History of Science as a Facilitator for the Study of Physics

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A Repertoire of Quantum Theory

By

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To my family: Simona and Edoardo,
lights of my life

TABLE OF CONTENTS

PREFACE

This proposal serves to enhance scientific and technological literacy, by promoting STEM (Science, Technology, Engineering, and Mathematics) education with particular reference to contemporary physics. The study is presented in the form of a *repertoire*, and it gives the reader a glimpse of the conceptual structure and development of quantum theory along *a* rational line of thought, whose understanding might be the key to introducing young generations of students to physics.

The historical development of quantum theory may be presented as a "physiological" extension of the concept of *natural radiation* (symbolized by Planck's constant), which led to a new interpretation of phenomena at micro-scale: the *quantization* of *energy* and *momenta*–as Max Planck formally laid it down in 1900–which Albert Einstein successively developed in 1905, and other physicists extended to wider domains of application: that is, to the *quantization* of *rotational energy* and to the structure of atoms, like Walther Nernst and Niels Bohr respectively did.

With regard to the formulation of Bohr's model of the hydrogen atom, I will focus on the momentous article "On the constitution of atoms and molecules" of 1913 (which is discussed in chapter IV) for shedding new light on one of the most controversial achievements in the history of physics–the Bohr model of the atom–which openly violated the causal relation between optical and mechanical frequency by the orbiting electron. The episode represented a further breakthrough (following Einstein's 1905 discovery of *photon*, see chapter III) along the "history of the relation" between radiation and matter, and it confirmed the hypothesis of an intimate connection between the atomic structure and Planck's constant. The issue at stake here concerns the "conceptual shift" of a universal constant of nature (Planck's *h*) from a mere "mathematical device"–as it was regarded in 1900–to a fundamental law of nature, from 1905 onwards, when it became the "symbol" of the energy quantization. Furthermore, I will provide a brief (and simplified) introduction to some fundamental issues of *quantum mechanics* (circa 1925-27): the concept of quantization, the measurement procedure, as well as the revision of the concepts of position and momentum, and the *uncertainty principle* by Werner Heisenberg.

Since the present study has a pedagogical purpose, throughout this survey I have been concerned with presenting scientific discoveries in connection with the circumstances and backgrounds underlying the implementation of experiments, without overlooking the relationships between the relevant theoretical work and the related experimental domain. In this regard, I decided to introduce the discoveries of the *neutrino* and the *neutron* in the early 1930s, giving account of the backgrounds underlying the experiments that confirmed their existence. On the one side, when Wolfgang Pauli introduced the hypothesis of the existence of neutrino, he expressed complete dissatisfaction, because at the time this particle was unexpected. Whereas the discovery of the *neutron* by James Chadwick was the *climax* of a multiple-step process that started in 1903.

Furthermore, in the case of Enrico Fermi's discovery of the *slow neutrons* in 1934–which led to the controlled nuclear fission–I will stress both the importance of the cultural background and the institutional relations, which provided the framework for Fermi's group success.

This is to say: we are used to think of scientists as exceptionally gifted individuals without realizing the importance of the economic, social, political and cultural conditions to their major achievements.

In my view, this is an aspect of the history of science that may offer interesting suggestions and causes for reflection to students. For this purpose I will integrate the discussion about scientific discoveries with scientists' personal and scientific correspondence, quotations from *Nobel lectures*, samples of minutes and letters to disclose the "backstage" of science in one of the most exciting and vibrating periods of the history of physics.

Finally, I will focus on two fundamental contributions to the formulation of quantum electrodynamics: Richard Feynman's formulation of a space-time view of quantum electrodynamics and Julian Schwinger's *quantum action principle* which underlies his "functional-based approach" to quantum electrodynamics. The two scientists confronted each other with the construction of the mainframe of contemporary particle physics, that is, the so-called *Standard Model*, which is up-to-now the best theory for explaining the behaviour of relativistic quantum phenomena and the structure of matter.

Acknowledgements

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Abbreviated Titles of Periodicals

Naturwiss.	Naturwissenschaften
Z. Phys.	Zeitschrift für Physik
Proc. Roy. Soc. (London)	Proceedings of the Royal Society (London)
Ann. d. Phys.	Annalen der Physik
Verh. d. Deutsch. Phys. Ges.	Verhandlungen der Deutschen Physikalischen Gesellschaft
Sitz.ber. Preuss. Akad. Wiss.	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften

CHAPTER I

THE HEURISTIC VALUE OF THE ATOMISTIC DOCTRINE

The atomistic doctrine from time to time addressed and anticipated issues that have become fundamental in modern and contemporary physics, by serving also an important heuristic function in pre-modern physical sciences. Yet atomism had a discontinuous success in the history of physics and chemistry, due to the limits of man's capacity to visualize phenomena at micro level. Given the importance of atomism for the history of physics, and quantum physics–in particular–I shall begin this repertoire by presenting the main ideas and conceptions implicit in atomism. In fact, the concept of atom, with its ambiguities and misconceptions, was prodromic to the development of modern physics.

The concept of atom had been introduced by the ancient Greek philosophers, especially by Democritus of Abdera (born 470-460 B.C.?, died around 370 B.C.), to account for the complexity of natural phenomena and their changes. According to this view, there should exist innumerably many, unchangeable atoms having different shapes and sizes, which move about constantly. Atoms were regarded as the smallest constituents of all matter; the different kinds of matter consisted of different atoms, having different positions with respect to each other.

In ancient times, the atomic view of nature had been propagated by Epicurus of Samos (341-270 B.C.) and Lucretius Carus (96-55 B.C), but in the philosophy of the Middle Ages it had not played a major role.

Atomism was rediscovered in the seventeenth century, notably by Pierre Gassendi (1592-1655), and then incorporated into the "new" science with the advent of the Modern Age: Robert Boyle (1627-1691) connected it with chemistry, and Isaac Newton (1643-1727) used it in mechanics and optics. These are two examples of the heuristic role of the concept of atom, which served as a guide for scientists who aimed at explaining the behaviour of matter. After that, the atomic hypothesis did not contribute essentially to the progress of science in the following hundred years.

This could be ascribed to the fact that nothing was known about the specific properties of atoms. But the situation changed when the chemist Antoine Laurent Lavoisier (1743-1794) made a fundamental contribution to the process of combustion, which he recognized as being connected with the binding of oxygen by certain substances.

Results from a series of experiments led Lavoisier to express his conclusion and to formulate the law of conservation of mass in chemical reactions (1773). He then defined a number of substances as elementary ones or elements, because they could not be separated by chemical methods; they included some of the best-known metals like silver, gold, mercury, antimony and zinc.

Contemporary to Lavoisier, Joseph Louis Proust (1754-1826) made a new important step in establishing the law of definite proportions, which stated that the elements in a given compound were present in a fixed proportion by weight. This law was first formulated explicitly by John Dalton (1766-1844), who has the merit of having brought atomism into chemistry through his works between 1803 and 1808. Dalton argued, specifically, that the ultimate particles in a chemically homogeneous substance had the same weights and the same shape. He then set forth a table of relative weights of the atoms for a number of elementary substances, derived by the chemists of his time from the analysis of water, ammonia, carbon dioxide and other compounds. Furthermore, Dalton added to Joseph Proust's law of definite proportions the law of multiple proportions (1803), stating: if a given amount of weight of a chemical substance combines with different amounts of weight of another element to form compounds, the ratios among them can be represented by the ratios of small integers[1].

The laws of Proust and Dalton found support in an observation of Joseph Louis Gay-Lussac (1778-1850), from which he derived the law of combining gases (1808): when gases combine with each other, they do so in simple proportions of their volumes.

Following Gay-Lussac's law, Amedeo Avogadro (1776-1856) drew a far-reaching conclusion: under identical conditions of temperature and pressure, equal amounts of gases contain the same number of molecules, which goes under the name of Avogadro's law (1811).

The validity and importance of Avogadro's hypothesis was not acknowledged right away, and this neglect caused considerable confusion in chemistry during the following decades.

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[1] *Cf.* Jagdish Mehra and Hans Rechenberg, *The Historical Development of Quantum Theory* (New York: Springer-Verlag, 1982), Vol. 1, Part I, p. 12.

Only when Stanislao Cannizzaro (1826-1910) accepted Avogadro's hypothesis fully in 1858 was he able to establish a consistent nomenclature for chemical substances. However, some opposition arose against Cannizzaro's proposals because there seemed to be exceptions to Avogadro's hypothesis[2].

Some years later, especially the scientists who worked on dissociation processes, like Jacobus van't Hoff (1852-1911) and Walther Nernst (1864-1941), finally returned to advocate the atomic hypothesis. To the title of his book on *Theoretical Chemistry*, Nernst wanted to add: "from the point of view of Avogadro's rule"[3]. This was an important acknowledgement for the concept of atom, for the majority of the chemists–since Dalton's time–had given up the belief in the atomic hypothesis. The reason was that chemists were inclined to interpret the results of Lavoisier, Proust and Dalton as expressing simple ratios not necessarily connected with the existence of ultimate particles (atoms).

In the meanwhile, some chemists joined forces with physicists to provide further support to the atomic hypothesis, by discovering certain properties–such as the specific heat of solids from 1819, via the rule of Pierre Dulong (1785-1838) and Alexis Petit (1791-1820)–which were used to determine the chemical composition of molecules.

Another hint in this direction came from the researches carried out by Johann Döbereiner (1780-1849) who–in 1817–discovered the so-called law of triads (a group of three elements), and the *relative atomic mass* of the middle element in each triad. Furthermore, André Dumas (1800-1884) also contributed by the mid-1840s to finding relations between the atomic weights of elements and their properties.

It was towards the end of the 1860s that two chemists–Dmitri Mendeleev in 1869 and Julius Meyer in 1870–proposed the *Periodic System of Elements*, in which natural elements were basically arranged according to rising atomic weights.

Notwithstanding the recognized importance to the elaboration of the *Periodic Table*, influential scientists and philosophers continued to express strong reservations against the atomic hypothesis.

To sum up, the development of physics during the nineteenth century generally did not tend to favour the atomic constitution of matter. Rather, the results in optics and electrodynamics pointed to the necessity of continuum theories (like Maxwell's theory of electromagnetism). But one

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[2] *Ibid*. p. 13.

[3] Walther Nernst, *Theoretische Chemie vom Standpunkte der Avogadroschen Regel und der Thermodynamik* (Stuttgart: F. Enke, first ed. 1893).

field of research challenged the dominant "anti-atomic" trend: the kinetic theory of gases (from which Max Planck started to elaborate his first theory of radiation), which actually met with fundamental issues that would be developed later by the quantum theory.

It is worth anticipating that the main assumptions involved in the kinetic theory of gases were the following: a gas consists of molecules, which may be represented roughly by elastic spheres; the molecules move with a certain velocity in straight lines until they collide with each other or the "wall" of a container. In this regard, the gas pressure could be explained immediately by the elastic impacts of the molecules on the wall of that container; the kinetic energy of the molecules was assumed to be proportional to the absolute temperature, which provided a relation for calculating the velocity of the molecules.

Rudolf Clausius (1822-1888) and James Clerk Maxwell (1831-1879) improved the kinetic theory of gases in the mid-nineteenth century. In particular, Maxwell removed the assumption in August Kröning's and Clausius' treatments that all molecules possess the same velocity by showing that the velocities of the molecules were distributed according to a certain law.

Maxwell, Ludwig Boltzmann (1844-1906) and others succeeded in deriving the detailed properties of gases, such as internal friction, diffusion and heat conduction from the kinetic theory. In spite of these important results, at the end of nineteenth century, the "atomic hypothesis" did not convince yet the great majority of physicists.

Ernst Mach (1838-1916), Wilhelm Ostwald (1853-1932) and Pierre Duhem (1861-1916)–for example–raised doubts over the reality of atoms and molecules as constituents of matter, arguing that physical phenomena could rather be described in terms of "energy" considerations.

The two opposing sides (Boltzmann, on the one hand, and the "partisans" of the so-called "energetics hypothesis", on the other) confronted each other at the Lübeck's *Assembly of Natural Scientists* in September 1895.

Boltzmann firmly defended his hypothesis, by claiming that none of the existing physical theories could be developed on the basis of Ostwald's assumptions[4]. He was convinced that the attacks of the "energeticists" were based on a misunderstanding, for this reason he could not doubt the validity of the theory of gases and the atomic hypothesis inherent to it.

[4] Ludwig Boltzmann, "Zur Energetik" (On the energetics), *Ann. d. Phys.*, 1896, 58 (3): 595-598 (published in issue No. 7 of 21 June 1896).

> In my opinion it would be a great tragedy for science if the theory of gases were temporarily thrown into oblivion because of a momentary hostile attitude toward it, as was for example the wave theory because of Newton's authority. I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered[5].

As it is evident, such a dogmatic opposition to the kinetic theory frustrated Boltzmann's hypothesis regarding the atomic constitution of matter. And the absence of a direct proof of the atomic hypothesis may have been one of the causes of his suicide in 1906. But Boltzmann was right, and a proof had already been found in 1905 by a still unknown scientist (at the time), Albert Einstein (1879-1955) who–with his quantitative theory of Brownian motion (random movement of particles suspended in a fluid, in a liquid or in a gas, discovered by the Scottish botanist Robert Brown in 1827)–gave full support to Boltzmann's hypothesis and to the existence of atoms.

What counts as evidence today is related to the fact that Boltzmann was able to grasp the discontinuous nature of microphysical phenomena and to build on that a new theory that the ideological trend of the epoch refused to accept, because of a preconceived opinion against the concept of atom.

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[5] Boltzmann, *Vorlesungen über Gastheorie. II Teil: Theorie van der Waals'; Gas mit zusammengesetzten Molekülen; Gasdissociation; Schlussbemerkungen* (Lectures on the theory of gas. 2nd part: Van der Waal's theory; gas with compound molecules; gas dissociation; concluding remarks). Leipzig: J. A. Barth, 1898, p. v.

CHAPTER II

THE DISCOVERY OF PLANCK'S CONSTANT AND THE BREAKTHROUGH OF QUANTUM THEORY

Quantum theory concerns the study of the structure of microphysical world. And one of the chief aspects of quantum theory is the attention devoted to mutual interactions and motions of matter in space and time.

Whereas in classical physics we can neglect the consequences of the interaction between two bodies (specifically, if it is required by the conditions of the experiment, the interaction between two physical bodies can be reduced to zero), we are not allowed to underestimate these interactions in quantum physics, where even the same process of observation and the means by which we observe phenomena can affect the experiment.

New empirical facts accumulated since the end of the nineteenth century have shown that there exists in nature a lower limit of interaction that cannot be surpassed. This lower limit is negligible on the macro scale, but it becomes fundamental when we handle interactions among atoms and molecules, that is, at the micro level. In fact, there are finite energy-elements $h\nu$, which characterize the interaction between the matter and the radiation: that is, only a determinate amount of energy can be transferred from matter to radiation and vice versa, according to the law

$$E = h\nu, \tag{2.1}$$

where h is a universal constant and ν is the frequency. It was the German physicist Max Planck (1858-1947) who introduced the constant h that has become characteristic of quantum phenomena, as it gives the lower limit of interactions between matter and radiation.

2.1 Max Planck and the formulation of the first blackbody law

The historical process that led Max Planck to discover the constant of nature *h* deserves a proper discussion. There is, in fact, a common misconception among many commentators and historians about the meaning of the constant *h* at the time Planck introduced it in 1900-1901.

Beyond a shadow of a doubt, Planck introduced the constant *h* that has become characteristic of quantum phenomena; he associated finite energy-elements $h\nu$ with harmonic oscillations at the frequency ν; he provided a proof for the blackbody law. Most important, Planck discovered a new method that led to the formulation of quantum theory. However, it is worth noticing that the introduction of energy-elements does not presuppose a discontinuity of the energy of the resonator.

On 14 December 1900, Planck presented his new radiation law at the German Physical Society in Berlin. He started his speech by emphasizing the necessity of using Boltzmann's probability arguments in the blackbody theory, and he soon after dealt with the distribution of a given amount of energy E, among N cavity resonators with frequency ν.

> If E is considered as an infinitely divisible quantity, the distribution can be made in an infinite number of ways. However, we consider – and this is the most important point of the entire calculation – E as being composed of a completely definite number of finite, equal parts, and make use for that purpose of the natural constant[1] $h = 6.55 \cdot 10^{-27}$ (Erg · Sec^2). This constant, when multiplied by the common frequency ν of the resonators, yields the energy element ε in ergs; and by dividing E by ε we obtain P, the number of energy elements, which have to be distributed among the N resonators. If the quotient (E/ε) thus calculated does not happen to be an integral number, then one has to take for P an integer close to it (the quotient)[2].

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[1] Planck introduced the notion of "elementary quantum of action" with the following words: "I want to designate this [i. e. the constant h] as the elementary quantum of action [elementares Wirkungsquantum] or as "element of action" [Wirkungselement], because it has the same dimension as the quantity which owes its name to the Principle of Least Action [Planck, *Vorlesungen über die Theorie der Wärmestrahlung* (Lectures on the theory of heat radiation), Leipzig: J. A. Barth, 1906, p. 154]. I point out that in English-speaking countries the notion of "quantum of action" remained uncommon for many years.

[2] Max Planck, "Zur Theorie des Gesetzes der Energieverteilung im Normalspectrum" (On the theory of energy distribution in normal spectrum), *Verh. d. Deutsch. Phys. Ges.*, 1900, 2 (2): 237-245 (presented on 14 December 1900, published in issue No. 17), pp. 239-240. Reprinted in Planck, *Physikalische Abhandlungen und*

How did Planck come to this formulation?
A scientist's biography may give some clues about the *process of discovery* underlying the formulation of a theory, which, in this case, introduces a new relation among phenomena. As a matter of fact, Planck's social and cultural milieu may help to explain his conservative attitude, that is, the reason for which he did not accept discontinuity in physics.

Max Karl Ernst Ludwig Planck was born in Kiel on 23 April 1858, the son of a law professor at the university of that city; he had received his early education in Kiel and Munich and had studied physics and mathematics at the University of Munich (1874-1877) and Berlin (1877-1878). Among his professors were Philipp von Jolly in Munich, Hermann von Helmholtz and Gustav Kirchhoff in Berlin.

Planck obtained his doctorate, summa cum laude, from the University of Munich, and became *Privatdozent* in Munich the following year. In 1885 he accepted a call to an *Extraordinariat* (associate professorship) at the University of Kiel, and four years later he moved to the University of Berlin, where he was promoted to a full professorship of theoretical physics in 1892. Planck devoted his early scientific career to the investigation of one general topic, the second law of thermodynamics, especially the concept of entropy and its application to problems of physical and chemical equilibrium, such as phase transitions and electrolytic dissociation. His first public papers already exhibited the characteristic features of his later work: on the one hand, he carefully worked out the details of his theories and calculated results that could be compared immediately with the available experimental data; on the other, he put great emphasis on clear definitions of the fundamental concepts. Having been deeply influenced by Rudolf Clausius, he had sought in particular to establish the "principle of the increase of entropy" in thermodynamics on the same level as the law of conservation of energy.

In this endeavour he had pointed out the crucial role of irreversible processes, i.e., the fact that in nature processes occur, such as the conduction of heat, which cannot be reversed completely. Planck's analysis of mechanical and thermodynamic concepts had brought him into disagreement with Wilhelm Ostwald and the partisans of "energetics".

For example, at the Lübeck's *Assembly of Natural Scientists* in 1895–where Ostwald and Georg Helm had propounded the views of the "energeticists" against Boltzmann's atomic hypothesis–Planck had been on Boltzmann's side. However, unlike Boltzmann, who had argued against

Vorträge, (Physical essays and lectures), Vol. I (Braunschweig: Vieweg & Sohn, 1958), pp. 698-706.

Energetik on the basis of the molecular hypothesis and the kinetic theory of matter, Planck had used thermodynamic reasoning in order to criticize Ostwald's concept of "volume energy". Indeed, Planck had adopted a very cautious attitude towards the molecular hypothesis and, in a paper entitled "Against the New Energetics", he had declared concerning the point: "I do not intend, at this point, to enter the arena on behalf of the mechanistic view of nature; for that purpose, one has to carry out far-reaching and, to some extent, very difficult investigation"[3].

At the time of the controversy about *Energetik* Planck had turned his attention to what was a new field of investigation for him: heat radiation. Several reasons may be cited why he had become interested in this field. First, there was the general interest of many physicists in the phenomena of electromagnetic waves after Heinrich Hertz' successful experiments.

A second reason was Planck's concern with the importance of thermodynamic arguments in electromagnetism. Thus, for example, in his inaugural address to the Prussian Academy on 28 June 1894, he had expressed the hope

> […] that we can obtain a closer understanding also of those electrodynamic processes, which are directly caused by the action of temperature and which show up especially in heat radiation, without having to follow the laborious detour through the mechanical interpretation of electricity[4].

Evidently, Planck had had the occasion to participate in many discussions between his Berlin colleagues, such as Willy Wien and Heinrich Rubens, who worked actively on the problem of heat radiation[5].

Max Planck was aware of Wien's law, which represented the existing observations extremely well. However, the derivation given by Wien did not satisfy Planck's taste completely. Planck, in fact, hoped to arrive at the same equation in a more systematic way, using fewer hypotheses than his predecessor.

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[3] Planck, "Gegen die neuere Energetik" (Against the new energetics), *Ann. d. Phys*., 1895, 57(3): 72-78 (dated December 1895, published in issue No. 1 of 15 December 1895), p. 73. Reprinted in Planck, *Physikalische Abhandlungen* (ref. 2), pp. 459-465.

[4] Planck, "Antrittsrede" (Inaugural speech), *Sitzber. Preuss. Akad. Wiss. (Berlin)*, pp. 641-644, (presented at the meeting of 28 June 1894), p. 643. Reprinted in Planck, *Max Planck in seinen Akademie-Ansprachen* (Planck's academic speeches), Berlin: Akademie Verlag, 1948, pp. 1-5.

[5] *Cf.* Jagdish Mehra, *The Golden Age of Theoretical Physics* (Singapore: World Scientific Publishing, 2001), Vol. 1, p. 27.

2.2 The state-of-the-art of physics on *fin de siécle*

When Planck started to study physics in the 1870s, Maxwell's theory of electrodynamics was the leading theory also in Germany, where Heinrich Hertz contributed, by means of experiments–which compared various electrodynamics theories–to give a "modernist" interpretation of Maxwell's system and to underpin its foundation.

Besides electromagnetism, the other fundamental domain of physics at the time was the thermodynamics of Rudolf Clausius and William Thomson, which was not immune to changes either. In this regard, Ludwig Boltzmann was developing a kinetic approach to thermal phenomena, putting forward a statistical conception of irreversibility. Boltzmann contributed to elaborate a probabilistic interpretation of the second law of thermodynamics (the entropy law). However, most German physicists did not follow Boltzmann's interpretation, as they propounded the idea of a macroscopic application of the two laws of thermodynamics (energy conservation and entropy). This situation changed at the turn of the century, when statistical and atomistic methods started to penetrate German physics[6].

As it is evident, Max Planck experienced and worked in a context of changes and divergences in theoretical conceptions, which undermined the same foundations of physics. On his side, Planck was interested in clarifying the meaning of the two laws of thermodynamics, and in doing so he aimed at applying them to a wider range of phenomena. More specifically, around 1897 Planck started to devote himself to the radiation problem, which attracted him in particular for the universal character of the distribution law (required by Kirchhoff's theorem).

It is worth reminding that in 1860 Gustav Kirchhoff had shown that the nature of the radiation in thermal equilibrium in an enclosure (a blackbody, that is to say: a cavity whose walls can emit or absorb light of every possible frequency) is completely independent of the properties of any material bodies, rather it depends on temperature only.

Planck approached this domain of research also in consequence of the metrological importance of the radiation problem, which was a means to measure the temperature of a blast furnace. We here can appreciate a straightforward example of interconnection between industrial revolution and science development.

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[6] *Cf.* Olivier Darrigol, "Continuities and discontinuities in Planck's *Akt der Verzweiflung*", *Ann. Phys.*, 2000 (9): 951-960, p. 952.

At any rate, by studying the thermalization of electromagnetic radiation, Planck aimed at a new understanding of thermodynamic irreversibility. In his dissertation of 1879, Planck had made irreversibility and the increase of entropy the essence of the second law of thermodynamics. In the wake of Boltzmann, Planck sought to give a dynamical justification of the entropy increase, although he doubted both the statistical interpretation of irreversibility and Boltzmann's gas-theoretical solution, which was based on atomistic considerations. Both of two solutions were, in fact, incompatible with Planck's *conservative* attitude, which made him inclined to stick to the "traditional" interpretation of the two laws of thermodynamics (which was not statistical at all). Coherently, Planck was seeking to obtain irreversibility by replacing Boltzmann's molecular model with a simple electromagnetic model.

Boltzmann, in fact, was able to derive in 1884 the so-called Stefan's law, which in 1879 had proved that the total energy density over all frequencies is proportional to the fourth power of the temperature. In order to derive theoretically Stefan's law, Boltzmann applied the second law of thermodynamics to radiation, treating it as a gas whose pressure was the radiation pressure of Maxwell's electromagnetic theory.

2.3 Planck's hypothesis of "Natural Radiation"

Returning to Planck, when in the years from 1897 to 1899 he set forth his program for a theory of radiation, this program was in continuity with his early work in thermodynamics for the irreversible approach of radiation to equilibrium. He aimed to show that a conservative system consisting of electromagnetic radiation in a blackbody, interacting with a collection of harmonic oscillators, could approach an equilibrium state without the need of any assumption–unlike Boltzmann–beyond the laws of electromagnetism. Specifically, Planck's idea was that electromagnetic radiation interacting with a system of electric resonators (oscillators) at every possible frequency should irreversibly evolve towards blackbody radiation.

Nevertheless, as Boltzmann himself pointed out to Planck, the laws of electromagnetism did not determine the irreversible approach of radiation to equilibrium. Additional assumptions were needed: statistical assumptions about the disordered character of the initial state such as Boltzmann had made in the kinetic theory of gases. It was in this framework of new ideas that Planck introduced the hypothesis of natural radiation *h*, according to which the partial vibrations of the radiation and the oscillator remained completely incoherent[7].

The introduction of natural radiation made the large-scale evolution of the system an irreversible process. This procedure became known as Planck's electromagnetic *H-theorem*, because in its demonstration Planck used functions of the oscillator and radiation energy that had the same form of Boltzmann's *H-function*, that is

$$S = K \ln W. \tag{2.2}$$

Where S is the entropy, K is Boltzmann's constant, the symbol *ln* stands for the *natural logarithm*, and W is the probability density of the energy over a set of oscillators: the so-called complexion, a definition used also by Boltzmann in 1877. With the difference that: for Planck a "complexion" was given by a correspondence between an oscillator and the number of the energy-elements possessed by this oscillator. For Boltzmann, the correspondence was between a molecule and the discrete energy of the molecule.

We have now arrived at the very crucial question regarding Planck's revolutionary work in 1900, which essentially concerns the method that Planck used for deriving his distribution law: *in what ways did Planck depart from Boltzmann's methods in his statistical calculation of the entropy using energy quanta?*

Planck, in fact, made a fundamental departure from Boltzmann's method, which precisely consists in the variety of complexions considered in the calculation of *W*. On the one side, Planck took for his *W* the total number of complexions for all sets w_r of resonators. On the other side, Boltzmann limited the choice concerning the *complexion* to the number of molecules carrying the energy. This inappropriate generalization of Boltzmann's method was the way to obtain Planck's distribution law[8].

Planck's relation seems to suggest an undue generalization from Boltzmann's method. The relation that here arises is a solution that Planck had to adopt or an *ad hoc* hypothesis that Planck would have formulated in whatever manner (maybe Planck would have turned to any suitable formula of Boltzmann's which had to do with the number of complexions), which had referred to Boltzmann's expression in order to

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[7] Martin Klein, "Max Planck and the Beginnings of the Quantum Theory", *Archive for History of Exact Sciences*, 1962, 1 (5): 459-479, p. 462.

[8] Darrigol, "Statistics and Combinatorics in Early Quantum Theory, II: Early Symptoma of Indistinguishability and Holism", *Studies in History and Philosophy of Biological Sciences*, 1991, 21 (2): 237- 298, pp. 253-254.

obtain the relation between entropy and probability. As Planck admitted some years later:

> But even if the absolutely precise validity of the radiation formula is taken for granted, so long as it had merely the standing of a law disclosed by a lucky intuition, it could not be expected to possess more than a formal significance. For this reason, on the very day when I formulated this law, I began to devote myself to the task of investing it with a true physical meaning. This quest automatically led me to study the interrelation of entropy and probability–in other words, to pursue the line of thought inaugurated by Boltzmann[9].

The quotation above leads us to deal with a fundamental question: how did Planck perceive his own discovery?

He was certainly aware of having introduced a new way of calculating entropies that bridged two domains of physics: radiation theory and gas theory. Specifically, the constant K in the equation (2.2) had to be the same in both realms. However, in 1900-1901, Planck did not make any mention of the meaning of the constant *h*. In particular, he did not say that the energy of a resonator could only be an integral multiple of $h\nu$, introducing–in so doing–the concept of discontinuity in physics, as most historians and even scientists have incorrectly argued.

Planck himself defined the introduction of the *new* constant *h* as a "lucky intuition" or an "act of desperation", and in that context (of discovery) he ascribed to it only a formal character, whose real meaning would be clarified later on.

Another point to stress in relation to Planck's decision of introducing the hypothesis of natural radiation is: *what if Planck had done what he did not, ascribing to "complexion" the same meaning as Boltzmann's?*

By using the so-called counterfactual, we may answer that Planck would get a perfect application of Boltzmann's method, which would have led him to the Rayleigh-Jeans law for the electromagnetic radiation in a blackbody and its contradictory results. Indeed, the Rayleigh-Jeans law agrees with experimental results at low frequencies, but it disagrees with experiments at high frequencies. This argument upholds the claim of an *ad hoc* hypothesis that Planck might have introduced in order to avoid the wrong consequences of Boltzmann's statistical thermodynamics.

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9 Planck, *Wissenschaftliche Selbstbiographie* (Leipzig: Barth, 1948), p. 41. Reprinted in Planck, *Physikalische Abhandlungen und Vorträge*, Vol. III (Braunschweig: Vieweg & Sohn, 1958), pp. 374–401. English translation: Planck, *Scientific Autobiography and Other Papers* (New York: Philosophical Library, 1949).

Counterfactuals aside, Planck made a fundamental discovery in the history of physics, which he himself was not ready to recognize. His distribution law was accepted as describing the facts in a simple and adequate context (the blackbody spectrum), but the theory as such did not gain the due consideration at least until 1905, when Albert Einstein finally grasped the full significance of Planck's hypothesis.

The reasons of the delay in ascribing to Planck's law the importance it deserved were mostly scientific: first, the theory of radiation was not the centre of interests in physics in 1900. For example, scientists had other priorities at the time: X-rays were discovered in 1898; radioactivity in 1896, the electron in 1897; radium in 1898. Nevertheless, we can identify also an extra-scientific motivation underlying Planck's difficulty in putting forward his thesis. Planck was midway between Boltzmann's atomic mechanical view of the world and the anti-atomistic program supported by Ostwald, Mach, and Duhem, who denied the importance of the whole program of Boltzmann's kinetic theory of gases. Planck stood on Boltzmann's side versus the "energetics" school, in spite of his doubts on Boltzmann's work at that time. But his hesitancy had a price.

To sum up, the case of the original relation that Planck's constant had established–among the frequencies in blackbody radiation–is emblematic. Later, it was replaced by Einstein's derivation in 1905, and then extended by Einstein himself to the attempt of a discrete selection of mechanical states in 1906.

The introduction of Planck's constant–a new constant of nature–is hence the starting point of a "conceptual chain" of relations inherent in the structure of a new theory with respect to both thermodynamics and Boltzmann's relation.

CHAPTER III

EINSTEIN'S CONTRIBUTION TO QUANTUM THEORY

Albert Einstein was the right man in the right place to receive the implications of Planck's ideas, as well as he was bold and ambitious enough to develop them in a variety of directions. Anticipating his contemporaries, Einstein was well aware of the revolutionary implications of Planck's work, as he himself confirmed many years later, recalling those days: "It was as if the ground had been pulled out from under one, with no firm foundation to be seen anywhere upon which one could have built"[1].

But Einstein took some time before turning to Planck's radiation formula. For the reason that from 1900 to 1905 Planck's radiation law was generally considered to be neither more nor less than a successful representation of the data. Only in 1905 things began to change, the main reason being the failure of the Rayleigh-Jeans law.

To summarize: in 1900 Planck discovered the blackbody radiation law; in 1905 Einstein discovered light-quanta without using Planck's law. In particular, Einstein extracted the light-quantum postulate from an analogy between radiation in the Wien regime (according to which the blackbody radiation curve for different temperatures peaks at a wavelength inversely proportional to the temperature) and a classical ideal gas of material particles. In 1906, Einstein completed the first paper of the quantum effects in the solid state. This paper was fundamental for the formulation of the third law of thermodynamics (according to which, it is impossible for any process to reduce the entropy of a system to its absolute zero-value in a finite number of operations) by Walther Nernst, and it laid the basis for the successive studies on the quantization of rotational energy, which led to the formulation of Niels Bohr's first atomic theory.

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[1] Peter A. Schilpp (ed.), *Albert Einstein: Philosopher-Scientist. The Library of Living Philosophers*, Vol. 7 (Evanston, IL: The Library of Living Philosophers, 1949), p. 45.

3.1 Einstein's cultural background and his early works on radiation and matter

Between 1900 and 1904, Einstein started to submit to the journal *Annalen der Physik* a series of papers dealing with problems of the foundations of thermodynamics and kinetic theory, from which, in 1905, he finally drew two important conclusions: i) particles suspended in a fluid must execute an irregular motion even if the fluid is at rest (Brownian motion); ii) he arrived at an important conclusion concerning the nature of radiation (light-quantum hypothesis):

> According to the assumption considered here, when a light ray starting from a point is propagated, the energy is not continuously distributed over an ever increasing volume, but it consists of a finite number of energy quanta, localized in space, which move without being divided and which can be absorbed or emitted only as a whole[2].

As it is evident, there is an important difference between Planck and Einstein with regard to energy quanta. Einstein put forward a *revolutionary* hypothesis of the existence of localized energy quanta in radiation. By contrast, Planck had based his derivation of the energy distribution in blackbody radiation entirely on Maxwell's electromagnetic theory of light, in continuity with *classical physics*.

How did Einstein come to such a conclusion? The answer may be found in the peculiar personality of the young Albert as well as the cultural and social milieu in which Einstein grew up, far away from the academic world.

Albert Einstein was born on 15 March 1879 in Ulm, Württenberg, Southern Germany, the son of the Jewish merchant Hermann Einstein and his wife Pauline Koch. The family moved to Munich the following year, where Hermann Einstein opened a small electro-technical workshop together with his brother Jakob. In Munich Einstein received his early education. He became a pupil of the Catholic elementary school, and then he attended the Luitpold-Gymnasium. Several months after the family had moved to Milan in 1894, Einstein left the Gymnasium; he first joined the family in Italy and was then sent to Switzerland to complete his education.

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[2] Albert Einstein, "Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt", *Ann. d. Phys.*, 1905, 17 (4): 132-148, p. 133. English translation: "On a heuristic point of view about the creation and conversion of light", in Dirk ter Haar, *The Old Quantum Theory* (London: Pergamon Press, 1967), 91-107.