

Essay review

The evolution of Pauli's exclusion principle

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Michela Massimi, *Pauli's exclusion principle: The origin and validation of a scientific principle*, Cambridge University Press, Cambridge, ISBN 0521839114, 2005 US\$75, £45 hardback, xiv + 211pp.

1. The Pauli exclusion principle for electrons

In 1925 the Austrian physicist, Wolfgang Pauli, published the first, restricted, version of what has since come to be called the Pauli Exclusion Principle (PEP). Quantum Mechanics was being discovered and would be completely formulated within the next 2 years, but the framework within which Pauli was then working was what we call the Old Quantum Theory (see Ruark & Urey, 1964). In that theory atoms were conceived as planetary systems in which negatively charged electrons were bound in Bohr–Sommerfeld quantized orbits around a tiny, massive, positively charged nucleus. Emission of radiation occurred when a bound electron dropped to an orbit of lesser energy, the lost energy being carried away by a Planck–Einstein photon. Absorption of radiation occurred when an incident photon provided just the right energy for an electron to jump to a higher energy orbit.

Pauli proposed that, besides the integer-valued quantum numbers (in modern notation) n , l and m_l which, together, characterized the size, shape and spatial orientation of an electron's orbit, the electron also possessed a 'classically indescribable two valuedness', represented by an additional two valued quantum number, m_s , and no two electrons bound in an atom could have the same set of these four quantum numbers. This insight of Pauli was based on an analysis, published in the preceding year by E.C. Stoner (Enz & von Meyen, 1994, p.168; Duck & Sudarshan, 1997, pp. 43–48), of the phenomenology of atomic spectral lines from the perspective of the Bohr–Sommerfeld theory. In the paper Stoner came within a hairs breadth of enunciating the electron PEP himself. In particular,

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Stoner made the crucial observation that the collections of electron orbits, called subshells, labeled by a quantum number pair, (n, l) , were never occupied by more electrons than $2(2l + 1)$, i.e., twice the number of orbits in the subshell. The atoms of the inert, noble elements could then be understood as only occurring when certain subshells ($l = 1$) were filled.

Both Stoner and Pauli were working in a confusing atmosphere in which the complexities of spectral line splitting for alkali metal and alkaline earth atoms, in the presence or absence of external magnetic fields, had provoked rather ad hoc schemes going beyond Bohr–Sommerfeld theory (Tomonaga, 1997, pp. 1–42). Angular momentum quantum numbers, sometimes two valued, were attributed to the collection of completed subshell, inner electrons, the so-called ‘core’, which in the chemically adjacent noble gases had total angular momentum zero. The individual electron was regarded as an essentially pointlike, structureless entity (for which *rotational motion* would be meaningless) and only the less understood and more complex core could be regarded as harboring the puzzling, but seemingly necessary, extra quantum number. Thus, when Pauli interpreted Stoner’s work as strongly suggesting associating a two valuedness with *each* electron he dubbed it ‘classically indescribable’.

Immediately upon hearing of the idea, R. Kronig suggested to Pauli that the role of the new electron quantum number could be understood if it represented an internal angular momentum of the electron with a doubled magnetic moment that he thought could be understood from relativity. Pauli, however, dismissed the idea as ‘amusing’ and this eventually dissuaded Kronig (Fierz & Weisskopf, 1960, pp. 5–39). Subsequently, Uhlenbeck and Goudsmit had the same idea and submitted it for publication, failing to stop the publication at the last minute when they learned from Lorentz that classical electron theory posed severe obstacles to generating the required angular momentum. Thus, did the spin $\frac{1}{2}$ electron, satisfying the PEP, enter physics. Great clarification in understanding atomic spectra and the electron structure of the chemical elements of the periodic table ensued.

With the discovery of quantum mechanics it was quickly recognized that electrons would automatically satisfy the exclusion principle if multi-electron state functions were antisymmetric under interchange of any two electrons (Fierz & Weisskopf, 1960, pp. 199–248). In 1926, Heisenberg and Dirac independently showed that no transitions could ever occur between symmetrized and antisymmetrized state functions for identical particles and that symmetrized state functions would lead to Bose–Einstein statistics. Fermi showed that identical particles subject to the PEP would display the statistical behavior we now call Fermi–Dirac. Dirac obtained the same result for particles restricted to antisymmetrized state functions and, with the discovery of his relativistic wave equation for spin $\frac{1}{2}$ particles, showed that relativity did, indeed, account for the doubled magnetic moment (Tomonaga, 1997, pp. 43–62).

In time people came to call particle types restricted to symmetrized state functions, bosons, and those restricted to antisymmetrized state functions, fermions. For particles of a given type, then, an essential question was were they bosons or fermions? In 1926 the matter was settled only for photons and electrons.

2. Protons, neutrons, positrons, neutrinos and mesons

In 1927 Hund conceived the idea of determining the spin and statistics of protons by examining the band spectra of the hydrogen molecule, H_2 (Enz & von Meyen, 1994, p. 173;

Tomonaga, 1997, pp. 63–77). The spectral frequencies produced by the two electrons would be influenced in different ways if the *spatial* dependence of the proton–proton state function was symmetric or antisymmetric under proton interchange. On the other hand, the ratios of the intensities of the spectral lines would be influenced in different ways if the *spin* dependence of the two proton state function was symmetric or antisymmetric under proton interchange and the magnitude of the intensity ratios could determine the proton spin. Within the year Hori carried out the difficult measurements and determined that protons have spin $\frac{1}{2}$ and were subject to the PEP. Protons were fermions.

Until 1932 most people thought that atomic nuclei were composed of protons and electrons although it was hard to understand (because of the uncertainty principle) how an electron could be confined to such a tiny volume by protons. If it was so, then this would make a nucleus an integral-angular momentum-boson if the totality of constituent protons and electrons was even and a half integral-angular momentum-fermion if the totality were odd. But this conclusion also gave rise to problems, most conspicuously with lithium and nitrogen isotopes.

Consequently, when, in 1932, Chadwick discovered the massive, electrically neutral, neutron among the ejecta from heavy nuclei bombarded by helium nuclei, it was a pressing question to determine its spin and statistics (Tomonaga, 1997, pp. 150–161). Was the neutron an integral spin boson and, therefore, possibly a proton–electron bound state itself, or was it a fundamentally new constituent of nuclei? Fortunately deuterium was also discovered in the same year by Urey and Brickwedde and its nucleus, the deuteron, was best understood as a proton–neutron bound state with zero relative orbital angular momentum. Using an analysis of the band spectra of the D_2 molecule similar to Hori’s analysis of H_2 , it was determined by 1934 that the deuteron was a spin 1 boson. This required the neutron to be a fermion with spin $\frac{1}{2}$ or $\frac{3}{2}$ (Tomonaga, 1997, pp. 150–161).

The lower value was not experimentally established until 1947, but the success in developing early nuclear physics with the presumption that nuclei consisted of spin $\frac{1}{2}$ protons and neutrons convinced everyone of the lower value early on. The discovery of the positron by Anderson was also made in 1932. This positively charged particle with the mass of the electron was recognized as the partner of the electron predicted by Dirac’s earlier analysis of the negative energy solutions to his famous equation. As such, it also had to be a spin $\frac{1}{2}$ fermion.

In 1934 Fermi published a useful theory of β decay that employed a hypothetical very light neutral particle previously proposed by Pauli in 1931 in a desperate attempt to resist the challenge to energy conservation from the continuous β ray energy spectrum. Fermi called the particle a neutrino and treated it as a spin $\frac{1}{2}$ Dirac particle (Fierz & Weisskopf, 1960, pp. 249–303; Tomonaga, 1997, pp. 162–183).

In 1935, motivated by the example of the massless photon acting as a ‘carrier’ of the long-range electromagnetic force between electrons, positrons and protons, Yukawa proposed an integral spin (ultimately zero spin) boson particle, with mass about 200 times that of the electron, as the ‘carrier’ of the short-range nuclear force between protons and neutrons. In 1936 Anderson and Neddermeyer discovered a ‘heavy electron’ in cosmic rays of about Yukawa’s predicted mass and Oppenheimer and Serber suggested (incorrectly, as it turned out) that the heavy electron might really be Yukawa’s meson (Pais, 1986, pp. 429–434; Tomonaga, 1997, pp. 162–183).

3. The spin-statistics connection

Experimental resolutions concerning the existence and nature of the neutrino, Yukawa's meson (now the *pion*) and the heavy electron (now the *muon*) did not arrive for 10 more years, but by the late thirties it was almost universally held that electrons, positrons, protons, neutrons and the neutrino were spin $\frac{1}{2}$ fermions subject to the generalized PEP, while the photon and Yukawa's meson were integral spin bosons not subject to the PEP. This atmosphere, coupled with the Ehrenfest and Oppenheimer conclusion that 'tightly bound' composite structures containing odd (even) numbers of fermions would, themselves, display fermion (boson) statistics, led to a recognized need to ground the apparent spin-statistics connection in a derivation from first principles, i.e., from the principles of the still fledgling relativistic quantum field theory (Fierz & Weisskopf, 1960, pp. 48–77).

Spin-statistics theorems began emerging in 1936 with Pauli contributing in that year and then, again, in 1940 with what is widely regarded as the first sound proof (Tomonaga, 1997, pp. 131–149; Fierz & Weisskopf, 1960, pp. 199–248). But dissatisfaction with existing proofs, either because of the status of the premises, the complexity and sophistication of the arguments, or, indeed, challenges to the logic of the arguments, has maintained a sporadic effort to improve and simplify such proofs (Duck & Sudarshan, 1997). Indeed, Richard Feynman famously apologized to the readers of his 'Lectures in Physics' for not having a simple, intuitive proof of the spin-statistics theorem that we can really understand?

4. The book

4.1. Content

In the book under review the author proposes to provide a philosophically grounded account for the rise of the PEP from its initial form as a limited restriction on atomic electrons to its present status as necessarily applicable to all half integral spin quanta of relativistic quantum field theory, if not synonymous with the general spin-statistics theorem itself. The philosophical perspective adopted by the author takes its departure, primarily, from the Marburg school neo-Kantian philosopher, Ernst Cassirer. The aspect of Cassirer's philosophy most relevant is his emphasis on the regulative status of concepts and principles in scientific theories over a constitutive status, if any. I found this aspect of the book very welcome as examining the application of Cassirer's philosophy to problems of contemporary science has seemed, to me, unduly neglected.

In the more philosophical sections of the book the author pits Cassirer and some views of Gerd Buchdahl against views of Kuhn on incommensurability, Quine on under-determination and, more recently, Michael Friedman on the constitutive status of relativized a priori principles, as foils to champion, successfully I think, the regulative character of the PEP and scientific principles in general.

For example, in Chapter 3 the author argues against Kuhn's incommensurability thesis applied to the transition from the Old Quantum Theory to Quantum Mechanics. In an argument that takes into account the later modifications of Kuhn's views, but which might have benefited from some additional editing, the author concludes "..., Kuhn conflated the regulative *as if* with *is*. He took the genus–species relationships among kind concepts/

kind terms not as fulfilling a merely regulative demand in the Kantian sense (i.e., *as if* nature were ordered according to those taxonomic relationships), but rather as fixing an order of things in nature in the Aristotelian/neo-Platonic sense (i.e., nature *is* so ordered).” (italics in the original).

This example is sufficiently representative of the philosophical conclusions reached in the book that I was surprised to find no mention of Hans [Vaihinger \(1935\)](#), the neo-Kantian author of “The Philosophy of As If”.

The more historical sections of the book focus on the formulation and subsequent evolution of the PEP in 20th century physics. Here I encountered a puzzling dichotomy. The history just preceding the first formulation of the PEP is nicely balanced between experimental and theoretical considerations. But once the PEP is launched for electrons and the connection with Fermi–Dirac statistics theoretically established in 1926, the author effectively abandons experimental physics until the emergence of the parastatistics challenge to quarks in the 1960s.

This feature of the book prompted the writing of Section 2, in which I sketch the establishment of the applicability of the PEP to protons and neutrons via experimental studies in molecular physics. None of this appears in our book. Yet it would seem essential to the growth of the status of the PEP. Some of the rest of the material in Section 2 is discussed in the book but there is no mention of Yukawa or the emerging awareness of a spin-statistics connection prior to the theorems as described in Section 3.

The book returns to empirical considerations when it takes up the parastatistics challenge but, oddly, the focus is only modestly on the empirical considerations that influenced the introduction of the spin-statistics saving ‘colored’ *quarks*. More detailed consideration is devoted to the experimental searches in the late 1980s and 1990s for spin-statistics violations among atomic *electrons*! This choice was puzzling since during the arguments in the 1960s over parastatistical versus statistically normal quarks, people held strongly opposing views and one did not know how things would turn out. The later tests for spin-statistics violations among atomic electrons, while they would have been revolutionary had violations been found, had nothing to do with quarks and were very much a quieter activity. Almost no one expected any violations.

On the theoretical side, I was disappointed that the author did not follow the development of attempts to improve on Pauli’s 1940 proof of the spin-statistics theorem. The valuable sourcebook on this topic by [Duck and Sudarshan \(1997\)](#) is listed in the bibliography, but it is only referred to once in passing and no use is made of its post 1940 material. Perhaps the author is not sympathetic to Feynman’s apology.

4.2. Polish

The preceding criticisms can, perhaps, be put down to differences of perspective between the author and this reviewer. Unfortunately, the book is more seriously flawed by an anomalously large number of technical lapses. Many are just typos, but many are more substantive and some suggest a serious lack of understanding of the scientific material. The only sections escaping this charge are Chapter 3, mentioned above, and an excellent 9 page section from pp. 128 to 137. In the remaining 153 pages of text I found more than 50 pages with at least one technical lapse apiece! I’ll cite several of the more glaring ones (along with possibly unnecessary corrections) to give the flavor.

On p. 3 a footnote declares that the ‘light principle’ of special relativity “... fixes the finite value for the velocity of light.”

(The light principle asserts the *invariance under inertial frame change* of the vacuum speed of light. It does not fix the value of that speed.)

On p. 8 a footnote tells us the modern electronic energy-level quantum numbers “are n , l , m , s and the fourth quantum number is the spin s .” (The quantum numbers are n , l , m_l and m_s and the fourth quantum number is not the spin, but the z -component of the spin.)

On p. 15 we are told “The Michelson–Morley experiment gave negative evidence for the motion of light through ether; ...”

(It gave negative evidence for the motion of the *Earth* through the ether.)

On p. 37 Eq. (2.6) employs the same symbol, r , for two very different quantities.

On p. 49 the same kind of ambiguous use of a symbol, m in this case, in a simple equation, (2.11), occurs, but here *the author draws the readers attention to the ambiguity in a footnote rather than removing the ambiguity!*

This instance puzzled me, but imagine my surprise when, while collaterally reading Tomonaga’s (1997) book, “The Story of Spin”, I found, on p. 16, the same ambiguity in, essentially, the same equation, (1–30), and, once again, pointed out to the reader by the author rather than removed! Amazing!

On p. 72 we read “... the number of sublevels into which the spectral term splits was known to be $2(2k-1)$, i.e., $2n^2$.” [The correct connection is $2n^2 = \sum_{k=1}^n 2(2k-1)$.]

On p. 125 the commutation relations among creation and annihilation operators of Eq. (4.14) are given without the relevant conditions on the indices. The operators of Eqs. (4.15, 16) are written without regard for the reordering of non-commuting factors under conjugation.

On p. 152 the meson and baryon spin predictions of the quark model are described without mention of the important presumption of zero relative orbital angular momentum between the quarks. Also strangeness conservation is related to quarks without the qualification that it only holds for purely strong and electromagnetic interaction processes.

On p. 168: First, axial vector and vector currents are conflated. Second, we read, “The neutral pion is a meson consisting of up (and down) quarks (or antiquarks); ...”. [They consist of up (or down) quarks (and antiquarks).] Third, a decay amplitude is claimed proportional to the “average of the electric charges of the u and d quarks involved:”. (The correct average is of the *squares* of the electric charges.) Fourth, in a footnote we read, “... described by four-vector operators that, ... could be vector (V), axial vector (A), scalar (S), pseudoscalar (P), and tensor (T).” [A ‘four-vector’ operator can only be V or A, never S, P or T. The context of the passage (discussion of early weak interaction theory) indicates that the qualifying term, ‘four-vector’ should not have preceded the word, ‘operators’.]

There are several figures in the book taken from research publications or textbooks and while we are told *what* they refer to we are not told *how* to read them and in some cases they are inappropriate for the accompanying text.

5. Conclusion

The subject of this book is deeply interesting and the philosophical perspective from which the subject is approached, both apropos and illuminating. On balance, however, I have the impression of a book written under extreme conditions of pressure and schedule deadlines; and proof read, if at all, under the same conditions. Sadly, it shows.

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