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# The Bose-Einstein statistics: Remarks on Debye, Natanson, and Ehrenfest contributions and the emergence of indistinguishability principle for quantum particles

## Abstract

The principal *mathematical* idea behind the statistical properties of black-body radiation (photons) was introduced already by L. Boltzmann (1877/2015) and used by M. Planck (1900; 1906) to derive the frequency distribution of radiation (*Planck's law*) when its discrete (quantum) structure was additionally added to the reasoning.

The fundamental *physical* idea – the principle of indistinguishability of the quanta (photons) – had been somewhat hidden behind the formalism and evolved slowly.

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Here the role of P. Debye (1910), H. Kamerlingh Onnes and P. Ehrenfest (1914) is briefly elaborated and the crucial role of W. Natanson (1911a; 1911b; 1913) is emphasized.

The reintroduction of this Natanson's statistics by S. N. Bose (1924/2009) for light quanta (called photons since the late 1920s), and its subsequent generalization to material particles by A. Einstein (1924; 1925) is regarded as the most direct and transparent, but involves the concept of grand canonical ensemble of J. W. Gibbs (1902/1981), which in a way obscures the *indistinguishability* of the particles involved.

It was ingeniously reintroduced by P. A. M. Dirac (1926) via postulating (imposing) the transposition symmetry onto the many-particle wave function.

The above statements are discussed in this paper, including the recent idea of the author (Spałek 2020) of transformation (transmutation) – under specific conditions – of the indistinguishable particles into the corresponding to them distinguishable quantum particles.

The last remark may serve as a form of the author's *post scriptum* to the indistinguishability principle.

**Keywords:** *black body radiation, Planck's law of radiation, particle indistinguishability, quantum statistical physics, Natanson statistics, Bose-Einstein statistics*

# Statystyka Bosego-Einsteina: Uwagi na temat wkładu P. Debye'a, W. Natansona i P. Ehrenfesta oraz wyłonienie się zasady nierozróżnialności cząstek kwantowych

## Abstrakt

Zasadnicza idea *matematyczna* opisu własności statystycznych promieniowania ciała doskonale czarnego (fotonów) wprowadzona została już przez L. Boltzmanna (1877/2015) i użyta przez M. Plancka (1900; 1906) do uzasadnienia wyprowadzenia rozkładu po częstościach dla tego promieniowania (prawo Plancka), jeśli jego dyskretna (kwantowa) struktura została dodatkowo dodana do tego rozumowania.

Fundamentalna idea fizyczna – zasada nierozróżnialności kwantów (fotonów) jest w pewnym stopniu ukryta w tym formalizmie i ewoluowała powoli.

Tutaj omawiamy krótko rolę P. Debye'a (1910), H. Kamerlingha Onnesa i P. Ehrenfesta (1914), a przede wszystkim podkreślamy zasadniczy wkład W. Natansona (1911a; 1911b; 1913).

Ponowne wprowadzenie tej statystyki przez S. N. Bosego (1924/2009) dla kwantów światła (zwanych fotonami od końca lat dwudziestych XX wieku) i następującej po niej statystyki A. Einsteina (1924,1925) dla cząstek materialnych jest uważane za najbardziej bezpośrednie i przejrzyste, ale zawiera koncepcje *dużego rozkładu kanonicznego* J. W. Gibbsa (1902/1981) i do pewnego stopnia przesłania także zasadę nierozróżnialności cząstek.

Tę zasadę wprowadził ponownie w sposób genialny P. A. M. Dirac (1926), włączając (narzucając) symetrię względem przestawień pary współrzędnych cząstek (inwersji) wielocząstkowej funkcji falowej.

Powyższe stwierdzenia są przedyskutowane w tej pracy, włącznie z niedawno sformułowaną ideą autora (Spałek 2020) *przekształcenia (transmutacji)* – w specyficznych warunkach – cząstek nierozróżnialnych w korespondujące z nimi, rozróżnialne cząstki.

Ta ostatnia uwaga ma służyć jako *post scriptum* autora do zasady nierozróżnialności.

**Słowa kluczowe:** *promieniowanie ciała doskonale czarnego, rozkład Plancka dla promieniowania, nierozróżnialność cząstek, kwantowa fizyka statystyczna, statystyka Natansona, statystyka Bosego-Einsteina*

## 1. Motivation

The Bose-Einstein statistics is a well-established branch of quantum condensed matter physics[1], particularly after the discovery in 1995 of Bose-Einstein (BE) condensation for practically ideal atomic gasses[2]. From a theoretical point of view, its fundaments are solid and now

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[1] The very term "Bose-Einsteinische Statistik" was coined at the latest in 1925. The English term "Bose-Einstein statistics" was used only in 1950, earlier, the term "Einstein-Bose statistics" was in usage – cf. Kokowski 2019, pp. 408–409.

[2] See: Anderson, et al. 1995; Davis, et al. 1995. The very term "Einstein condensation" was probably coined by F. London (1938).

are based on the combinatorial symmetry of the many-particle wave function with respect to the transposition of particle-pair coordinates[3].

Imposition of this symmetry on such a multi-particle state resolves the well-known fundamental puzzle why even an ideal (noninteracting) gas of those particles exhibits a phase transition, here in the form of BE condensation. Namely, the imposed symmetry on the wave function introduces the quantum coherence into macroscopic state and those correlations, in turn, induce phase transition on the thermodynamic scale. Simply put, the transition results from a competition between the tendency of forming the coherent ground state with minimum energy and the entropy part ($-TS$) of the resultant Gibbs free energy of that state at temperature $T > 0$. Nevertheless, questions related to the principle of quantum-mechanical particles *indistinguishability* are often analyzed in physical terms and in particular, its relation to the entanglement and coherence of particles in a practically noninteracting (but still non-separable) situation.

Related to this question is that about the origin of particle indistinguishability in its historical context. This last question is relevant to the works of P. Debye (1910), W. Natanson (1911a; 1911b; 1913), H. Kamerlingh Onnes and P. Ehrenfest (1914/1915) with a different thoroughness, i.e., well before the paper of S. N. Bose (1924/2009), A. Einstein (1925/2015a; 2015b), and P. A. M. Dirac (1926).

This story can thus throw some light also on the sociological aspects of science, although this in not the intention of this paper. Instead, we comment *briefly* (i.e., without going into details) on the achievements of the first four pioneers of the quantum statistics (Debye, Natanson, Kamerlingh Onnes and Ehrenfest) and their impact on *its today's understanding*.

As we remark at the end, the principle of *particle indistinguishability* as the basic assumption may be tested experimentally. The experimental testing of the basic principles on which whole theory is based, is what distinguishes the physical approach from a purely mathematical theory.[4]

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[3] Dirac 1930, §§ 62, 67–69.

[4] It is often perceived that the indistinguishability is related to the states rather than to particles (cf. Bach 1997, p. 8). In my opinion, this is a simplified view since the physical states represent physical particles and the measured physical properties are described in terms of particle occupancies. I comment this view below.

## 2. The issue of indistinguishability of identifiable objects (particles)

The starting expression for the total number of configurations of particles in the so-called ideal gas state, which appears in all pioneering papers on quantum statistics[5] (and even to some degree, in Boltzmann's paper in 1877[6], cited by M. Planck[7]) can be rewritten nowadays in the form

$$W_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \equiv \binom{n_i + g_i - 1}{g_i - 1}; \quad W = \prod_i W_i \,. \tag{1}$$

In this expression $W_i$ is the number of arrangements of $n_i$ particles in the single particle state "$i$" in which $g_i$ is the state degeneracy (the number of available states with the same energy $\varepsilon_i$ for each particle in that state). Also, $W$ is the total number of configurations for the whole system. This formula is valid when we say that the $g_i$ states are boxes and there is no way of knowing in which box each particle is placed. This formula has an intuitive interpretation, apparently ascribed to H. Kamerlingh Onnes and P. Ehrenfest (1914) that the system of $n_i$ particles has $g_i - 1$ dividing walls (for bosons) and $n_i$ is the number particle in those boxes. We cannot distinguish in between which pair of separating walls the given particle is placed; **this situation is phrased as the principle of their indistinguishability**. We can move thus the border walls among the particles freely and hence the total number of arrangements (permutations) of particles and dividing walls is $(n_i + g_i - 1)!$. Now, the number of equivalent arrangements of the walls and particles among themselves separately are $(g_i - 1)!$ and $n_i!$, respectively. In result, the number of physically distinct an equally probable macro arrangements is given by (1). Essentially, this was the Boltzmann's idea of starting with the number of such arrangements under the proviso that we

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[5] I have been following partly the reasoning elaborated in Mehra, Rechenberg 1982, vol. I, part 2, pp. 558–560.

[6] We can find in Boltzmann (1877/ reprinted 1909, pp. 164–223, here p. 181, and (Eng. transl.) 2015, p. 1983) a similar formula $J = (\lambda + n - 1; \lambda)$, where $\lambda$ – a total number of molecules, and $n$ – a total number of fictious "quanta", cf. Enders 2016, Section 3.5.

[7] Planck 1900, p. 147. A good exposition of his ideas is presented in: Planck 1915, particularly in the Sixth Lecture, pp. 87–96. Although Planck (1900) refers to Boltzmann's (1877) "complexions", his "complexions" are different – cf. Boltzmann 1877; reprinted 1909, pp. 164–223; (Eng. trans.) 2015. For details, see Enders 2016, Section 3.6.

have, in principle, no knowledge in which box the particle is, so we count those arrangements as if their particular box has not been fixed. This is the heart of the issue.

A methodological remark is in place at this point. Namely, the problem of particles (in)distinguishability should not be regarded as an impossibility to identify them, as we still have the ability to count them, as well as to attach the energy or momentum and spin to each of them. So, it is the *indistinguishability* in the sense of Eq. (1) of *identifiable,* but otherwise non-recognizable individual particles in their condensed gas or liquid state.

Now, the basic question is who was the first to formulate this statistics clearly and properly. Here, immediately, the question to be raised is whether the indistinguishability in the black-body radiation case concerns the radiating and absorbing container walls or else, is this the property of the radiation itself? This question was not understood unequivocally during the years 2005–2014, during which the distribution function of radiation frequencies was rederived many times and applied to reinterpret Planck's law. *This is because the concept of radiation--quanta state was not clearly established well as of then.* On the other hand, the symmetry principle of many-particle wave function introduced by Dirac is employed to the states, not to particles. This issue is still an interesting one (cf. Bach (1997)). Also, Planck guessed the form (1) without stressing the indistinguishability as the *fundamental* principle. Note also that in the standard "particle-number language" (second quantization), employed in Appendix A, this principle does not show up clearly when calculating the average number of quanta of given frequency.

## 2.1. P. Debye's contribution

The first person, in my view, who applied the formula (1) directly to the radiation in the cavity was P. Debye (1910). He identified the number of states $g_i$ with the (continuous) number of radiation modes $N_\nu$ so that its number in the frequency interval $[\nu, \nu + d\nu]$ is

$$N_\nu d\nu = \frac{8\pi\nu^2 V}{c^3}, \qquad (2)$$

where $c$ is the velocity of light. Obviously, this is the number of waves accommodated in volume $V$. Then, he has rewritten Eq. (1) in the form

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$$W = \prod_{\nu} \frac{[N_\nu d\nu + N_\nu f_\nu d\nu]!}{[N_\nu d\nu]![N_\nu f_\nu d\nu]!}, \tag{3}$$

where $f_\nu$ is the desired frequency distribution of radiation frequencies $\nu$, in agreement with Planck's *ansatz*. Now, adding the conservation of the total system energy as a constraint within the variational approach of Boltzmann, he arrived at

$$f_\nu = \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}, \tag{4}$$

where $k_B$ is (nowadays universal) the Boltzmann constant, $T$ absolute temperature, and $h$ the Planck universal constant. Obviously, the Planck relation between energy of quanta and their frequency, $\varepsilon_\nu = h\nu$, had to be included extra. Debye approach was essentially correct, without an irrelevant term (–1) in the numerator and the denominator of Eq. (1) though.

### 2.2. Natanson: First formulation of the principle of indistinguishability

Another path of the same derivation was proposed by W. Natanson (1911a; 1911b) by considering the maximal entropy of a system of *indistinguishable* wave packets, each of energy $h\nu$ among a given number of *receptables* (modes, resonators) of energy, which can be identified as a distinguishable reference number. His method of approach is original and differs from that of L. Boltzmann (1877/2015 (Eng. transl.)), A. Einstein (1906/1989b (Eng. transl.)), and P. Debye (1910). It is not trivial at all and there is no point in presenting it in detail here[8]. After a long and detailed discussion of the limits of small and large number of quanta present in a given mode, he proposes a universal form (4) and discusses in detail thermodynamic properties in his 88-page book (1913), which was unfortunately written in Polish and never translated into any other language (see however his original work 1911a (in English) & 1911b (in German)).

As a good side remark I should quote from J. Mehra and H. Rechenberg (1982, p. 151, fn. 211):

[8] For a further elaboration see: Spałek 2005 (in Polish).

> Natanson's derivation did not deviate formally from the one given by Einstein (1906) or Debye (1910) as far as the application of the hypothesis of energy packets (or quanta) was concerned. However, he claimed that his assumption about considering the distribution of indistinguishable energy packets (quanta) among distinguishable receptables of energy (which replaced Planck's resonators) provided the proper definition of equally probable states in radiation theory.

Parenthetically, the term (-1) from (1) is included correctly in Natanson's work.

In summary, only the explicit inclusion of the indistinguishability principle enlightens the difference between the original approach due to Boltzmann, defining the classical statistics, and its quantum correspondent. To put it bluntly, the hypothesis of Planck regarding energy quanta and the subsequent concept of light quanta (photons)[9] as particles by A. Einstein (1905) must be supplemented with the indistinguishability principle of Natanson to make it complete.

Here the indistinguishability principle means that we cannot identify in principle to which mode (resonator, receptable) photon belongs to. In other words, it is as if the photon can be present in any mode even though it has a particle nature. In consequence, when determining the statistical entropy of such a gas we have to count as equivalent all possible agreements of photons among the modes (states). This takes its final shape in the form of a symmetrization principle of the multiparticle wave function with respect to either particle coordinate including spin (in the coordinate representation), or with respect to the complete sets of possible quantum numbers for a single particle including again spin (in the occupation-number representation). Originally, the principle in such a form was formulated by P. Dirac (1926; 1930, chap. XII). The latter is called the second-quantization representation and was clearly elaborated by V. A. Fock (1932; 1957/2004).

[9] The term "photon" was coined only in 1916, but noticed in the late 1920s, cf. Kragh 2014; Lewis (1926).

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### 2.3. A methodological remark: Natanson versus others

One may ask: How was it possible that the statistical principle expressed through Eq. (1) had not been understood properly earlier? The author's interpretation is as follows: The formula (1) was applied to a cavity filled with the (standing) waves. Then the question regarding which radiating atom of the cavity border the wave (photon) emerges from cannot be answered. In that language, $n_i$ is the number of photons of frequency $v$ and $g_i \equiv g_v$ is the number of radiating atomic states, which differs from the number of modes in the cavity. The conceptual jump of Natanson is that we attached exclusively the meaning of Eq. (1) to the properties of radiation itself. In other words, Eq. (1) describes the number $W_i$ of the ways the $n_i$ photons can be distributed among the available **states** calculated in terms of the number of possible radiation modes in the cavity. Parenthetically, all this type of analysis speaks implicitly for the dual (complementary) nature of photons, phrased explicitly much later in 1927 and 1928 by N. Bohr (1928, p. 580, fn. 1) in a quite different context. Namely, $g_v$ represents the number (density) of possible wave modes, whereas the number of particles is singled out at the same time.

## 3. Concluding remarks

In the literature the work of H. Kamerlingh Onnes and P. Ehrenfest (1914) is often quoted as the one providing a simple meaning to the photon statistics.[10] Those authors quote neither the work of P. Debye (1910) nor the works of W. Natanson (1911a; 1911b; 1913) preceding it. The present author regards the 1914 paper by H. Kamerlingh Onnes and P. Ehrenfest as, at best, a subsidiary work with respect to the original works of Debye and Natanson. It must be mentioned that the work of Natanson has been practically ignored. The question why is it so, was addressed in e.g., two recent papers in this journal (i.e., *Studia Historiae Scientiarum*) by N. Nagasawa (2018) and M. Kokowski (2019), who illustrate to some extent the sociological aspect of science mentioned earlier.

It may be interesting to some readers to mention that recently there appeared a possibility of direct testing the indistinguishable *versus* distinguishable particles dilemma, raised by the present author. It is connected

[10] But cf. fn. 9, above.

with the fact, first predicted theoretically[11], and then confirmed experimentally[12] that the mass of quasiparticles in a system of the so-called strongly correlated fermions depends on their spin direction ($\sigma = \uparrow$ or $\downarrow$). The effective mass difference $|m_\uparrow - m_\downarrow|$ in the spin polarized state of their milieu is large and proportional to the average spin polarization (magnetic moment) $m$ of the system. Therefore, by tracing the effective mass evolution from the spin unpolarized ($m = 0$) state (when $m_\uparrow = m_\downarrow$) to the state with $m > 0$ (when $m_\downarrow \gg m_\uparrow$), we can see the transmutation of indistinguishable particles with respect to the spin quantum number to their distinguishable, but still quantum, corresponding particles (i.e., correspondants). The particles are then distinguishable by their masses and momenta.[13] The work is in progress.[14] All this recent work is for fermions; the same should apply to correlated bosons with nonzero spin, in e.g., to cold atomic lattices.

## 4. Final note

The material concerning the works of Władysław (Latinized: Ladislas) Natanson is available also on request to author.

After this paper was submitted I have learnt about interesting article of Simon Saunders: The concept "indistinguishable", published in *Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics*, vol. 71, pp. 37–59 (2020), in which the concepts considered here were overviewed critically in detail. I am grateful to my colleague Mariusz Sadzikowski for turning my attention to this paper and to Simon Saunders for insightful correspondence on the topics raised in this and his article.

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[11] Cf. Spałek, Gopalan 1990; Korbel, Spałek, Wójcik, Acquarone 1995.

[12] Cf. Sheikin *et al.* 2003; McCollam *et al.* 2005.

[13] I would like to add an additional comment. Namely, I talk here about (in) distinguishability with respect to the spin degrees of freedom only. With respect to other degrees of freedom they may be still indistinguishable. A beautiful example is the Born-Oppenheimer theorem as applied to the hydrogen molecule, where the orbital degrees of electrons and protons are distinguishable, with no anti-symmetrization of the corresponding orbital part of the wave function, but anti-symmetrization of its spin part, as the spins of the electron and the proton are indistinguishable! Cf. Born, Oppenheimer 1927; Schutte 1971; Tuckerman 2019.

[14] J. Spałek 2020.

## 5. Acknowledgments

The author is grateful to Dr. Danuta Goc-Jagło for her technical help. The complete set of papers by Władysław Natanson is deposed at the Library of the Faculty of Physics, Astronomy, and Applied Computer Science of the Jagiellonian University (Kraków, Poland).

I am grateful to our Head Librarian, Ms. Maria Pawłowska for her help in browsing through the works of Natanson, Debye, Einstein, Kamerlingh Onnes, Ehrenfest, and Planck.

I am also grateful to Prof. Michał Kokowski for editing the article and improving the bibliography, as well as for proposing to summarize briefly in this article the more detailed account of Natanson's works presented in my earlier work (J. Spałek 2005).

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## Appendix A: Bose and Einstein analysis of the Bose-Einstein distribution function for quantum particles using the grand – canonical – ensemble formalism

Below we reproduce a textbook derivation of Planck's law for comparison as a supplement to the discussion in main text.

### A1. Derivation

There are two ways of thinking about the Bose-Einstein distribution for photons.[15] One of them is based on assuming, after M. Planck and A. Einstein, that the energy of radiation state of frequency $\nu$ is composed of discrete quanta, each of energy $E = h\nu$. In actual situation, that radiation may contain many such quanta leading to their total energy $E_n = nh\nu$, with $n = 0,1,2,3 \ldots$. Now, in order to calculate the average number $\overline{n} \equiv \overline{n}(\nu)$ of those quanta in the radiation being at equilibrium with

[15] Cf. fn 9, above.

the surroundings (e.g. in a cavity), we treat their energy in an analogous manner Boltzmann treated the statistical energy distribution of classical particles. That means that we determine the probability $P(\nu)$ for the thermal system of having energy $E_n$, i.e.

$$P(\nu) = \frac{e^{-\beta E_n}}{\sum_{n=0}^{\infty} e^{-\beta E_n}} = \frac{e^{-nh\nu}}{\sum_{n=0}^{\infty} e^{-\beta nh\nu}}\ , \tag{A1}$$

where $\beta = (k_B T)^{-1}$ is the inverse absolute temperature in energy units ($k_B$ is the universal Boltzmann constant). In effect, the statistical average number of particles $\overline{n}(\nu)$ is

$$\overline{n}(\nu) = \sum_{n=0}^{\infty} nP(\nu). \tag{A2}$$

A relatively simple algebra leads then to the expression

$$\overline{n}(\nu) = \frac{1}{e^{\beta h\nu} - 1}\ .$$

This is the celebrated formula for the frequency distribution of photons. To calculate the thermodynamic (internal) energy distribution (density) we use the formula

$$U(\nu) = h\nu \cdot \varrho(\nu) \cdot \overline{n}(\nu) \tag{A3}$$

where the first factor is the energy of the simple quantum (photon) $h\nu$, $\varrho(\nu)$ is the number of available states (modes) that are occupied by $\overline{n}(\nu)$ waves (photons). This last quantity can be easily determined and was provided by Planck for cavity (vessel) of volume $V$ in the form

$$\varrho(\nu) = 8\pi \frac{h^3 \nu^2}{c^3} V, \tag{A4}$$

where $c$ is the speed of light. The quantity $U(\nu)$ can be measured directly in the theory and agrees with experiment. In this manner, it has been proved that the distribution $\overline{n}(\nu)$ *cannot* be the Boltzmann distribution. This is essentially Bose's (1924/2009) original derivation. Finally, one can determine the full thermodynamics of such a gas of photons by calculating the total (internal) energy from the formula

$$U = \int_0^{\infty} d\nu\, U(\nu) = AT^4 \tag{A5}$$

to recover directly the Stefan-Boltzmann law with $A$ being a constant.

A similar method has been subsequently applied by A. Einstein (1924; 1925)[16] for the case of material particles, but only after he explicitly included in his considerations an additional condition amounting to the material particle number conservation, did he discover the celebrated particle condensation called now the *Bose-Einstein condensation*.[17] But that is a separate story. Also, a separate but parallel story concerns the emergence of the Fermi-Dirac statistics.

**A2. Final remarks**

Firstly, the method of the derivation contains the quantum element $E_n = nh\nu$. This assumption is absolutely fundamental in nature, obtained easily from the wave equation for the massless bosons. Secondly, the energy $E_n$ of quanta complexes are treated as classical objects following the Boltzmann distribution. This mixture of quantum and classical aspects of the problem somewhat obscures the picture. In a way, it is analogous to Bohr's concept of the hydrogen atom, in which the quantization of a classical angular momentum $L_n$ of the electron circling around the nucleus ($L_n = nrp$, $p$ – particle classical momentum, $r$ – orbit radius) is mixed with the classical equilibrium condition of balancing the electrostatic attraction of electron to the nucleus with the centrifugal mechanical force due to rotational motion around it.

Amazingly enough, this type of derivation in our statistical case suffices to determine statistical-mechanical properties of the gas by using the average particle number in each quantum state. The method is insufficient when the knowledge of the wave function is explicitly required. In such a case, the principle of quantum-mechanical indistinguishability is required explicitly. One may say that the analysis of W. Natanson (1911a; 1911b; 1913) from one side and those of P. Debye (1910) and H. Kamerlingh Onnes and P. Ehrenfest (1914) from the other fulfill this last requirement, even though the explicit knowledge of the particle wave function is not required. In any case, a resolution of this ambiguity would require a separate analysis.

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[16] See Einstein 1924 / 2015a, Doc. 283 (reprinted); 2015b, DOC. 283 (Engl. transl.); 1925 / 2015a, Doc. 427 (reprinted); 2015b, Doc. 427 (Engl. transl.).

[17] See fn.2.

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