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Was Bose-Einstein Statistics Arrived at by Serendipity?

Bose-Einstein statistics is the statistical mechanics of *bosons,* i.e., of particles such that if there are several of them the wavefunction is symmetric under exchange of any pair of them. Thus

$$\psi(x_1,x_2 \ldots x_i \ldots x_k,x_n) = \psi(x_1,x_2 \ldots x_k \ldots x_i,x_n)$$

for any i and k where each x_i represents all the coordinates of the ith particle including spin or other internal variables.

All particles with integral spin are bosons: light quanta, deuterons, alpha particles, ^{4}He atoms, etc. All particles with half integral spin have antisymmetric functions and are called fermions: electrons, protons, neutrons, neutrinos, etc.

The notion of a boson originated with a paper by S. N. Bose in June 1924 (*1*), a year before the invention of quantum mechanics, two years before wave mechanics, three years before the Uncertainty Principle (*2*). How could this be? How could the notion even be formulated without the notion of wavefunction? It is my contention that it arose from an elementary mistake in statistics that Bose made. Einstein at first copied that mistake without paying much attention to it. He then realized the mistake but saw that it must have a deep meaning since it gives the right answer. A clear justification only came with the working out of quantum mechanics.

Bose's paper is entitled "Planck's Law and the Hypothesis of Light Quanta."

Planck's law, of course, is the law describing radiation in thermodynamic equilibrium with matter at a given temperature, the so-called black body radiation. It states that the energy density of radiation, as a function of the temperature of the box and of the frequency of the radiation is given by

$$\rho(\nu,T)\mathrm{d}\nu = \frac{8\pi h\nu^3\,\mathrm{d}\nu}{c^3}\cdot\frac{1}{e^{h\nu/kT-1}}$$

$$\text{or } \rho = c\,x^3\frac{1}{e^x - 1}$$

$$\text{with } \frac{h\nu}{kT} = x$$

For $x \ll 1$ this becomes $\rho = C\,x^2$ (Raleigh-Jeans' law).

For $x \gg 1$ it becomes $\rho = C\,x^3\,e^{-x}$ (Wien's law).

For $x \gg 1$ (large quanta, low temperature) the distribution looks like a Maxwell distribution of energy in an ideal classical gas. Einstein had pointed that out in 1905 (*3*) and had used this limiting form of the law to infer that radiation in some way behaved like discrete quanta. In 1905 the idea of light consisting of particles was an outrageous idea. Too much was known at that time about light as electromagnetic waves to allow room for doubt. Indeed even eight years later at a time when the usefulness of Einstein's proposal in explaining the photoelectric effect had been fully comfirmed it was still considered outrageous by the physics community. When Planck, Nernst, Rubens, and Emil Warburg got together in 1913 to nominate Einstein for membership in the Prussian Academy of Sciences they felt the need to apologize for this speculative extravagance of their nominee. They thought that matter could occur in quantized states but not radiation floating around in free space. In contrast Einstein pushed the idea of light quanta further and further. In 1917 in his famous paper introducing spontaneous and radiation-induced transition probabilities of molecules (*4*) he showed that during such absorption and emission acts the molecules must receive a recoil momentum $p = h\nu/c$ if radiation is not to dislocate the thermal equilibrium of the molecules. In other words, radiation must be emitted not like a spherical wave but like a bullet shot out in one direction.

Bose (*1*) took the ultimate leap to treat radiation as an ideal gas of light quanta showing that simply maximizing the entropy led to Planck's law. He arrived at Planck's law by a consideration which made no reference at all to the interaction of light with matter.

How did he do this conjurer's trick? To see the point of Bose's paper we must consider how one calculates entropy in statistical mechanics. There are several procedures, some more elegant, some more cumbersome, some more abstract, some more visualizable. They all involve something like this: we define a state of the system under consideration in some coarse-grained fashion: the macrostate. We then find out in how many ways this macrostate can be realized by specifying it microscopically, looking at the state of each molecule individually. We assume that these microstates are all equally probable, count the number, W, and get the entropy

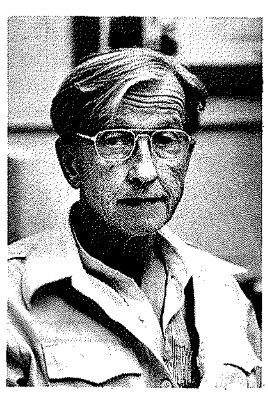
$$S = k \log W$$

We then maximize the entropy under some constraints, for instance by requiring the total energy and the total particle number to be fixed. The macrostate which has the largest entropy is the equilibrium state.

The tricky part in this procedure is the correct enumeration of the equally probable microstates. Bose proceeded as follows: any one light quantum has a location in space, x, y, z, and a momentum, p_x, p_y, p_z such that

$$p_x{}^2 + p_y{}^2 + p_z{}^2 = \left(\frac{h\nu}{c}\right)^2 \qquad (1)$$

In the quantum phase space with the coordinates x, y, z, p_x, p_y, p_z it is constrained with respect to x, y, z to the real volume, V, and with respect to p_x, p_y, p_z to a spherical shell of



Max Delbruck is best known for his pioneering work in molecular biology. His work on the reproduction and genetics of bacterial viruses employed his background in theoretical physics obtained from his PhD work at the University of Gottingen. After receiving his degree in 1930, he was a Rockefeller Foundation Fellow both in Europe and at the California Institute of Technology (1937–39) where he first became interested in the bacterial virus problem. He was professor of physics at Vanderbilt University until 1947 when he became professor of biology at the California Institute of Technology. He was awarded the Nobel Prize in Medicine in 1969.

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radius $h\nu/c$ and thickness $(h/c)\mathrm{d}\nu$. This spherical shell has the volume in momentum space

$$4\pi\left(\frac{h\nu}{c}\right)^2\frac{h\mathrm{d}\nu}{c}$$

Multiplying by V to get the volume in phase space, dividing by h^3 to get the number of quantum cells in this phase volume and multiplying by 2 to take into account two alternative states of polarization we get

$$Z_\nu = 8\pi\frac{V\nu^2}{c^3}\mathrm{d}\nu$$

as the number of cells available to each quantum in the frequency interval $\mathrm{d}\nu$.

Clearly, the next step should be to find the number of ways in which a certain number of quanta can be distributed over these cells in accordance with the specifications of the macrostate. The quanta should be treated as statistically independent entities as in the case of the classical statistical mechanics of ideal gases. In other words the microstate should be defined by saying into which cell each photon has been put. At this point Bose's mind goes foggy. Instead of carrying out the program as indicated he looks at each *cell* to see how *many quanta* are in it and in this way defines the microstate.

To illustrate with Tom, Dick, and Harry and their distribution over two rooms, we should define a microstate as shown in Figure 1, while Bose defines it as shown in Figure 2, a method which on our counting subsumes the three cases shown in Figure 3. Surely if you consider these three characters as entities perambulating independently through the three rooms it would make no sense to define the microstate in Bose's way.

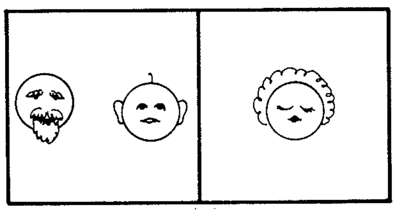

Figure 1. Tom and Dick in living room, Harry in kitchen.

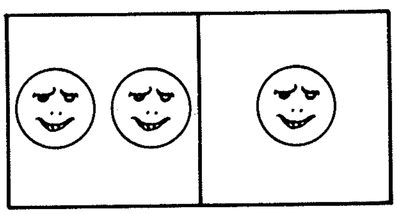

Figure 2. Two men in living room, one in kitchen.

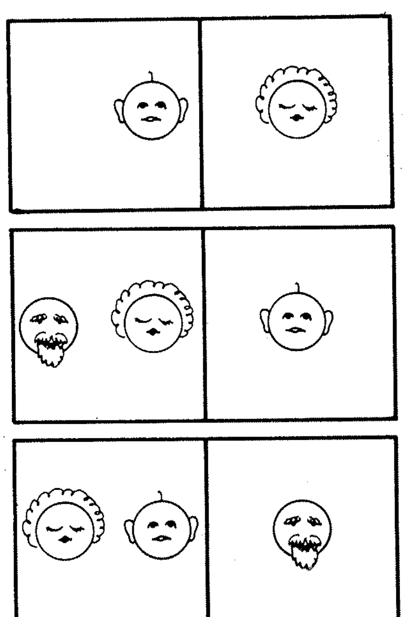

Figure 3. Harry, Dick, Tom alone in kitchen, respectively, the two others in living room.

Z. f. Physik 26 : 178 – 181 (1924)

Accompanying Letter from Bose to Einstein dated June 4, 1924!!

Plancks Gesetz und Lichtquantenhypothese.

Von Bose (Dacca-University, Indien). !!

(Eingegangen am 2. Juli 1924.)

Der Phasenraum eines Lichtquants in bezug auf ein gegebenes Volumen wird in „Zellen" von der Größe h^3 aufgeteilt. Die Zahl der möglichen Verteilungen der Lichtquanten einer makroskopisch definierten Strahlung unter diese Zellen liefert die Entropie und damit alle thermodynamischen Eigenschaften der Strahlung.

Figure 4. Title section of Bose's paper, as published.

(Übersetzt von A. Einstein.)

Anmerkung des Übersetzers. Boses Ableitung der Planckschen Formel bedeutet nach meiner Meinung einen wichtigen Fortschritt. Die hier benutzte Methode liefert auch die Quantentheorie des idealen Gases, wie ich an anderer Stelle ausführen will.

Figure 5. End of Bose's paper, as published, with Einstein's footnote.

The fact is that Bose does his peculiar counting without drawing attention to its oddity and arrives by straightforward procedures at Planck's law.

Bose mailed his manuscript from Dacca (India at that time, now Bangladesh) to Einstein (in Berlin) with a covering letter dated June 4, 1924 (Fig. 4). There was no airmail service in those days. I estimate that it took three weeks to make its way from Dacca to Berlin, getting there around June 25.[1] Einstein translated the paper and sent it in for publication in the *Zeitschrift für Physik* where the manuscript was received on July 2, i.e., about one week after Einstein had received the original. There is evidence of haste in Einstein's handling of the paper in that Bose is not credited with his initials. Also the paper is astoundingly brief and abrupt. It has no literature references. I have a strong suspicion that Einstein cut it short, perhaps even rewrote it, but the original of the manuscript is not available so I cannot prove my point. At the end of this four-page paper there is a highly unusual footnote (Fig. 5), a kind of thunderbolt that says, "Translated by A. Einstein" and "Note by translater: Bose's derivation of Planck's law in my opinion constitutes an important step forward. The method here employed also yields the quantum theory of the ideal gas as I will show in another place." Who would not like to have such a footnote to his paper!

The other place referred to was the Proceedings of the Prussian Academy of Sciences where Einstein submitted his paper entitled "Quantum Theory of the Monatomic Ideal

[1] Bose also sent Einstein a second paper (*1b*) which Einstein translated and submitted to *Z. f. Physik* five days after the first. This paper also had a postscript by Einstein, but this time the postscript pointed out that the point of view taken by Bose regarding the interaction of light and matter was not tenable, giving a whole page of arguments against it.

Einstein never even bothered to acknowledge that he had received this MS from Bose, let alone that he had translated it and sent it in for publication with his negative comments. Several months later, when Bose inquired whether this MS might have been lost in the mail, Einstein calmly replied "No, no, it has long since been published and the reprints by mistake have been sent to me. You can pick them up when you get to Berlin."

Gas" on July 10, i.e., a week after submitting Bose's paper (5).

It is a powerful mathematical paper giving the complete theory of the ideal Bose gas, except for one item. It is tersely written and difficult to read not least because it abounds with misprints and numerical errors. It adopts Bose's definition of the microstate, manifestly unaware that something bizarre is being done. At the end it draws attention to the following paradox, implicit in the theory. Consider a mix of two ideal gases. Its pressure, according to this theory, is the sum of the pressures of the two separate gases. That is reasonable indeed. The pressure of each gas, however, at fixed temperature and volume is *not* porportional to the number of molecules. Therefore, if by some magic the molecules are gradually made alike, the pressure should change abruptly when the two kinds of molecules become alike (it should diminish). In other words, the pressure of a Bose gas is less than that of a classical gas. Qualitatively it can be seen how this result follows from the theory. Consider a box with n molecules and at a temperature so low that all the molecules except one are in the lowest state, E_0. On Bose's counting there is only one such state defined by $n-1$ particles in the lowest state, E_0, and one particle in the next higher state, E_1. In contrast, classically with distinguishable molecules, there are n ways of putting one molecule in state E_1. At the given energy, therefore, the entropy of the Bose-Einstein gas is much lower than that of the classical gas. This lowering of entropy implies that if the two gases are brought into heat exchange contact the Bose-Einstein gas will loose its energy to the classical gas, i.e., its pressure will go down. This pressure anomaly is contingent on the indistinguishability of the molecules.

We may remark, in passing, that these indistinguishability effects show up very strongly in such situations as the scattering of alpha particles by helium (it is twice higher than that given by the Rutherford formula) and in comparison of the spectra of the boson pair D_2 with that of the fermion pair H_2 and with that of the ordinary pair HD.

When Einstein noted this effect in his formulas he was nonplussed. He says, "I have been unable to resolve this paradox. The pressure effect appears as good as impossible."

It seems clear from the record that Bose was not aware that he counted the microstates in a peculiar way. My guess is that he simply made a mistake, the kind of mistake that is very easy to make in any statistical undertaking and especially in the present case when the whole business of cutting up the phase space of individual particles into cells of size h^3 is obviously a makeshift affair lacking the consistency of classical statistical mechanics with the continuously modifiable trajectories, Liouville's theorem, and the ergodic hypothesis to back up the procedure.

In the case of Einstein's paper, submitted as we saw within two weeks after receiving Bose's manuscript, the evidence is not quite as clear-cut. Overtly he makes no reference at all to the fact that he is counting in an odd way. At one point, however, he refers to the fact that the new statistics automatically yields Nernst's theorem, i.e., that the entropy goes to zero at absolute zero temperature. All the molecules would then be in the ground state and this state of the gas is a single state *"im Sinne unserer Zählung."* Does this mean that he is aware that he is counting in a funny way? I believe he was but in a vague way only. He is just aware that the Bose counting eliminates the factor $n!$ of classical statistics, a factor that had been known to be a thorn in the flesh of statistical mechanics since the days of Gibbs. He is not aware that it conflicts with the idea that the particles are independent of each other.

Einstein published a second paper on the Bose gas, submitted six months later, January 8, 1925 (6). This paper is written as a continuation of the first one with consecutive numbering of sections and equations. The first section contains perhaps the most astounding discovery of all statistical mechanics, the discovery that the Bose gas undergoes a phase transition at a critical density and temperature: a progressively larger fraction of the gas "condenses" (in phase space), i.e., a progressively larger fraction of the molecules accumulates in the state with zero momentum and fails to contribute to the pressure of the gas. He shows that this effect is hardly observable for any real gas because it occurs under conditions where their behavior is far from ideal. He speculates that the conduction electrons in a metal might constitute a Bose gas! This paper is almost simultaneous with Pauli's discovery of the exclusion principle for electrons in orbits around a nucleus and six months before Fermi's generalization of this notion to free electrons.

Of greater interest in the present context is the second section of Einstein's paper. It opens with the following sentence:

> Ehrenfest and other colleagues have criticized Bose's theory of radiation and my analogous one of the ideal gas because in these theories the quanta or molecules, respectively, are not treated as statistically independent structures, without our having emphasized this circumstance. This is perfectly true. If one treats the quanta as statistically independent in their localization, one gets Wien's radiation law. I will contrast the two methods for the case of gases to bring out the difference as clearly as possible.

He then proceeds to explain very clearly in what way the new counting method implies indirectly a certain hypothesis about "a mutual influence of the particles on each other of a kind which is at this time still completely mysterious."

These formulations indicate that when Einstein wrote the first paper in a tremendous rush he had indeed not paused to clarify in his own mind in what way Bose's counting implied a mysterious interaction at a distance between the particles. Most likely he had not pursued this question at all being simply fascinated with the success of producing Planck's law for a light quantum gas and seeing instantly that it would resolve some ugly questions for the real gas.

There are no letters preserved between Einstein and Ehrenfest from this period. Most likely Ehrenfest's intercession took place during a mutual visit in Leyden or in Berlin.

The second paper goes one remarkable step further. Einstein calculates the density fluctuations of the gas according to the new theory. He does so by an ingenious method he had thought up earlier for radiation. The method works backward and calculates the fluctuations from the entropy. He finds that this fluctuation consists of two additive parts. One part corresponds to the fluctuation expected for independent particles, the other part is independent of the density, and, he says, can be interpreted as "interference between waves to be associated with the particles." What???

What waves? It turns out that Einstein, sometime while he was working on the second paper, had received from Langevin a draft of Louis de Broglie's thesis. In this thesis de Broglie had conjectured that every particle had associated with it a wave, according to a fixed rule relating momentum of the particles and frequency of the wave. In a vague way de Broglie thought that a quantization of the electrons in the Bohr atom could thus be interpreted as standing waves. De Broglie's professor, Langevin, thought this was a pretty bizarre idea and decided to consult with his friend Einstein whether he should accept this thesis. Einstein immediately smelled that this was a good thing, encouraged Langevin to accept the thesis and referred to the thesis in his paper. Schrödinger learned of de Broglie's idea through Einstein's paper, was sufficiently intrigued to go to the trouble of getting a copy of the thesis, an effort in which he succeeded about November 1 (7) and in the sequel developed wave mechanics.[2] Anybody who has ever

[2] Schrödinger's first paper (2) on wave mechanics was submitted January 27, 1926, two months after he got de Broglie's thesis. The subsequent papers were submitted at a rate of one per month, on February 23, March 18, May 10, June 21. Pauli has told me that 48 hours after reading Schrödinger's first paper he wrote him a long letter containing all the results of the next four papers, but [illegible] dinger had these results, too.

tried to get hold of a French thesis will appreciate that obtaining de Broglie's thesis may well have constituted half the battle of inventing wave mechanics.

The later clarification of the wave-particle duality *and* of the odd statistical assumptions appropriate for bosons and fermions, respectively, occurred in terms of quantum mechanics of many particle systems. Quantum mechanics showed that the wavefunctions *must* be either symmetric or antisymmetric under exchange of the particles. More precisely, every transition probability from any symmetric to any antisymmetric state, and vice versa, is necessarily exactly zero. Nonrelativistic wave mechanics does not prescribe *which* particles must be bosons, which fermions. Relativistic arguments can be made requiring half-integral spin particles to be fermions and integral spin particles to be bosons (*8*).

This symmetry or antisymmetry requirement for the wavefunction implies, in the formalism of quantum mechanics, that exchange of any pair of identical particles does not change the probability distribution of *any observable quantity*. The exchanged state is *the same* as the original. Thus, the crazy assumption of Bose, that the particles should be drawn without individual features identifying them, is built into the basic structure of the formalism.

The formalism can be generalized in such a way that the particle *number* need not be preserved. In both statistics single particles can be created and annihilated, as photons are created in emission and annihilated in absorptions, as electrons and neutrinos are created in β-decay of radioactive substances, and as electrons and positrons are created in Dirac's theory of holes.

This loss of identity, indeed loss of existence, is a stark reminder that the object concept, which is so basic to our orientation in the real world, is whittled down and emaciated in quantum mechanics to a mere shadow of its former self. The object concept has been acquired by our biological ancestors many million years ago. The steps through which every infant develops it during the first two years of his life has been analyzed beautifully by Piaget and his school. That the normal infant *can* develop this concept, and *does* so very precisely,[3] is part of its genetic programming. The notion of an object that persists when not perceived is absolutely essential for our orientation and survival in the world.

Clarification of the meaning of quantum mechanics came in 1927 in terms of Heisenberg's Uncertainty Principle (*9*) and of Bohr's Complementarity Argument (*10*). The Uncertainty principle says that particles can be pinpointed but do not have trajectories. How so? The reason that these two seemingly contradictory statements are compatible lies in the fact that a series of pinpointings does not constitute a trajectory: every pinpointing act is an observation and constitutes a unique event involving some uncontrollable interactions. Each event of such a series has only a probabilistic relation to the outcome of alternative events, say, a diffraction test.

If particles do not have trajectories, that opens the *possibility* for their loss of identity. If I see a rabbit hiding behind a bush and a rabbit emerging from the bush I may be uncertain whether it is the same rabbit or not. I have no doubt, though, that closer observation could have decided the issue. Not so with electrons.

If one electron gets attached to an atom and subsequently one electron is passed on to another atom, I cannot say, in principle, whether it is the same electron or not. This statement does *not* follow from the Uncertainty Principle or from the Complementarity Argument. These two Principles merely show that loss of identity is a possibility. The possibility becomes a necessity only in the light of the complete quantum mechanical formalism. Thus, the loss of the category of identity should be considered as an additional characteristic of quantum mechanics, and perhaps its most eerie one.

Our intuitive understanding of the events in our environment balks at this demand of Reason. The demand violates, like so many other aspects of 20th century science, our preconceptions about the real world. Relativity theory itself afforded the most striking example of a formal theory demanding that we forego our intuitive understanding of space and time. This intuitive understanding is by no means something "learned" or "conventional." Far from it. It is deeply embedded in our natural makeup since long before our ancestors came down from the trees. It is *a priori* for the individual, but *a posteriori* in evolution. It evolved in adaptation to the environment (*11*). It is a fact that Einstein never became reconciled to the resolution of the quantum puzzles offered by the Complementarity Argument. Though he conceded after 1935 that the argument was logically consistent, he could not accept the fact that quantum mechanics is incompatible with a unique "objective reality." And, indeed, none of us can, intuitively. Our biologically inherited concrete mental operations do not permit us to do so. That we nevertheless can do science, i.e., construct formalisms which are highly successful in representing our scientific findings is still a miracle, an extension of the miracle for which Einstein coined the expression, "The most incomprehensible thing about the world is its comprehensibility."

Should we let matters rest with this expression of wonder and bafflement? Or, should we attempt a more positive approach? Einstein's saying was coined almost 50 years ago and it was coined by a man steeped in the traditions of physics, a tradition which takes the human mind for granted and takes Nature (with a capital N) for granted, two agonists locked in a peculiar struggle, one trying to ferret out the "secrets" of Mother Nature and Mother Nature jealously trying to guard them. That, indeed, was Einstein's attitude throughout and, like Newton's corresponding statement, it reflects the awe and wonder at the success of the scientific enterprise. It comes naturally to anybody who is led into the problems of physics via the route of its history. Bohr, too, was very much caught up in it. Bohr does emphasize that we (the human mind and experimenter) play a dual role as "actor" and "onlooker" in the drama of existence. Yet, this dual role is taken for granted. Can we now, 50 years later, and armed with new insights on the origin and evolution of life, on the structure and evolution of our cognitive capabilities, take a new look at this question and perhaps formulate it in somewhat less of a defeatist style? That would seem to me to be a highly worthwhile undertaking.

[3] There exist several good summaries of Piaget's work. The most comprehensive is Flavell, J. H., The Developmental Psychology of Jean Piaget (*12*). Especially useful, part II, "The Experiments," chapter 9 on quantity, logic, number, time, movement, velocity; chapter 10 on space, geometry.

Much simpler are two undergraduate tests:

(a) Ginsburg, H. and Opper, Sylvia, 1969. Piaget's theory of intellectual development. An introduction. Prentice Hall, 237 pp.

(b) Phillips, John L. Jr., 1969. The origins of intellect. Piaget's theory. Freeman & Co., 149 pp.

Literature Cited

(1) (a) Bose, S. N., *"Planck's Gesetz und Lichtquantenhypothese," Z. f. Physik*, **26**, 178 (1924). (b) *Z. f. Physik*, **26**, (1924).

(2) Schrödinger, E., *"Quantisierung als Eingenwertproblem," Ann. J. Physik*, **79**, 361 (1926).

(3) Einstein, A., *"Über einen die Enzengung und Verwardlung des Lichtes betreffenden henristischen Gesichtspunkt," Ann d. Physik*, (4) **17**, 132 (1905).

(4) Einstein, A., *"Zur Quantentheorie der Strahlung," Physik. Zeitsch.*, **18**, 121 (1917).

(5) Einstein, A., *"Quantentheorie des einatomigen idealen Gases," Akad. d. Wiss. Berling, Sitzungiber phys. math. Kl.*, **22**, 261 (1924).

(6) Einstein, A., *"Quantentheorie des einatomigen idealen Gases, Zweite Abhandlung," Akad. d. Wiss. Berlin, Sitzungiber phys. math. Kl.* **23**, 3 (1925).

(7) Hanle, Paul A., "Erwin Schrödinger's Reaction to Louis de Broglie's Thesis on the Quantum Theory," *Isis*, **68**, 606 (1977).

(8) Pauli, W., "The Connection between Spin and Statistics," *Phys. Res.*, **58**, 696 (1940).

(9) Heisenberg, W., *"Über den anschaulichen Inhalt der Quantonmechanischen Kinematik und Mechanik.," Z. f. Physik*, **43**, 172 (1927).

(10) Bohr, N., "The Quantum Postulate and the Recent Development of Atomic Theory," *Nature*, **121**, 580 (1928).

(11) Lorenz, K., *"Kant's Lehre vom Apriorischen im Lichte gegenwärtiger Biologie. Blätter für deutsche Philosophie 15.94–125,"* (1941). Eng. trans. by Charlotte Churye *in* Bertalanffy and Rapaport (*Editors*) General Systems VII. Soc. for General Systems Research, Ann Arbor, MI, 1962, p. 37.