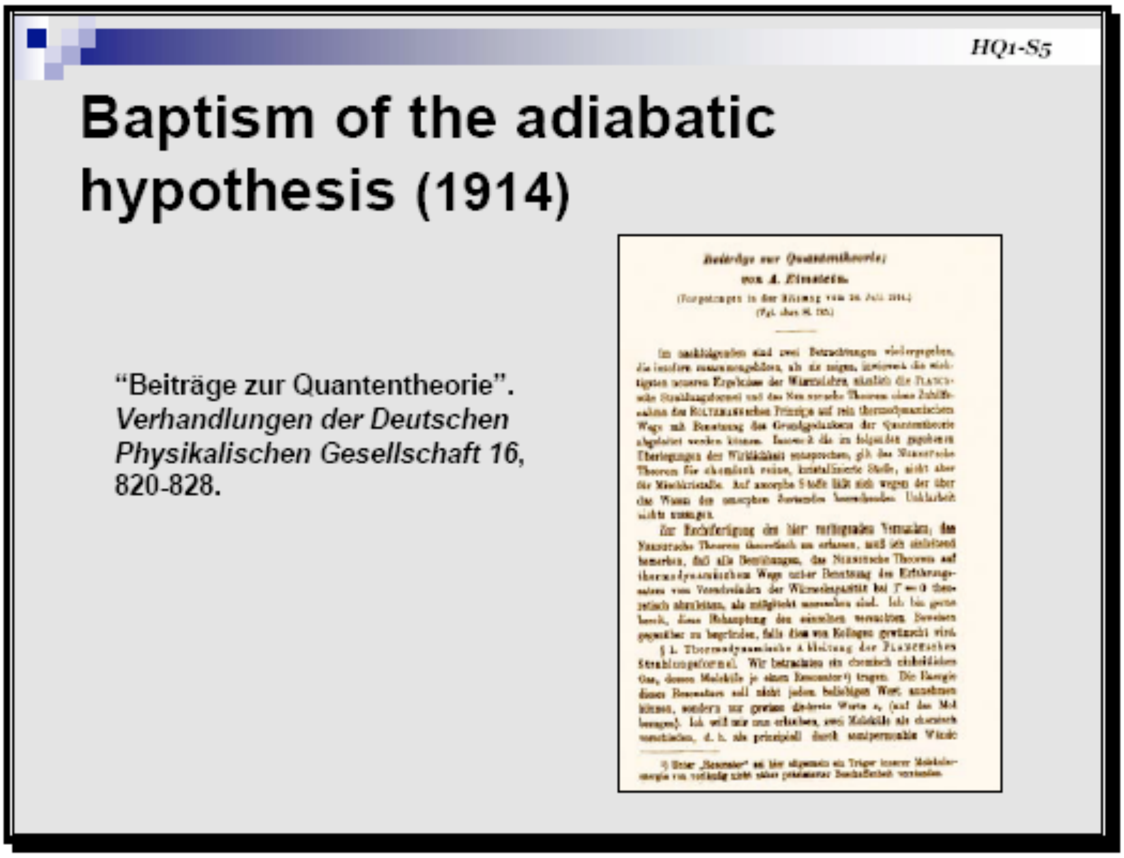
- considered a quantized system of harmonically vibrating electric dipoles in the presence of a strong orienting field (the dipole behaves like a Planckian resonator);

- after diminishing the value of the orienting field adiabatically, from a finite number to zero, saw that, as in this last state the electric dipoles did rotate, it was possible to connect adiabatically the vibration and the uniform rotation, and stated that the allowed quantum motions became (other) allowed quantum motions after an adiabatic transformation;

- and with this, he could deduce, as he knew the quantization of the energy for the vibrating molecules, thanks to the quantization of the adiabatic invariant at this point, the quantization for the rotating molecules.

This is the germ of the adiabatic hypothesis, although in this paper Ehrenfest scarcely justified it. It was in the second work of 1913, where he fully justified that supposition. In all likelihood, this is the work that contains the earliest version of the adiabatic hypothesis, although Ehrenfest did not call it this way.

We cannot dwell upon this point, but it must be pointed out that in this stage of his research, Ehrenfest did think that the quantization of the adiabatic invariant was compatible with the validity of Boltzmann's principle. In fact, in the 1911 paper he got to Wien's displacement law and also to the necessity of quantizing the adiabatic invariants by imposing, among other things, Boltzmann's principle. But later research, started by Ehrenfest in the summer of 1913, led him to realize that this compatibility may not be so obvious. So in 1914 he opened another line of investigation to see in which cases would Boltzmann's statistical foundations of the second law of thermodynamics be valid (see slide $S4/2$). Ehrenfest could not obtain a definitive result, but he could prove that the previous uses of Planck's, Debye's, and Einstein's of this principle were valid.

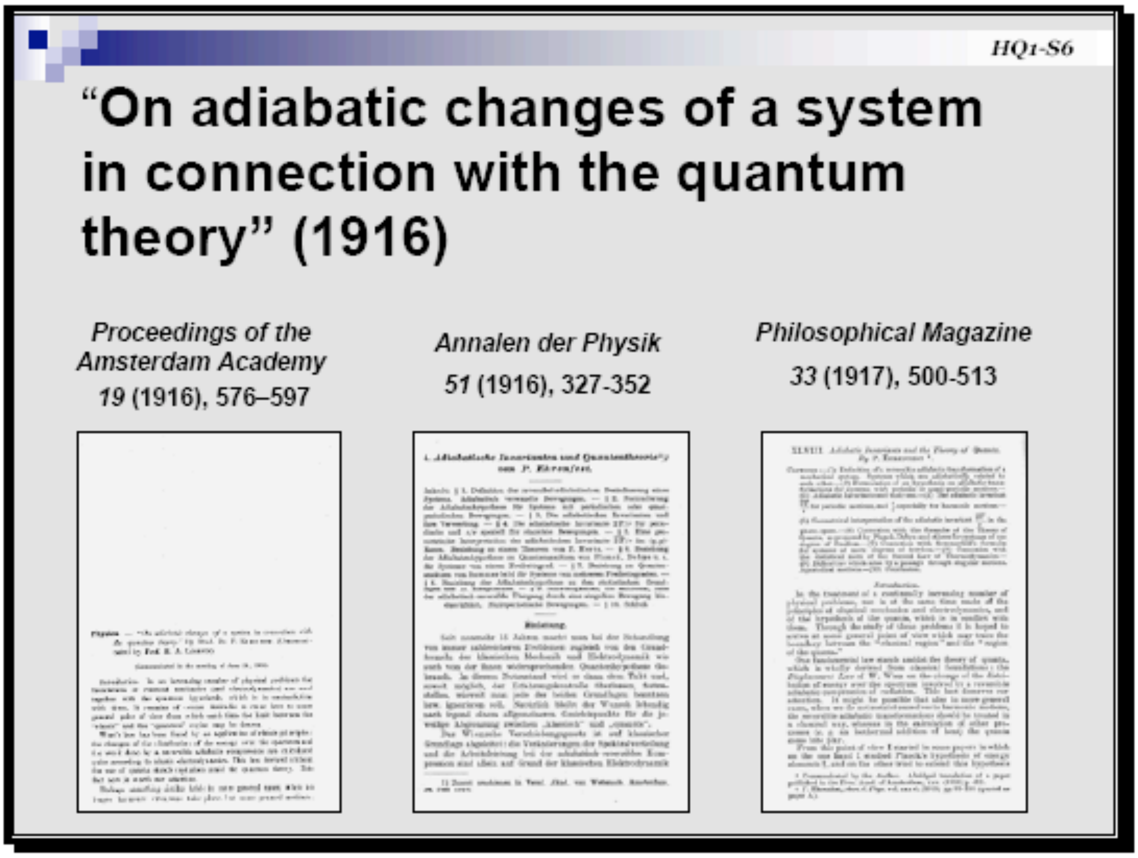


Ehrenfest did not call the adiabatic hypothesis this way in 1914, it was Einstein who did, and used it for the first—and, as far as we know, last—time in his quantum researches in a paper published in 1914. This paper—that contains an erroneous application of the hypothesis—was consequence of an intense dialogue that these two friends kept in the first months of 1914 about the adiabatic idea.

Apart from this Einstein's contribution, the results obtained by Ehrenfest had no visible incidence whatsoever during the next few years. Not even Sommerfeld nor Planck would worry about proving the compatibility of their respective quantum rules of 1915 with the adiabatic hypothesis. Probably compelled by this ignorance, Ehrenfest decided to gather all his previous results in a new paper and publish it in three different journals, as he thought that the adiabatic hypothesis should furnish with a basis on which to generalize the quantum theory.

“On Adiabatic Changes of a System in Connection with the Quantum Theory” (1916)

These are the front pages of the three versions of the paper written in 1916, which are practically the same (we will quote the version of *Philosophical Magazine*):



The main contents are the following:

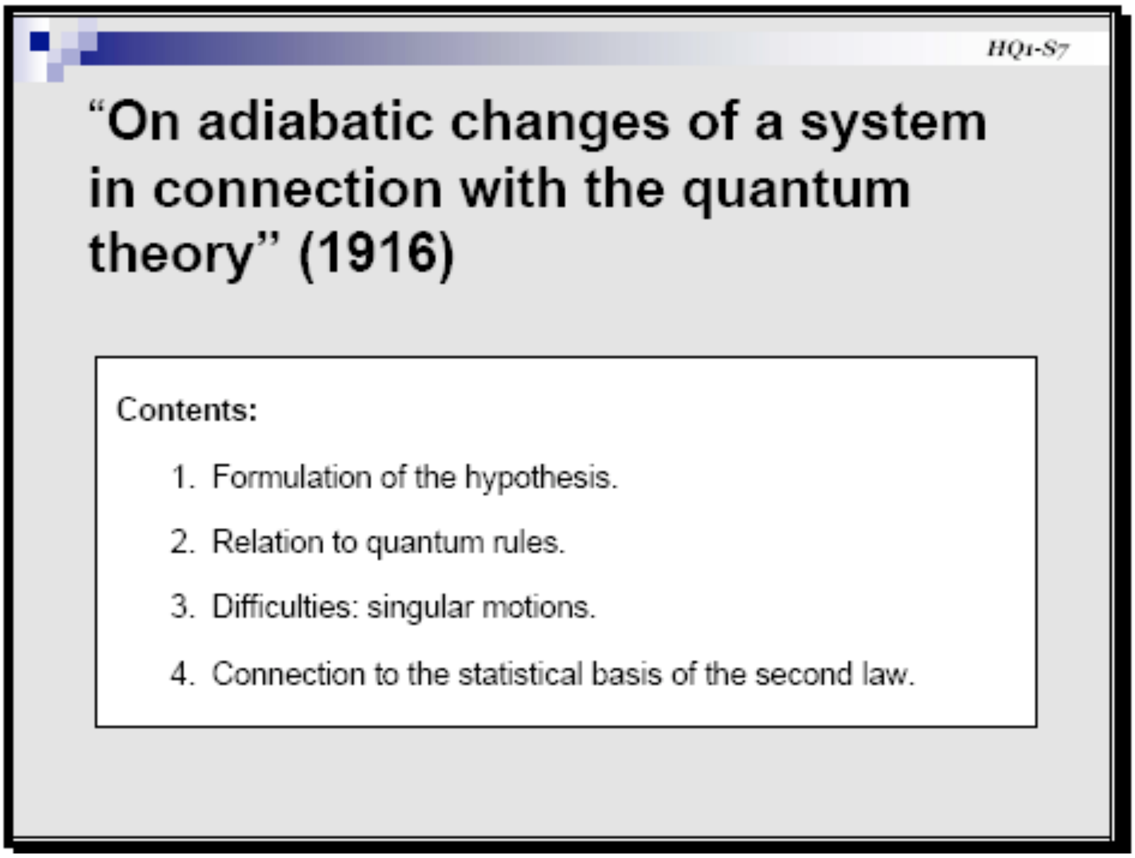
1. Formulation of the hypothesis.

2. Its relation to other quantum rules. This being the principal novelty respect to prior Ehrenfest's results. At this point he shows that his hypothesis agrees with the quantization rules proposed by Planck, Sommerfeld, and Debye.

3. Examination of some difficulties that appear in the application of the hypothesis: the singular motions.

4. Connection between the adiabatic hypothesis and the statistical interpretation of the second law of thermodynamics.

In this new presentation, Ehrenfest calls the hypothesis by its name, and offers an accurate formulation of it. Moreover, contrary to the 1913 papers, the way of presenting the results is systematic. Let's see shortly its contents, bearing in mind that this is the most complete version that Ehrenfest gave of his hypothesis.



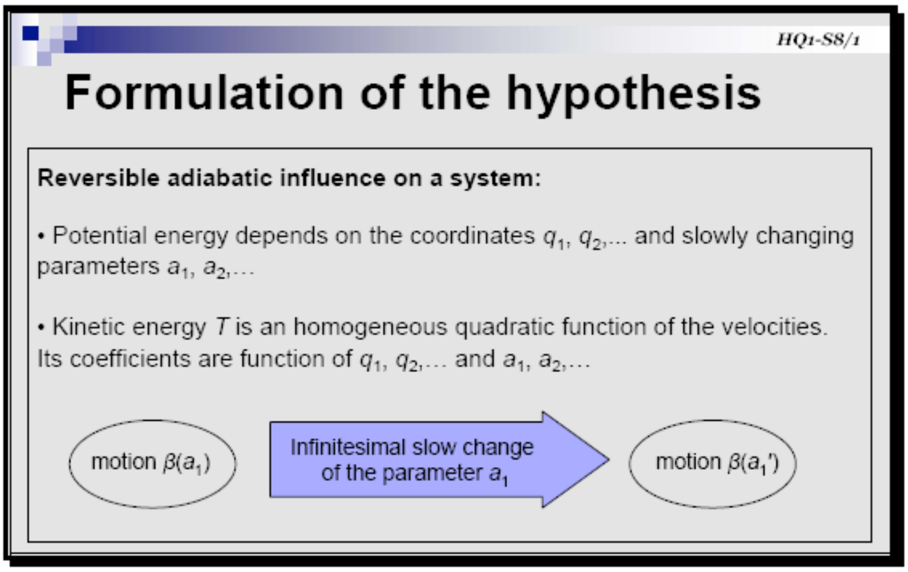
Formulation of the Hypothesis

Before the formulation, Ehrenfest defines a “reversible adiabatic affection of a system”. To do that, he considers:

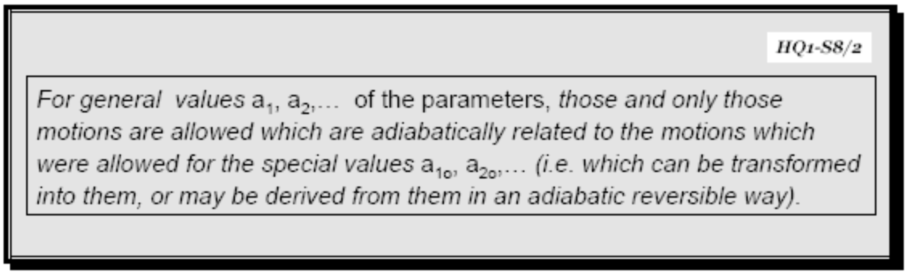
- A potential energy that depends on the coordinates $q_1, q_2, \ldots,$ and on certain parameters $a_1, a_2, \ldots$ “the values of which can be altered infinitely slowly”.

- A kinetic energy T, which is an homogeneous quadratic function of the velocities $\dot{q}_1, \dot{q}_2, \ldots$, and the coefficients of which are functions of $q_1, q_2, \ldots,$ and may be of $a_1, a_2, \ldots$

Ehrenfest defines a reversible adiabatic influence on a system as an infinitively slow change of the parameters $a_1, a_2 \ldots$

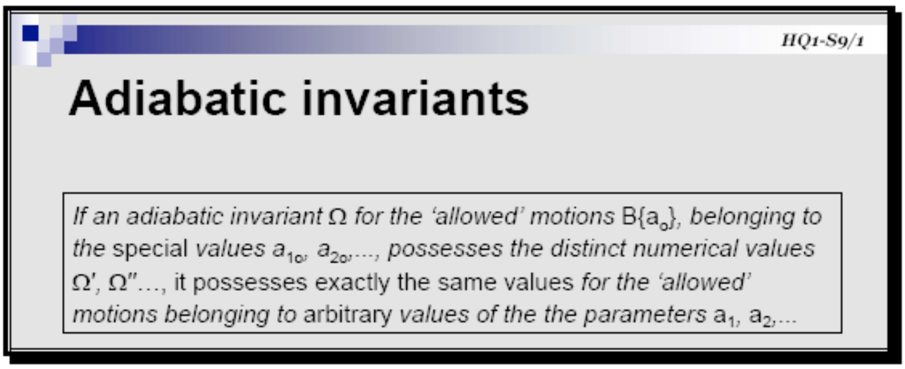


Given this definition, Ehrenfest enunciates his hypothesis:



This perfectly fits what Ehrenfest had supposed in his first paper of 1913, when he deduced for the first time the quantization of the energy of a system of rotating dipoles, by using an adiabatic transformation.

It is obvious that the adiabatic invariants play a very important role in this procedure. Ehrenfest referred to them in this way:



This statement implies that quantum rules must be enunciated through these quantities, because they must characterize the allowed motions.

As an example of an adiabatic invariant, Ehrenfest gives one for periodic motions, obtained from a mechanical theorem of Boltzmann's, Clausius', and Szily's, which is:

$$\delta' \int_0^P 2T\, dt = 0$$

(δ' stands for the variation during an adiabatic transformation; P is the period of the motion, and T the kinetic energy). From this theorem, Ehrenfest obtains the following adiabatic invariant:

$$\frac{2\bar{T}}{\nu}$$

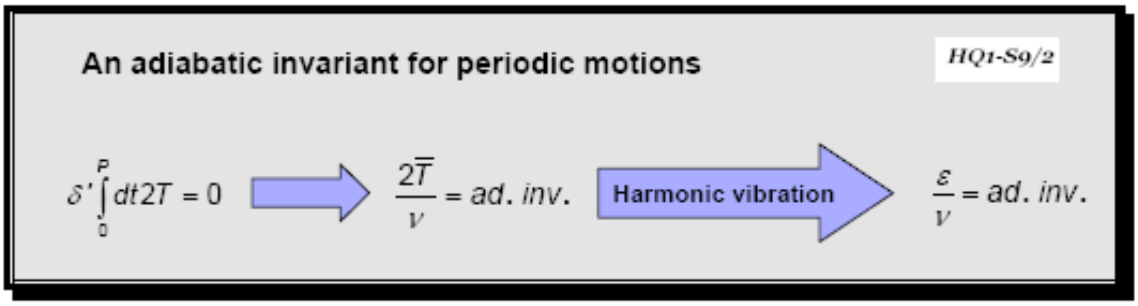
(ν is the frequency of the motion, and $\bar{T}$ the mean value of the kinetic energy during a period). Moreover, in the case of harmonic vibration, this invariant becomes:

$$\frac{\epsilon}{\nu}$$

(ϵ is the total energy, that is, the kinetic and the potential ones), being this expression perfectly related to Planck's quantization of energy done in 1900:

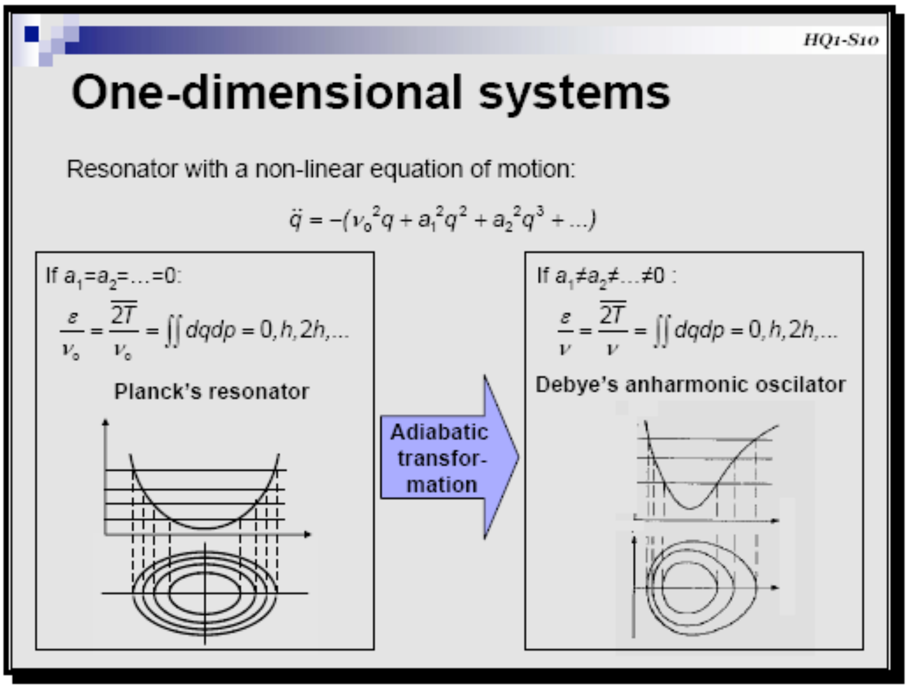
$$\frac{\epsilon}{\nu} = 0, h, 2h, 3h, \ldots$$

Summarizing:



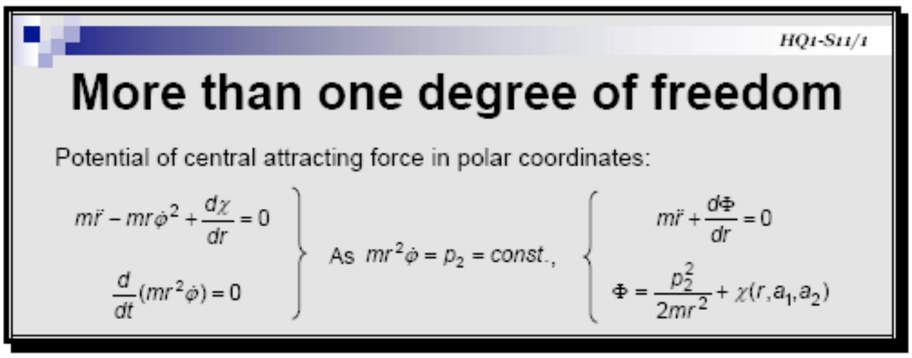
Relation to Quantum Rules

To connect his hypothesis with Planck's and Debye's quantization rules, Ehrenfest proposed an example referred to a one-dimensional system that consisted of a non-linear oscillator. By imposing $a_1 = a_2 = 0$ (see slide S_{10}), it is possible to recover the equation of motion of an harmonic oscillator, i.e., of a Planck's resonator. In this case, the potential energy curve is a parabola, and the allowed motions describe ellipses on the phase plane.



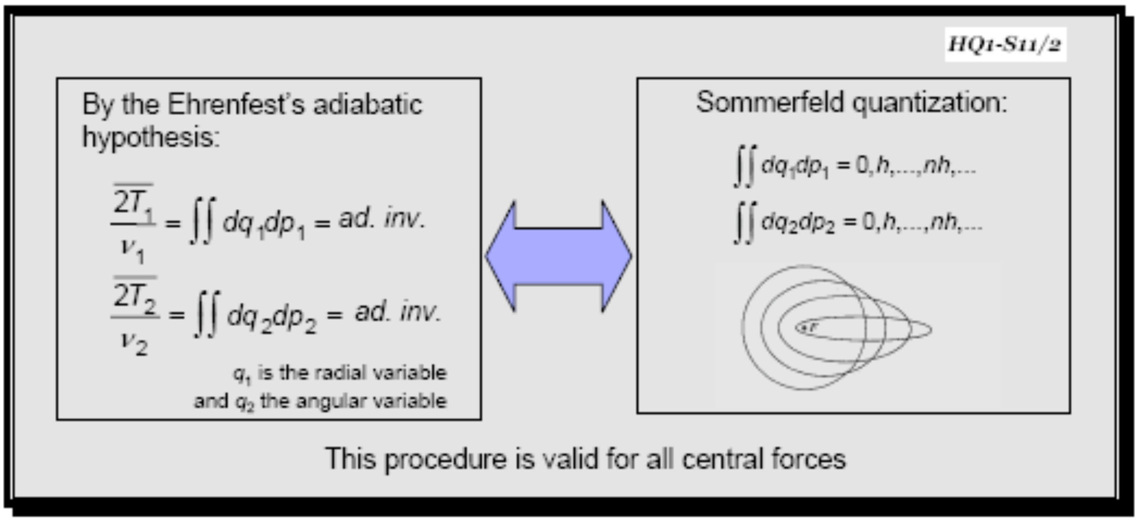
Reversing the reasoning, by considering an adiabatic change of the value of the parameters $a_1, a_2 \ldots$ from zero to any finite value, we can see how the equation of motion that it is obtained corresponds to an anharmonic oscillator. According to Debye's quantization, the allowed motions are defined by the closed curves represented on the corresponding phase plane, which are quite different from those of Planck's. As the quantities that remain constant during an adiabatic transformation are the quantities on which the quantization must be applied, both quantization rules, Planck's and Debye's, have to be equivalent to Ehrenfest's adiabatic hypothesis.

To connect his hypothesis with the Sommerfeld quantization rules, Ehrenfest considers a central system that can be described by the following equations of motion:



These equations correspond to a Kepler system in polar coordinates, and $\chi(r, a_1, a_2, \ldots)$ is the potential corresponding to an attractive central force. The second equation of motion means $mr^2\dot{\phi} = p_2$ that is constant under variation of time. With this result, the two previous equations are clearly equivalent to a following unique one-dimensional equation for the radial coordinate r, which oscillates between two fixed values. In effect, as it is easily seen, this last expression (see slide $S11/1$) is analogous to that one describing the one-dimensional oscillator, and because of that Ehrenfest can apply his adiabatic hypothesis to this motion in the same way he had in the previous example.

Having taken account of the fact that p_2 is also invariant under variations of the parameters $a_1, a_2 \ldots$, Ehrenfest obtains a second quantization rule (see slide $S11/2$). On the other hand, by applying independently the Sommerfeld quantization rules to the Kepler system in polar coordinates, the quantization has exactly this form for each one of the coordinates:



Hence, both ways to quantize are, in this case, equivalent. Ehrenfest also states this procedure to be valid for all central forces, since any central force can be connected to the Kepler system adiabatically by changing infinitively slowly the corresponding parameters on which the central potential depends.

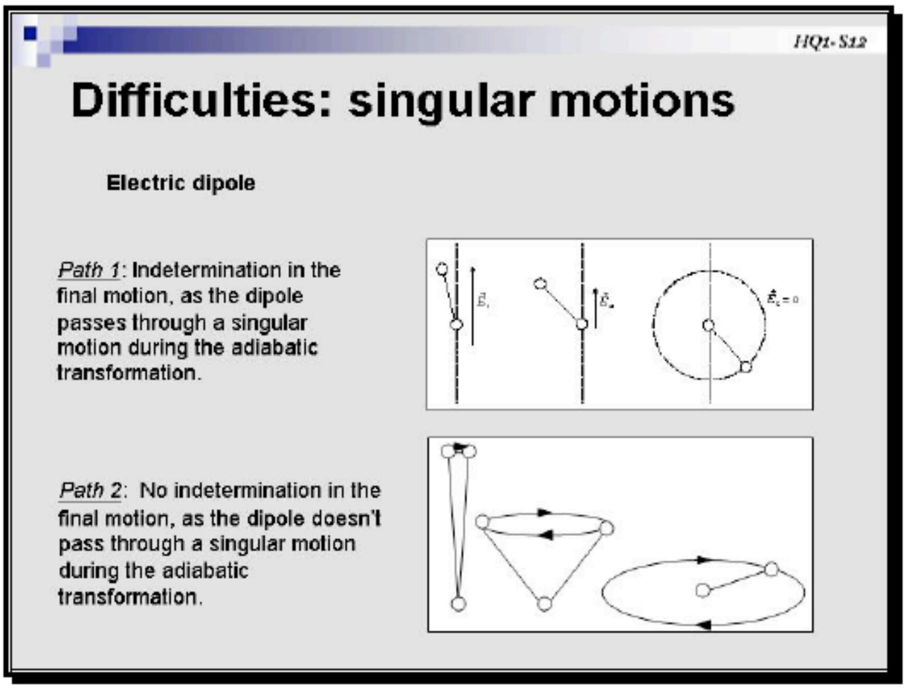
Up to this point, Ehrenfest has proved the compatibility of his hypothesis with all different quantization rules that had appeared until that moment. The only quantization rule that Ehrenfest does not mention is Bohr's one, probably because he thought of it unfavourably by then.

Difficulties: Singular Motions

However, in applying the hypothesis some difficulties appear. By analyzing the adiabatic transformation of the movement of an electric dipole from a vibration to a rotation by diminishing the orienting field $\vec{E}$, it is possible to better understand these difficulties (see slide S_{12}). In path 1, just in the transition movement between vibration and rotation, a motion with an infinite period emerges, in which it is impossible to define an infinitively slow change, that is, an adiabatic transformation, as the change rate is always defined in reference to the period of motion. Then, Ehrenfest's adiabatic hypothesis cannot be applied at this point. As a visible consequence of this fatal ambiguity, after this motion, the electric dipole can rotate clockwise or counter clockwise.

Ehrenfest proposes an alternative transformation to shun this problem (see *path 2*). In this picture, the dipole does not oscillate in a single plane, but it does so conically, so that after varying the value of the electric field adiabatically, from a finite number to zero, the final motion has no indetermination and the electric dipole has not passed through a singular motion.

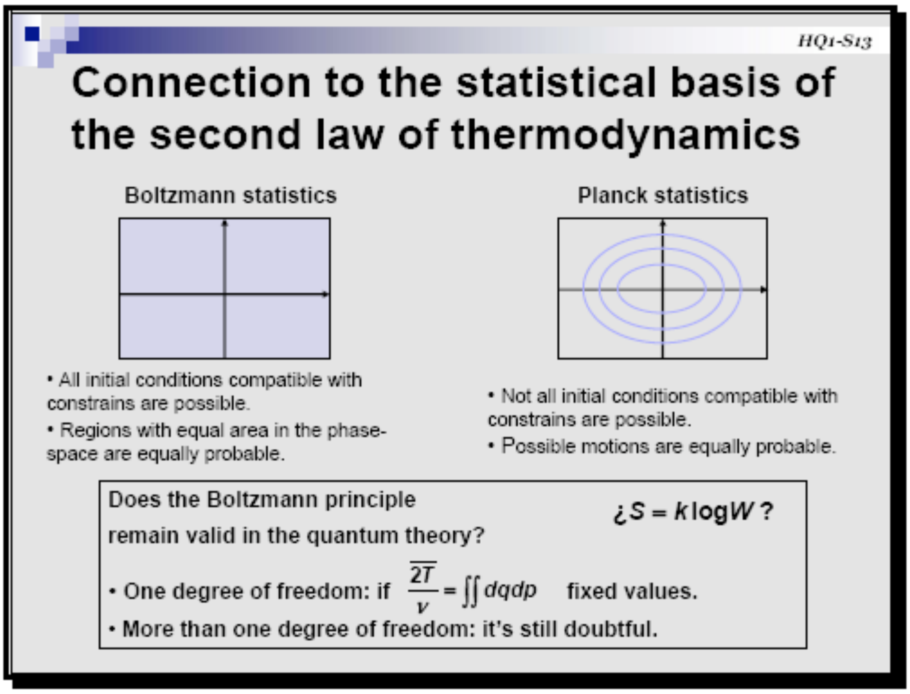
This second path avoids the ambiguity, but does not get rid of this dark point in the whole coherence of the Ehrenfest adiabatic hypothesis. In principle, it would be necessary to justify the plausibility of *path 1*. Ehrenfest hints that solving this question could be related to a possible extension of the application of his hypothesis to aperiodic motions.



Connection to the Statistical Basis of the Second Law

As we have commented above, in the paper of 1914, Ehrenfest wondered about the compatibility between the quantum theory and the statistical interpretation of the second law of thermodynamics, as the suppositions from which Boltzmann's and Planck's statistics were constructed were quite different. In the first case, all initial conditions—compatible with the corresponding constraints—, are possible. On the contrary, in Planck's statistics, not all initial conditions—compatible with constraints—are possible, but only those represented by Planck's ellipses on the phase plane. In the case of Boltzmann's statistics, all regions with equal area on the phase plane are equally probable, while in the case of Planck's statistics, where not all movements are possible, allowed motions are equally likely.

After some calculations and considerations, Ehrenfest deduced in 1914, and exposed again in this 1916 paper, that the validity of Boltzmann's principle is ensured for systems with one degree of freedom if the quantization is applied to adiabatic invariants. This is not the case for systems with more than one degree of freedom, for which this validity—and henceforth its compatibility with the adiabatic hypothesis—still remains doubtful.



First Reactions (1916–1918)

In the first half of 1916 new developments of the Sommerfeld theory, which tried to give a solution to the dependence of the quantization on the coordinate system, were published. We are referring to the contributions by Epstein and Schwarzschild, who used the Hamilton-Jacobi theory to try and elucidate for which coordinate system Sommerfeld rules could be applied. These contributions dealt with multiperiodic motions, which are, in a sense, made up by partial periodic motions for each of its coordinates.

This kind of motions can be defined accurately through the Hamilton-Jacobi equation:

$$H\left(q_1,\ldots,q_n;\frac{\partial S}{\partial q_1},\ldots,\frac{\partial S}{\partial q_n}\right)+\frac{\partial S}{\partial t}=0$$

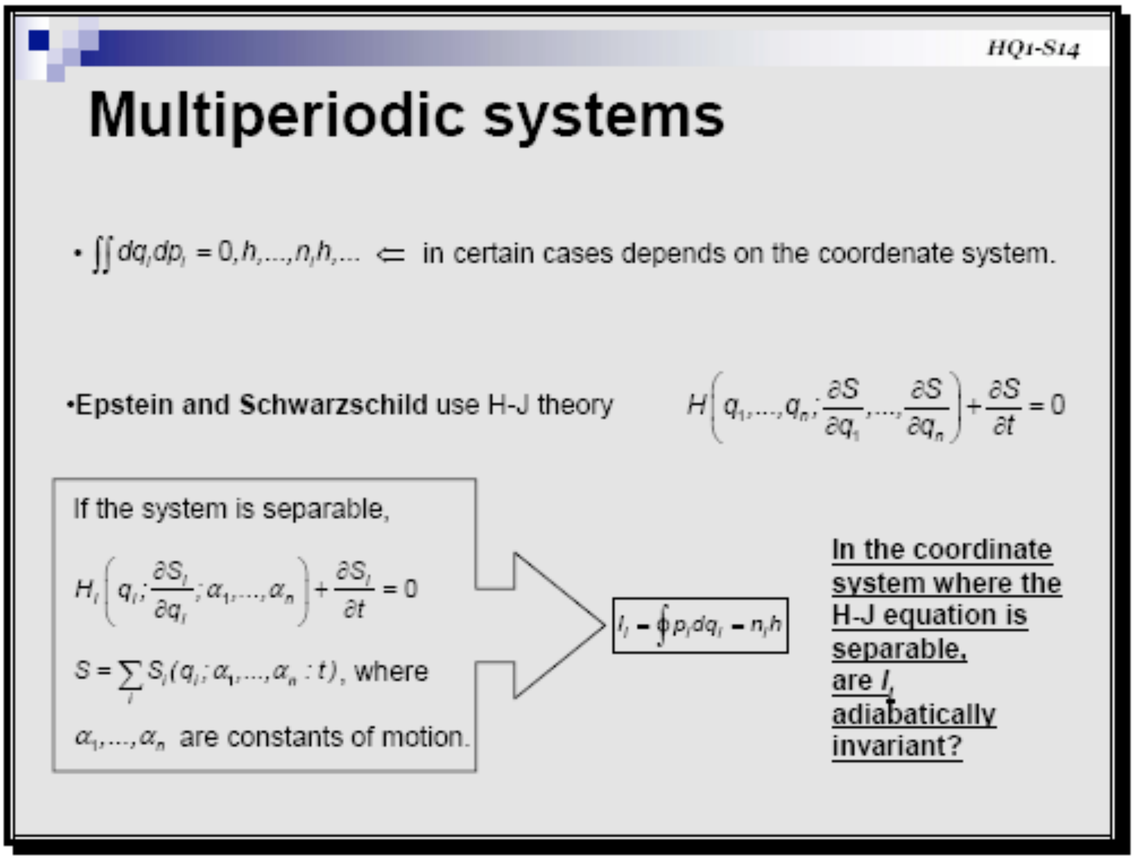
(S is the generatrix function of a transformation that converts the original coordinates $q_1 \ldots q_n$ into constants of motion). In the case of separable systems (systems where the Hamilton-Jacobi equation is separable), it is possible to obtain, in some coordinate systems, one Hamilton-Jacobi equation for each coordinate. That is:

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

(S_i only depends on the coordinate q_i, on n different constants of motion $\alpha_1 \ldots \alpha_n$, and on time t). In other words, in separable systems the generatrix function S has the form:

$$S=\sum_i S_i\left(q_i;\alpha_1,\ldots,\alpha_n;t\right).$$

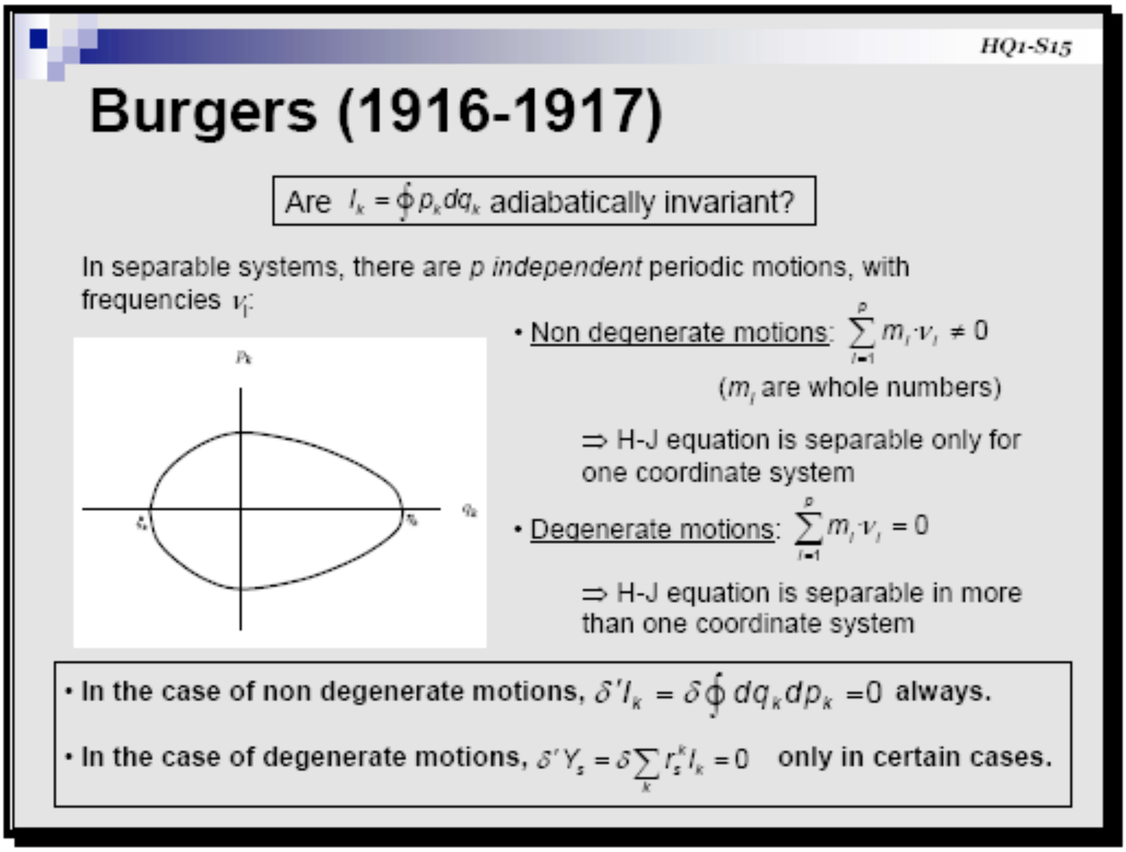
Epstein and Schwarzschild stated that only in such cases was it possible to apply the quantization to the different phase integrals without ambiguities: the correct quantization was that one obtained in the coordinate system where the Hamilton-Jacobi equation was separable.



This new contributions reduced the problem to the so called 'degenerate motions'. This class of motions can be characterized through its 'proper' frequencies: frequencies of degenerate motions satisfy one or more 'commensurability relations', and frequencies of non degenerate ones does not (see slide S_{15}). In the former, the separation of variables can be done in more than one system of coordinates, so that an ambiguity remained in how quantization should be applied.

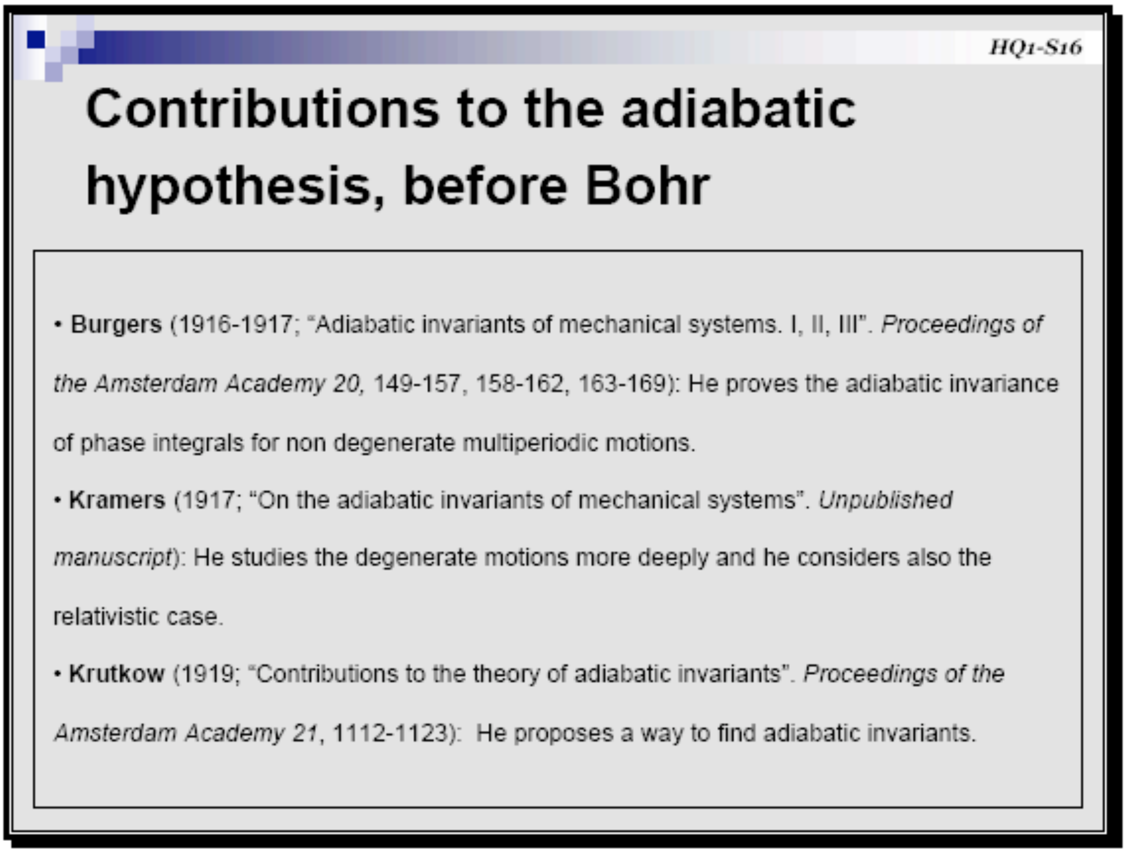
In the postscript of his 1916 paper, Ehrenfest wondered if the phase integrals referred by Epstein, Schwarzschild, and Sommerfeld were adiabatically invariant. It was for this reason that Ehrenfest entrusted his disciple Burgers with the task of finding an answer to this question.

Very soon, in December of the same year and January of the next one, Burgers obtained a definite result. He found that, in the case of non degenerate motions, the phase integrals were always adiabatically invariant, whereas in the case of degenerate motions, only certain linear combinations of these phase integrals were so only if the degree of degeneration (the number of commensurability relations) remained constant during the adiabatic transformation.



This contribution of Burgers must be considered, not as a new application of the Ehrenfest's hypothesis, but as a part of it, as it perfectly completed the exposition contained in the 1916 paper and contributed to improve its theoretical basis, extending the proof of the compatibility of the adiabatic hypothesis with the quantum rules which appeared after Ehrenfest had redacted his work.

Apart from Burgers, two former disciples of Ehrenfest, Kramers and Krutkow, also contributed to give foundation to the adiabatic hypothesis in similar ways. Kramers, who had been installed in the summer of 1916 in Copenhagen as Bohr's collaborator, tried to go further than Burgers, and began writing a manuscript where he was to study the adiabatic transformations in degenerate systems more deeply. In this manuscript, Kramers assesses that Burgers' proof could be generalized to relativistic systems. As far as we know, this manuscript was never published, but Kramers sent a copy to Ehrenfest in the summer of 1917.

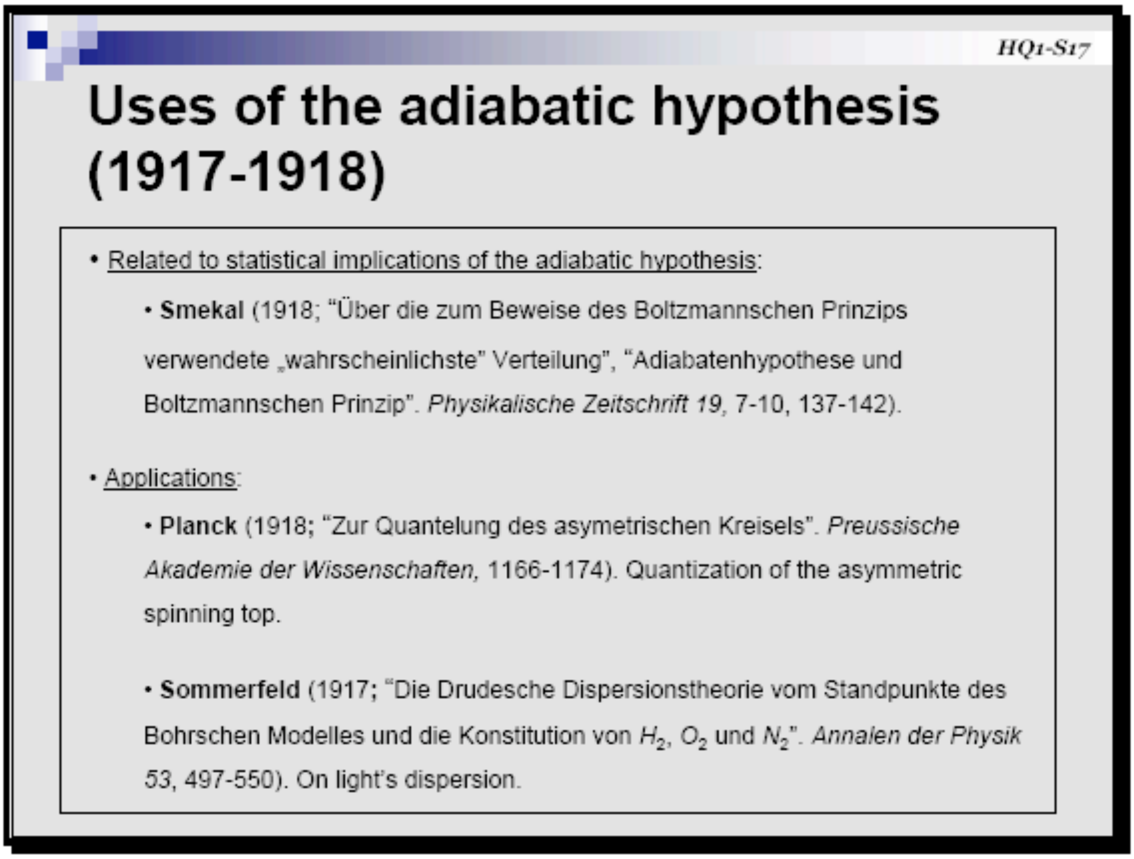


Krutkow, a friend of Ehrenfest's from his Russian days, who still resided in Saint Petersburg, was only partially aware of Burger's works. He did not know the contribution of 1918 by Bohr either. In late 1918 he sent a paper to Ehrenfest that scarcely contained any novelties, for in it Krutkow only proposed a new way to find adiabatic invariants (the action-angle variables introduced in the quantum theory by Schwarzschild—to which we will not refer here—had solved this particular question; moreover Burgers had proved in the third paper of his contribution to the Amsterdam Academy the compatibility between the Schwarzschild approach and the adiabatic hypothesis). Anyway, Ehrenfest decided to publish it in the *Proceedings of the Amsterdam Academy.*

But all of these contributions did not contain any new applications of the adiabatic hypothesis. They were destined for showing the harmony that existed between Ehrenfest's idea and the quantum theory. As far as we know, in 1917 and 1918, the adiabatic hypothesis was *used* only in five papers: two by Smekal, one by Planck, one by Sommerfeld, and one by Bohr.

Smekal, who was a young physicist when he moved to Berlin to finish his studies, published then, in 1918, two papers in the *Physikalische Zeitschrift* about the adiabatic hypothesis. They were basically centred on its statistical connections. Mainly he tried to generalize the considerations about the validity of Boltzmann's principle to systems with more than one degree of freedom.

Also in 1918, Planck used the hypothesis to choose one of the two possible quantizations found for the asymmetric spinning top (a rigid solid with three different moments of inertia). In this case, Planck privileged the quantization that was in agreement with the adiabatic hypothesis by Ehrenfest.

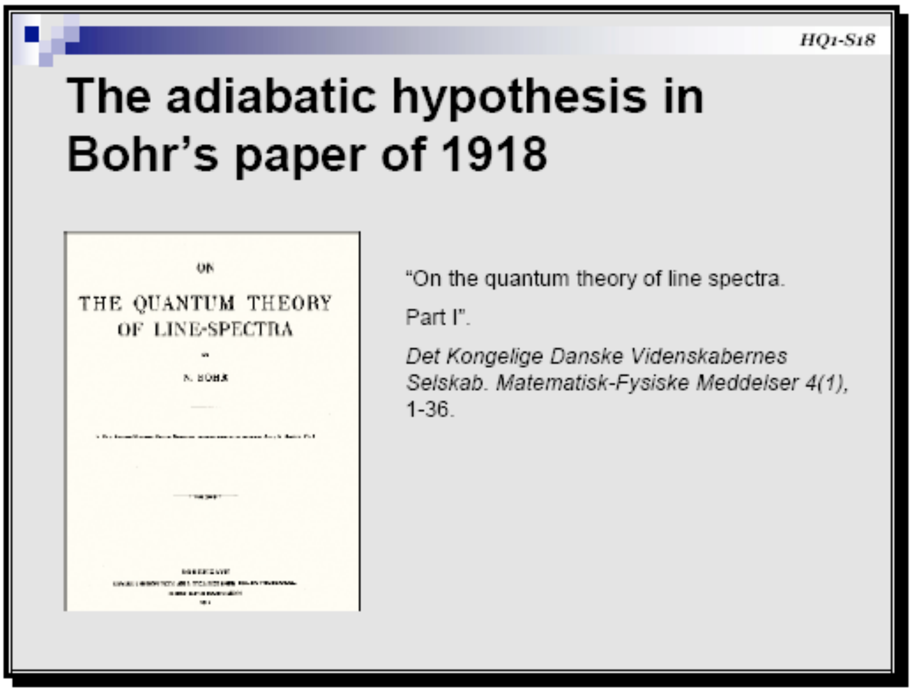


Sommerfeld used Ehrenfest's hypothesis to give a basis to his treatment of the magnetic field influence on the trajectory of the electrons in a paper on light's dispersion. Sommerfeld stated that Ehrenfest's rule, which restricted the quantization only to adiabatic invariants, ensured the validity of the mechanical laws during slow transformations.

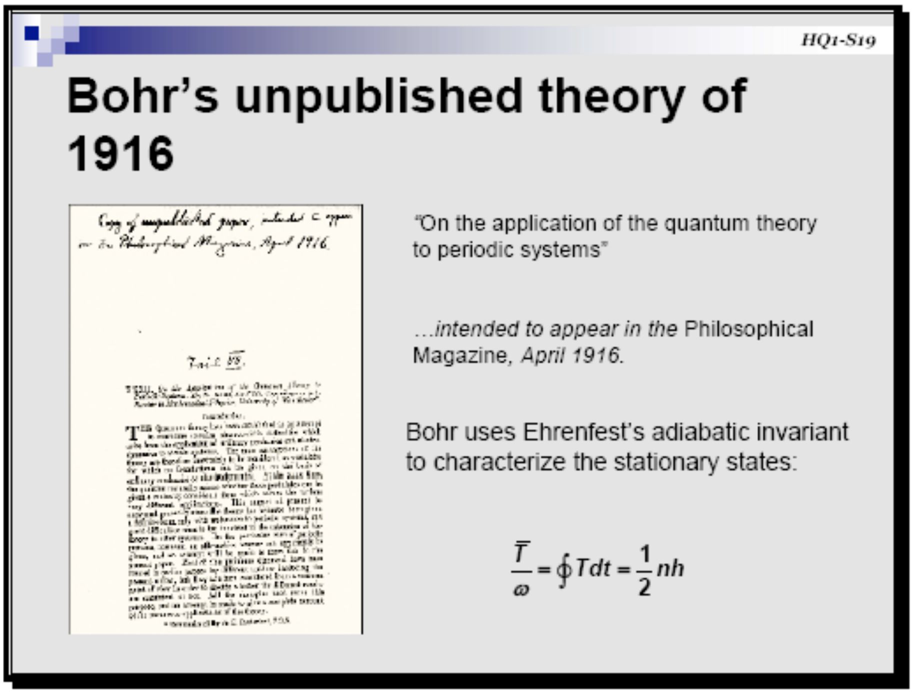
As we can see, all these uses are, in a way, minor uses. Because of that, we asses that the first response to Ehrenfest's publication was rather scarce, almost null. On the other hand, as we have seen, the works of Burgers, Kramers and Krutkow can not be considered as new applications or true reactions, because all of them contain attempts to give solid reasons to present the adiabatic hypothesis as a fundamental rule for the quantum theory. Moreover, only the papers by Burgers were often quoted in the following years. But this scenario changed abruptly when Bohr published his new theory.

The Adiabatic Hypothesis in Bohr's 1918 Paper

The first part of *On the quantum theory of line spectra* was published in April of 1918 as a memory of the Danish Real Academy. Its diffusion was not fast—the war had not finished yet—, but it gradually became one of the essential works of the quantum theory. This part contained the general theoretical basis of Bohr's theory, and the second one—published in December—contained a detailed analysis of the spectrum of the hydrogen atom. It was with the publication of the first part that a new stage of the role that Ehrenfest's adiabatic hypothesis played in the development of quantum ideas began.



However, this was not the first work where Bohr made use of Ehrenfest results. In early 1916, he had finished a renewed version of his quantum theory of 1913, now extended to all kind of periodic systems. However, when this paper was going to be published in the *Philosophical Magazine*, Bohr received by mail the recent Sommerfeld contributions and decided to restate the whole thing from scratch.



This paper of 1916 shows that Bohr knew Ehrenfest's work very well, except for the 1914 one about Boltzmann's principle. Two years later, in 1918, he is already a connoisseur of that paper and even uses some of the statistical considerations that appeared in it. In fact, in 1919, he explained to Sommerfeld that it was precisely the lack of a rich statistical approach to the quantum theory that had prevented him from reformulating quickly his results of 1916.

In this theory, Bohr used for the first time the mechanical theorem by Boltzmann-Clausius-Szily rescued by Ehrenfest for the quantum theory, and he proposed to quantize the adiabatic invariant to characterize the stationary states of periodic systems. That is to say, he proposed to generalize Planck's quantum hypothesis the same way as Ehrenfest did. But all of this remained unpublished.

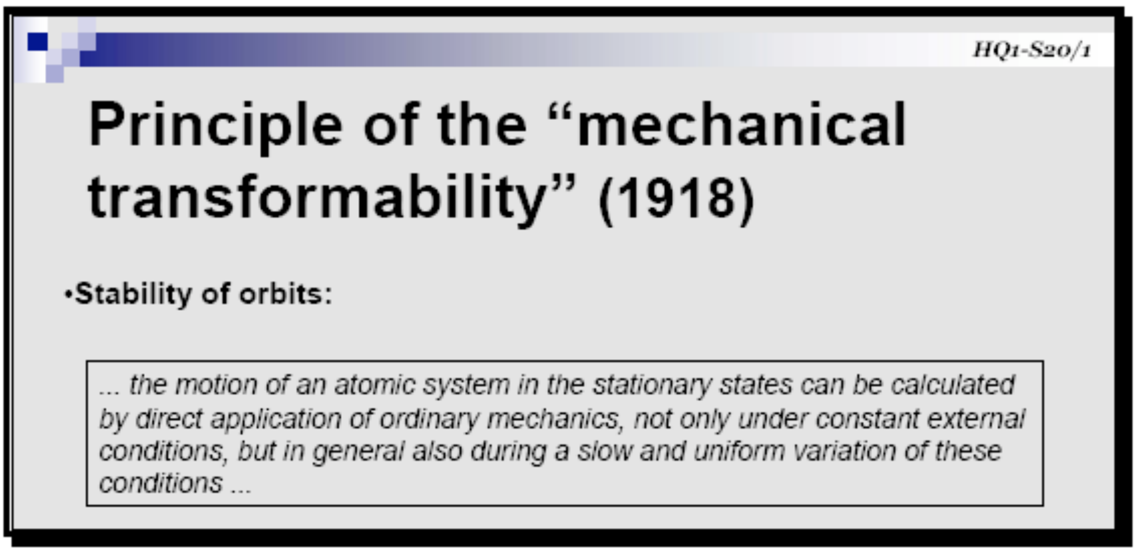
Coming back to Bohr's 1918 work, we must recall that it was based on two postulates. According to the first one, an atomic system could only exist permanently in a specific series of states corresponding to a discontinuous series of values for its energy, which were called 'stationary states'; any transition between two of these states implied a change in the energy of the system. According to the second one, the frequency of the energy emitted or absorbed during such a transition would have the value

$$\nu = \frac{E' - E''}{h}$$

where E' and E'' are the values of the energy of the two stationary states considered.

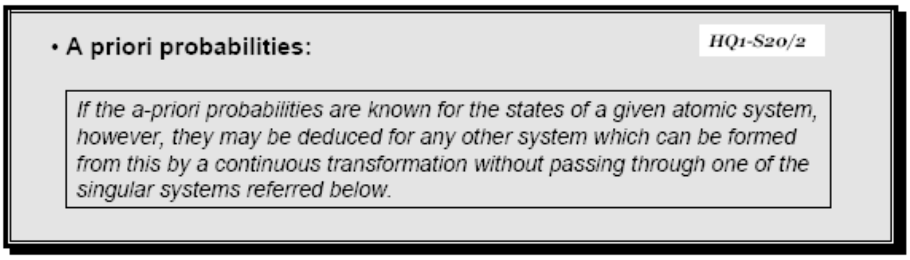
In this theory, Bohr included not only the contributions by Sommerfeld, Epstein, and Schwarzschild, but also the transition probabilities introduced by Einstein in 1916 and the principle of the "mechanical transformability", which is the name with which he rebaptized the Ehrenfest's adiabatic hypothesis.

Bohr wanted this principle to function as guarantee of the stability of the stationary states. Thus, according to it, the mechanical laws were valid, not only under constant external conditions, but also during infinitively slow changes of them, that is, during adiabatic transformations:



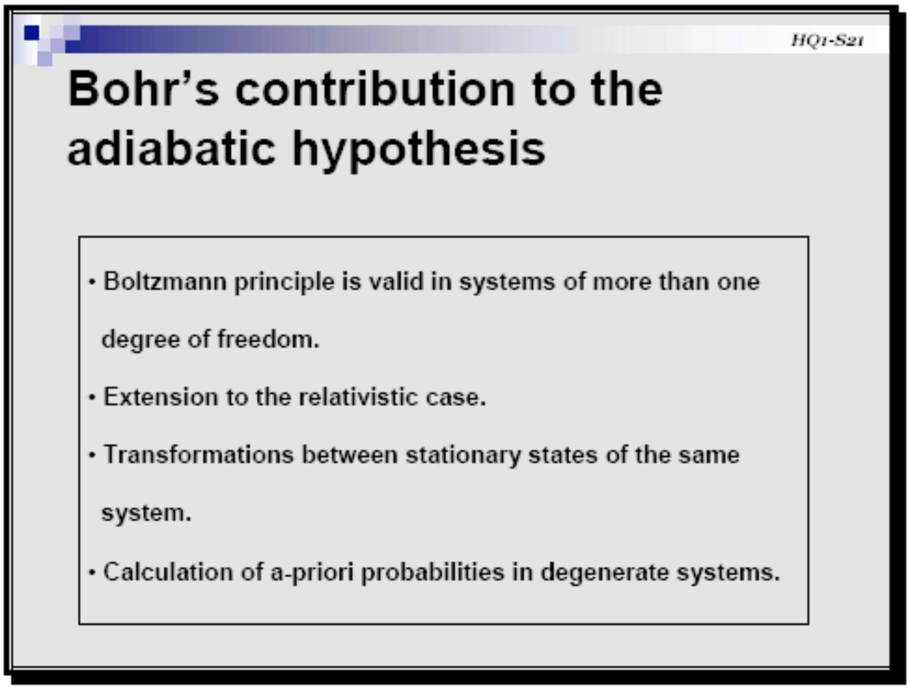
This implied that no small change of the motion could provoke quantum jumps, and that by them no emission or absorption processes could take place.

But the adiabatic hypothesis still had another crucial role:



(A "continuous transformation" means an "adiabatic transformation", and "the singular systems" are related to "the singular motions" to which we have referred above). This passage of Bohr's paper can be summarized as follows: during an adiabatic transformation, the a priori probabilities for the states remain constant. This assumption about the a priori probabilities of the stationary states links directly to the considerations that Ehrenfest introduced in 1914 and afterwards in 1916 about the validity of Boltzmann's principle. But while Ehrenfest limited the assessment of the validity of the statistical interpretation of the second law to systems with one degree of freedom, Bohr extends directly this validity to systems with more than one degree of freedom. We must remind that Bohr deals only with stationary states (quantum states) while Ehrenfest does not so.

Apart from these applications, Bohr contributed to extend the implications of the Ehrenfest's adiabatic hypothesis to more circumstances. For instance, he extended it to relativistic systems, he took profit of the characteristic situation of the degenerate motions to connect different stationary states of the same system, and he also conceived a way to calculate the a priori probabilities in a degenerate system.



Final Remarks

1. As we have shown, the Ehrenfest's adiabatic hypothesis had no considerable impact in the development of the quantum theory before the publication of Bohr's paper of 1918.

2. Despite his own developments, Bohr's use of the adiabatic hypothesis is very close to the original formulation. Because of that, Bohr's principle of mechanical transformability can be considered the most complete version of it.

3. Since 1918, the references to the adiabatic hypothesis increase. They emerged in so different fields as atomic models, specific heats of solids or quantization of aperiodic motions.

4. And, finally, we would like to conclude this talk pointing out that after his paper of 1916, Ehrenfest hardly worked anymore on the adiabatic hypothesis. The only subsequent publication that was related to it was a retrospective paper that the editors of *Die Naturwissenschaften* asked to him to include it in the number of 1923 devoted to celebrate the tenth anniversary of Bohr's atomic model.

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