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The puzzle of half-integral quanta in the application of the adiabatic hypothesis to rotational motion

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ABSTRACT

We present and discuss an interesting and puzzling problem Ehrenfest found in his first application of the adiabatic hypothesis, in 1913. It arose when trying to extend Planck's quantization of the energy of harmonic oscillators to a rotating dipole within the frame of the old quantum theory. Such an extension seemed to lead unavoidably to *half-integral* values for the rotational angular momentum of a system (in units of $\hbar$). We present the problem in its original form along with the (few) responses we have found to Ehrenfest's treatment. After giving a brief account of the classical and quantum adiabatic theorem, we also describe how Quantum Mechanics provides an explanation for this difficulty.

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1. Introduction

It is widely known that the role of Paul Ehrenfest in the old quantum theory was mainly related to the adiabatic hypothesis. Its historical relevance in the development of the old quantum theory has been discussed elsewhere (Klein, 1985; Navarro & Perez, 2004; Navarro & Pérez, 2006; Pérez, 2009). In this note, we focus on a problem which accompanied Ehrenfest for the (more than) 10 years during which he dealt with this hypothesis, and that, as far as we know, remained open within the frame of the old quantum theory. This problem –this "deep mystery"[1] as Jan M. Burgers[2] put it some years later—appeared in the very first application of the adiabatic hypothesis: in the extension of Planck's quantization (for a harmonic oscillator) to a rotating molecule.

In this paper we wish to describe how Quantum Mechanics—in particular, the wave mechanics of Schrödinger—provides an explanation for this difficulty and why the old theory did not—indeed, could not. To do that, we introduce the problem in the form used by Ehrenfest in 1913 (Section 2), and we give a brief account of the classical adiabatic theorem to establish the conditions which must apply for its validity (Section 3). In Section 4 we go into Niels Bohr's objection to Ehrenfest's application of the hypothesis, and in Section 5 we go back to Ehrenfest's later research and his last discussion of the adiabatic issue, in 1923, when he mentioned once more the conundrum we are discussing here (indeed, according to Burgers, Ehrenfest never stopped "turning around with it"[3]). In Section 6 we revisit Ehrenfest's dipole model and the paradox that he encountered when applying the adiabatic hypothesis to a system of rotating dipoles. We close the paper discussing how the issue must be treated from the point of view of Quantum Mechanics (Section 7).

2. The first application of the adiabatic hypothesis

The system of an electric dipole suspended in an electric field constitutes the first system in which Ehrenfest applied his idea of quantizing adiabatic invariants (Ehrenfest, 1959b). In 1911, in a long paper devoted to radiation, he had shown that adiabatic

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[1] Interview of Burgers by Kuhn, 6 September, 1962, p. 62 of the transcript. In *Archive for History of Quantum Physics*, microf. AHQP/OHI-1.

[2] Jan M. Burgers (1895–1981) was the first doctorate student of Ehrenfest. He had a crucial role developing the adiabatic hypothesis in the years 1916–1918. When he left Leiden in 1918 he began a new research career mainly dedicated to fluid mechanics.

[3] Interview of Burgers by Kuhn. See Footnote 1.

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invariance was the critical property behind Wien's displacement law, still valid within the quantum realm (Ehrenfest, 1959a). The quantization of the adiabatic invariants of black-body radiation assured the validity of Wien's law, and hence, consistency with the second law of thermodynamics. A few weeks after moving from Petersburg to Leiden, in the Christmas season of 1912 (he gave his inaugural lecture on 4 December), Ehrenfest described in his notebooks a mechanical theorem by Boltzmann–Clausius–Szily and its relation to the quantum hypothesis.[4] In other words, he found the germ of the principle later baptized by Albert Einstein the "adiabatic hypothesis." But he did not publish this result until November 1913. Before that, in May, he sent to the *Deutsche Physikalische Gesellschaft* a little calculation on the specific heat of molecular hydrogen, where he applied his new hypothesis. According to Klein (1985, p. 264):

> He did not rush into print with these ideas; what seemed so clear might, after all, not be correct. What he needed was a test case, a suitable physical problem on which he could try out his ideas…

We find the application of Ehrenfest's discovery in his notebooks, not in the paper. In the latter, he simply justifies the quantization of the kinetic energy of a rotator with a fixed axis by appealing to "… a very general point of view" (Ehrenfest, 1959b,p. 453, Footnote 1), which he does not describe. This quantization reads:

$$\frac{L}{2}(2\pi\nu)^2 = n\frac{h\nu}{2} \tag{1}$$

(L is the moment of inertia, ν the frequency of rotation, h Planck's constant, and n an integer). And for angular momentum p $(=L\omega=2\pi\nu L)$,

$$p = 0, \pm\frac{h}{2\pi}, \pm 2\frac{h}{2\pi}, \pm 3\frac{h}{2\pi}, \ldots \tag{2}$$

According to Ehrenfest's notebooks his attendance at the *Wolfskehl Lectures* of that same Spring (the *Gaswoche*) could have triggered the preparation of the paper, as he wrote it all at once when he returned to Leiden. But what is beyond any doubt is that replying to Einstein's paper with Otto Stern of 1913 on the same subject was Ehrenfest's goal (Einstein & Stern, 1996). This is what he said to his close friend Ioffé about this "trifle," obtained purely "by calculation"[5]:

> This is interesting, because it can be obtained *without* the introduction of the "absolute zero energy"! And the fact is that Einstein obtained his [and Stern's] curve by means of a not completely correct calculation, in which he turned out to have been bound to have recourse to this "absolute zero energy," to obtain again through a not very correct way the form of the curve of this sort [Ehrenfest here draws its horizontal asymptote]. Here, however, we achieve an absolutely correct calculation without employing the "absolute zero energy"!

Indeed, Einstein and Stern interest was in testing the existence of the zero point energy, a by-product of Planck's new ("second") quantum theory (Klein, 1985, pp. 266–267). Within Einstein's and Stern's approach all molecules in the hydrogen gas rotate with the same frequency $\nu(T)$. These authors argued that a rotating dipole absorbs and emits twice as much as a one-dimensional oscillator "for which the amplitude of the electric and mechanical moment equals the electric and mechanical moment of the dipole" (Einstein & Stern, 1996, p. 138). They obtained the frequency dependence on temperature equating the kinetic energy of the rotator:

$$\frac{L}{2}(2\pi\nu(T))^2$$

to two different expressions of the mean energy of a Planckian oscillator (for which the total energy is twice the mean kinetic energy), with or without zero point energy:

$$E = \frac{h\nu(T)}{e^{\frac{h\nu(T)}{\kappa T}} - 1} \tag{3}$$

or

$$E = \frac{h\nu(T)}{e^{\frac{h\nu(T)}{\kappa T}} - 1} + \frac{h\nu(T)}{2}. \tag{4}$$

Once one has obtained $\nu(T)$ for both cases—in fact, $T(\nu)$—, the specific heat c can be calculated through (3) and (4). Therefore:

$$c = \frac{dE}{dT} = \frac{dE}{d\nu}\frac{d\nu}{dT}.$$

At very low temperatures, c goes to zero with either an horizontal (4) or a vertical (3) asymptote (see Fig. 1). Eucken's measurements agreed much better with the curve obtained with a zero point energy.

In contrast, as Eq. (1) expresses, Ehrenfest sets the kinetic rotatory energy equal to the different allowed energies. Therefore:

$$\nu = n\frac{h}{4\pi^2 L} \rightarrow \epsilon_n = n^2\frac{h^2}{8\pi^2 L}.$$

Of course, now ν does not depend on T, but the most probable distribution of ν's does. The good agreement obtained by Einstein and Stern in the low temperature regime (where the curves asymptote horizontally), which was used by them as an argument in favor of the existence of the zero point energy, was obtained by Ehrenfest without resorting to it, just performing a properly statistical treatment.

In the early summer of 1913, once the paper was sent, the Ehrenfests visited Einstein in Zurich for some weeks. There they surely discussed Ehrenfest's new hypothesis, probably along with Stern and Karl F. Herzfeld, who by then were there too. In fact, in Ehrenfest's next paper on this subject, the first properly devoted to Boltzmann's mechanical theorem and its relation to quantum theory, an example suggested to Ehrenfest by Herzfeld is mentioned (Ehrenfest, 1959c).

It is in this paper, communicated to the *Amsterdam Academy* in November, that Ehrenfest justifies his previous extension of

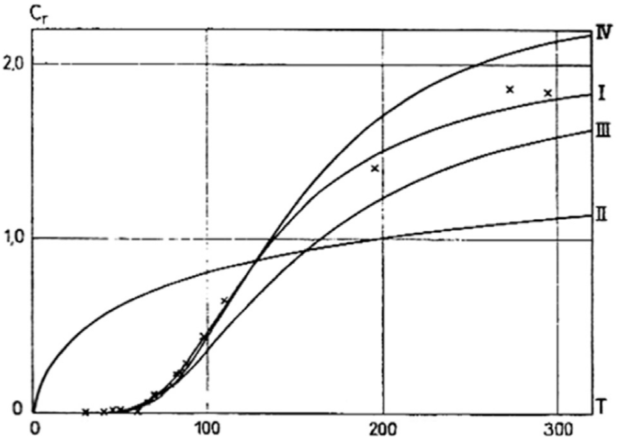

Fig. 1. Einstein and Stern's plots of the specific heat of diatomic hydrogen. Curves I, III and IV are obtained using a zero point energy; curve II without it. Small crosses represent Eucken's experimental data (Einstein & Stern, 1996).

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[4] For a history of the specific heat of hydrogen in quantum theory see Gearhart (2010). The episode of Ehrenfest's research we summarize in this Section is treated in more detail in Klein (1985, pp. 264–273), and Navarro & Pérez (2006).

[5] Ehrenfest to Ioffé, 22 May, 1913. In Moskovchenko & Frenkel (1990, p. 121).

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