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Historical Survey

1.1 Discovery of the Pauli Exclusion Principle and Early Developments

Wolfgang Pauli formulated his principle before the creation of the contemporary quantum mechanics (1925–1927). He arrived at the formulation of this principle trying to explain regularities in the anomalous Zeeman effect in strong magnetic fields. Although in his Princeton address [1], Pauli recalled that the history of the discovery goes back to his student days in Munich. At that time the periodic system of chemical elements was well known and the series of whole numbers 2, 8, 18, 32… giving the lengths of the periods in this table was zealously discussed in Munich. A great influence on Pauli had his participation in the Niels Bohr guest lectures at Göttingen in 1922, when he met Bohr for the first time. In these lectures Bohr reported on his theoretical investigations of the Periodic System of Elements. Bohr emphasized that the question of why all electrons in an atom are not bound in the innermost shell is the fundamental problem in these studies. However, no convincing explanation for this phenomenon could be given on the basis of classical mechanics.

In his first studies Pauli was interested in the explanation of the anomalous type of splitting in the Zeeman effect in strong magnetic fields. As he recalled [1]:

> The anomalous type of splitting was especially fruitful because it exhibited beautiful and simple laws, but on the other hand it was hardly understandable, since very

general assumptions concerning the electron using classical theory, as well as quantum theory, always led to the same triplet. A closer investigation of this problem left me with the feeling, it was even more unapproachable. A colleague who met me strolling rather aimlessly in the beautiful streets of Copenhagen said to me in a friendly manner, 'You look very unhappy'; whereupon I answered fiercely, 'How can one look happy when he is thinking about the anomalous Zeeman effect?'

Pauli decided to analyze the simplest case, the doublet structure of the alkali spectra. In December 1924 Pauli submitted a paper on the Zeeman effect [2], in which he showed that Bohr's theory of doublet structure based on the nonvanishing angular moment of a closed shell, such as K-shell of the alkali atoms, is incorrect and closed shell has no angular and magnetic moments. Pauli came to the conclusion that instead of the angular momentum of the closed shells of the atomic core, a new quantum property of the electron had to be introduced. In that paper he wrote, remarkable for that time, prophetic words. Namely:

According to this point of view, the doublet structure of alkali spectra … is due to a particular two-valuedness of the quantum theoretic properties of the electron, which cannot be described from the classical point of view.

This nonclassical *two-valued nature of electron* is now called *spin*. In anticipating the quantum nature of the magnetic moment of electron before the creation of quantum mechanics, Pauli exhibited a striking intuition.

After that, practically all was ready for the formulation of the exclusion principle. Pauli also stressed the importance of the paper by Stoner [3], which appeared right at the time of his thinking on the problem. Stoner noted that the number of energy levels of a single electron in the alkali metal spectra for the given value of the principal quantum number in an external magnetic field is the same as the number of electrons in the closed shell of the rare gas atoms corresponding to this quantum number. On the basis of his previous results on the classification of spectral terms in a strong magnetic field, Pauli came to the conclusion that a single electron must occupy an entirely nondegenerate energy level [1].

In the paper submitted for publication on January 16, 1925 Pauli formulated his principle as follows [4]:

In an atom there cannot be two or more equivalent electrons, for which in strong fields the values of all four quantum numbers coincide. If an electron exists in an atom for which all of these numbers have definite values, then this state is 'occupied.'

In this paper Pauli explained the meaning of four quantum numbers of a single electron in an atom, n, l, $j = l \pm 1/2$, and m_j (in the modern notations); by n and l he denoted the well known at that time the principal and angular momentum quantum numbers, by j and m_j—the total angular momentum and its projection,

respectively. Thus, Pauli characterized the electron by some additional quantum number j, which in the case of $l = 0$ was equal to $\pm 1/2$. For the fourth quantum number of the electron Pauli did not give any physical interpretations, since he was sure, as we discussed above, that it cannot be described in terms of classical physics.

Introducing two additional possibilities for electron states, Pauli obtained $2(2l + 1)$ possibilities for the set (n, l, j, m_j). That led to the correct numbers 2, 8, 18, and 32 for the lengths of the periods in the Periodic Table of the Elements.

As Pauli noted in his Nobel Prize lecture [5]: "…physicists found it difficult to understand the exclusion principle, since no meaning in terms of a model was given to the fourth degree of freedom of the electron." Although not all physicists! Young scientists first Ralph Kronig and then George Uhlenbeck and Samuel Goudsmit did not take into account the Pauli words that the electron fourth degree of freedom cannot be described by classical physics and suggested the classical model of the spinning electron. Below I will describe in some detail the discovery of spin using the reminiscences of the main participants of this dramatic story.

Kronig recalled [6] that on January 7, 1925, at the age of 20, he, as a traveling fellow of the Columbia University, arrived in the small German university town of Tübingen to see Landé and Gerlach. At the Institute of Physics Kronig was received by Landé with the remark that it was a very opportune moment, since he was expecting Pauli the following day and he just received a long and very interesting letter from Pauli. In that letter Pauli described his exclusion principle. Pauli's letter made a great impression on Kronig and it immediately occurred to him that additional to the orbital angular momentum l the momentum $s = 1/2$ can be considered as an intrinsic angular momentum of the electron. The same day Kronig performed calculations of the doublet splitting. The results encouraged him, although the obtained splitting was too large, by a factor of 2. He reported his results to Landé. Landé recommended telling these results to Pauli. Next day Pauli arrived at Tübingen, and Kronig had an opportunity to discuss with him his ideas. As Kronig [6] wrote: "Pauli remarked: '*Das ist ja ein ganz Einfall*',[1] but did not believe that the suggestion had any connection with reality."

Later Kronig discussed his ideas in Copenhagen with Heisenberg, Kramers, and others and they also did not approve them. Under the impression of the negative reaction of most authoritative physicists and some serious problems in his calculations Kronig did not publish his ideas about a spinning electron. In the letter to van der Waerden [7] Kronig wrote about the difficulties he met in his studies of the spinning electron:

> First, the factor 2 already mentioned. Next, the difficulty to understand how a rotation of the electron about its axis would yield a magnetic moment of just one magneton. Next, the necessity to assume, for the rotating charge of an electron of classical size, velocities

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[1] This is a very funny idea.

surpassing the velocity of light. Finally, the smallness of the magnetic moments of atomic nuclei, which were supposed, at that time, to consist of proton and electrons

Independent of Kronig, the Dutch physicists Uhlenbeck and Goudsmit after reading the Pauli paper on his exclusive principle also arrived at the idea of the spinning electron. In his address, delivered at Leiden on the occasion of his Lorentz Professorship, Uhlenbeck [8] told in detail the story of their discovery and its publication.[2]

According to Uhlenbeck, he and Goudsmit were greatly affected by the Pauli exclusion principle, in particular by the fourth quantum number of the electron. It was a mystery, why Pauli did not suggest any concrete picture for it. Due to their conviction that every quantum number corresponds to a degree of freedom, they decided that the point model for the electron, which had only three degrees of freedom, was not appropriate and the electron should be assumed as a small sphere that could rotate. However, very soon they recognized that the rotational velocity at the surface of the electron had to be many times larger than the velocity of light. As Uhlenbeck writes further,

> …we had not the slightest intention of publishing anything. It seems so speculative and bold, that something ought to be wrong with it, especially since Bohr, Heisenberg and Pauli, our great authorities, had never proposed anything of this kind. But of course we told Erenfest. He was impressed at once, mainly, I feel, because of the visual character of our hypothesis, which was very much in his line. … and finally said that it was either highly important or nonsense, and that we should write a short note for Naturwissenschaften and give it to him. He ended with the words 'und dann werden wir Herrn–Lorentz fragen'.[3] This was done. … already next week he (Lorentz) gave us a manuscript, written in his beautiful hand writing, containing long calculations on the electromagnetic properties of rotating electrons. We could not fully understand it, but it was quite clear that the picture of the rotating electron, if taken seriously, would give rise to serious difficulties. … Goudsmit and myself felt that it might be better for present not to publish anything; but when we said this to Erenfest, he answered: 'Ich habe Ihren Brief schon längst abgesandt; Sie sind beide jung genug um sich eine Dummheit leisten zu können.[4]

Thus, the short letter of Uhlenbeck and Goudsmit was transmitted by Erenfest to the editor of *Naturwissenschaften* and soon published [9]. Then in February 1926 they published a paper in *Nature* [10]. In the letter to Goudsmit from November 21, 1925 (see van der Waerden [7]), Heisenberg congratulated him with their paper but also asked him how he envisaged getting rid of the wrong factor 2 in the doublet splitting formula. Bohr, who was initially rather skeptic about the hypothesis of the spinning electron and did not approve the Kronig idea, gradually changed his mind.

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[2] English translation of an essential part of Uhlenbeck's address represented in Ref. [7].

[3] …and then we will also ask Mr. Lorentz.

[4] I have already sent your letter some time ago. You are both young enough and can afford yourself a foolishness.

The meeting with Einstein became crucial. In his letter to Kronig from March 26, 1926 (see van der Waerden [7]), Bohr writes:

> When I came to Leiden to the Lorenz festivals (December 1925), Einstein asked the very first moment I saw him what I believe about the spinning electron. Upon my question about the cause of the necessary mutual coupling between spin axis and the orbital motion, he explained that this coupling was an immediate consequence of the theory of relativity. This remark acted as a complete revelation to me, and I have never since faltered in my conviction that we at last were at the end of our sorrows.

Under the influence of Bohr's opinion on the idea of spinning electron, Heisenberg at last removed his objections.

However, Pauli did not! His deep intuition did not allow him at once to admit the hypothesis of the spin as an intrinsic angular momentum of the rotating electron. Pauli's objections resulted from the wrong factor 2 in the doublet splitting, but mainly from the classical nature of the spin hypothesis. After the Lorentz festival (December 1925), Pauli met Bohr in Berlin and in strong words expressed his dissatisfaction that Bohr changed his position. Pauli was convinced that a new "Irrlehre"[5] has arisen in atomic physics, as van der Waerden wrote in his recollections [7].

Meanwhile, in April 1926, a young English physicist Llewellyn Thomas, who had spent half a year in Copenhagen with Bohr, published a letter in *Nature* [11], where he presented a relativistic calculation of the doublet splitting. Thomas demonstrated that the wrong factor 2 disappears and the relativistic doublet splitting does not involve any discrepancy. In the end Thomas noted, "… as Dr. Pauli and Dr. Heisenberg have kindly communicated in letters to Prof. Bohr, it seems possible to treat the doublet separation as well as the anomalous Zeeman effect rigorously on the basis of the new quantum mechanics." Thus, this time Pauli was certain that the problem can be treated rigorously by the quantum mechanical approach. The relativistic calculations by Thomas finally deleted all his doubts.

In his Nobel Prize lecture Pauli recalled [5]:

> Although at first I strongly doubted the correctness of this idea because of its classical mechanical character, I was finally converted to it by Thomas [11] calculations on the magnitude of doublet splitting. On the other hand, my earlier doubts as well as the cautious expression 'classically non-describable two-valuedness' experienced a certain verification during later developments, as Bohr was able to show on the basis of wave mechanics that the electron spin cannot be measured by classically describable experiments (as, for instance, deflection of molecular beams in external electromagnetic fields) and must therefore be considered as an essentially quantum mechanical property of the electron.

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[5] Heresy.

It is now clear that Pauli was right in not agreeing with the classical interpretation of the fourth degree of freedom. The spin in principle cannot be described by classical physics. The first studies devoted to applying the newborn quantum mechanics to many-particle systems were performed independently by Heisenberg [12] and Dirac [13]. In these studies, the Pauli principle, formulated as the prohibition for two electrons to occupy the same quantum state, was obtained as a consequence of the antisymmetry of the wave function of the system of electrons.

It is instructive to stress how young were the main participants of this dramatic story. They were between 20 and 25 years. In 1925, the creators of quantum mechanics—Werner Heisenberg (1901–1976), Paul Dirac (1902–1984), Wolfgang Pauli (1900–1960), Enrico Fermi (1901–1954), and some others—were of the same age. Namely: Heisenberg—24, Dirac—23, Pauli—25, Fermi—24.

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In his first paper [12], submitted in June 1926, Heisenberg constructed the antisymmetric Schrödinger eigenfunction for the system of n identical particles (electrons) as a sum:

$$\varphi = \frac{1}{\sqrt{n!}} \sum (-1)^{\delta_k} \varphi_1\left(m_\alpha^k\right) \varphi_2\left(m_\beta^k\right) \ldots \varphi_n\left(m_\nu^k\right) \tag{1.1}$$

where δ_k is a number of transpositions in a permutation, P_k (a parity of permutation), and $m_\alpha^k m_\beta^k \ldots m_\nu^k$ the new order of quantum numbers $m_1 m_2 \ldots m_n$ after the application of permutation P_k. Heisenberg concluded that this function cannot have two particles in the same state, that is, it satisfies the Pauli exclusion principle. In the following paper [14], submitted in July 1926, Heisenberg considered a two-electron atom and from the beginning assumed that the Pauli-allowed wave functions must be antisymmetric. He demonstrated that the total antisymmetric wave function can be constructed as a product of spatial and spin wave functions and discussed two possibilities: A—the symmetric eigenfunction of the space coordinates is multiplied by the antisymmetric eigenfunction of the spin coordinates; B—the antisymmetric eigenfunction of the space coordinates is multiplied by the symmetric eigenfunction of the spin coordinates. Case A corresponds to the atomic singlet state with the total spin $S = 0$; case B corresponds to the triplet state with $S = 1$. Heisenberg presented detailed calculations for the atom He and the ion Li^+. These were first quantum mechanical calculations of the atomic states characterized by the total spin S of the atom defined by the vector addition of the spins of the individual electrons.

Dirac [13] began with the two-electron atom and noted that the states differing by permutations of electrons $\psi_n(1)\psi_m(2)$ and $\psi_n(2)\psi_m(1)$ correspond to the same state of the atom; these two independent eigenfunctions must give rise to the symmetric and antisymmetric linear combinations providing a complete solution of the

two-electron problem. Then Dirac considered the systems with any number of electrons and represents an N-electron antisymmetric function as a determinant[6]:

$$
\begin{vmatrix}
\psi_{n_1}(1) & \psi_{n_1}(2) & \dots & \psi_{n_1}(r) \\
\psi_{n_2}(1) & \psi_{n_2}(2) & \dots & \psi_{n_2}(r) \\
\dots & \dots & \dots & \dots \\
\psi_{n_r}(1) & \psi_{n_r}(2) & \dots & \psi_{n_r}(r)
\end{vmatrix}
\tag{1.2}
$$

After presenting the many-electron wave function in the determinantal form Dirac wrote: "An antisymmetrical eigenfunction vanishes identically when two of the electrons are in the same orbit. This means that in the solution of the problem with antisymmetrical eigenfunctions there can be no stationary states with two or more electrons in the same orbit, which is just Pauli's exclusion principle. The solution with symmetrical eigenfunctions, on the other hand, allows any number of electrons to be in the same orbit, so that this solution cannot be the correct one for the problem of electrons in an atom."

In the second part of his paper [13], Dirac considered an assembly of noninteracting molecules. At that time it was supposed that molecules are resembled electrons and should satisfy the Pauli exclusion principle. Dirac described this assembly, in which every quantum state can be occupied by only one molecule, by the antisymmetric wave functions and obtained the distribution function and some statistical quantities. It should be mentioned that these statistical formulae were independently published by Fermi [16] in the paper submitted several months earlier than the Dirac paper [13]. Fermi also considered an assembly of molecules and although his study was performed within the framework of classical mechanics, the results were the same as those obtained by Dirac who applied the newborn quantum mechanics. This concluded the creation of the statistics, which is at present named the *Fermi–Dirac statistics*.

In the same fundamental paper [13], Dirac considered the assembly described by the symmetric wave functions and concluded that he arrived at the already known Bose–Einstein *statistical mechanics*.[7] Dirac stressed that the light quanta must be described by the symmetric wave functions and he specially noted that a system of electrons cannot be described by the symmetric wave functions since this allows any number of electrons to occupy a quantum state.

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[6] It is important to note that the determinantal representation of the electronic wave function, at present widely used in atomic and molecular calculations, was first introduced in general form by Dirac [13] in 1926. In 1929, Slater [15] introduced the spin functions into the determinant and used the determinantal representation of the electronic wave function (so-called Slater's determinants) for calculations of the atomic multiplets.

[7] This statistics was introduced for the quanta of light by Bose [17] and generalized for particles by Einstein [18, 19].

Thus, with the creation of quantum mechanics, the prohibition on the occupation numbers of electron system states was supplemented by the prohibition of all types of permutation symmetry of electron wave functions except for antisymmetric ones.

The first quantum mechanical calculation of the doublet splitting and the anomalous Zeeman effect for atoms with one valence electron was performed by Heisenberg and Jordan [20] in 1926. They used the Heisenberg matrix approach and introduced the spin vector s with components s_x, s_y, and s_z with commutations relations the same as for the components of the orbital angular moment l. The spin–orbit interaction was taken as proportional to $l \cdot s$. The application of the perturbation theory led to results, which were in full accordance with experiment.

In 1927, Pauli [21] studied the spin problem using the wave functions. Pauli introduced the spin operators s_x, s_y, s_z acting on the wave functions, which depend on the three spatial coordinates, q, and a spin coordinate. Pauli took s_z as a spin coordinate. The latter is discrete with only two values. Therefore, the wave function $\psi(q, s_z)$ can be presented as a two-component function with components $\psi_\alpha(q)$ and $\psi_\beta(q)$ corresponding to $s_z = 1/2$ and $s_z = -1/2$, respectively. The operator, acting on the two-component functions, can be presented as a matrix of the second order. Pauli obtained an explicit form of the spin operators, representing them as $s_x = 1/2\sigma_x, s_y = 1/2\sigma_y$, and $s_z = 1/2\sigma_z$, where σ_τ are the famous *Pauli matrices*:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1.3}$$

Applying his formalism to the problem of the doublet splitting and the anomalous Zeeman effect, Pauli obtained, as can be expected, the same results as Heisenberg and Jordan [20] obtained by the matrix approach.

The Pauli matrices were used by Dirac in his derivation of the Schrödinger equation for the relativistic electron [22]. However, for most of physicists the two-component functions that do not transform like vectors or tensors seemed very strange. As van der Waerden recalled [7]: "Erenfest called these quantities *Spinors* and asked me on his visit to Göttingen (summer, 1929): 'Does a Spinor Analysis exist, which every physicist can learn like Tensor Analysis, and by which all possible kinds of spinors and all invariant equations between spinors can be written down?' " This request made by an outstanding physicist was fulfilled by van der Waerden in his publication [23].

After these publications, the first stage of the quantum mechanical foundation of the Pauli exclusion principle and the conception of the spin could be considered as completed. Although it is necessary to mention very important applications of the group-theoretical methods to the quantum mechanical problems, which were developed at that time by John von Neumann and Eugene Wigner [24–27]. Very soon the three remarkable books on the group theory and quantum mechanics were
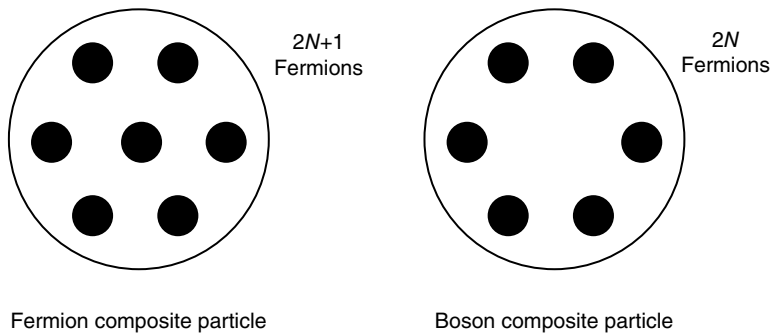
Fig. 1.1   The statistics of composite particles

published; first by Herman Weyl [28] and then by Wigner [29] and by van der Waerden [30].

The discovery of various types of elementary particles in the 1930s allowed formulating the Pauli exclusion principle in a quite general form. Namely:

The only possible states of a system of identical particles possessing spin s *are those for which the total wave function transforms upon interchange of any two particles as*

$$P_{ij}\Psi(1,\ldots,i,\ldots j,\ldots,N) = (-1)^{2s}\Psi(1,\ldots,i,\ldots j,\ldots,N), \tag{1.4}$$

that is, it is symmetric for the integer values of s *(the Bose–Einstein statistics) and antisymmetric for the half-integers (the Fermi–Dirac statistics).*

The Pauli exclusion principle formulated above also holds for composite particles. First, it was discussed by Wigner [31] and independently by Ehrenfest and Oppenheimer [32]. The latter authors considered some clusters of electrons and protons; it can be atoms, molecules, or nuclei (at that time the neutron had not been discovered yet and it was believed that the nuclei were built from electrons and protons). They formulated a rule, according to which statistics of a cluster depends upon the number of particles from which they are built up. In the case of odd number of particles it is the Fermi–Dirac statistics, while in the case of even number it is the Bose–Einstein statistics, see Fig. 1.1. It was stressed that this rule is valid, if the interaction between composite particles does not change their internal states; that is, the composite particle is stable enough to preserve its identity.

A good example of such stable composite particle is the atomic nucleus. It consists of nucleons: protons and neutrons, which are fermions because they both have $s = 1/2$. Depending on the value of the total nuclear spin, one can speak of boson nuclei or fermion nuclei. The nuclei with an even number of nucleons have an integer value of the total spin S and are bosons; the nuclei with an odd number of nucleons have a half-integer value of the total spin S and are fermions.

A well-known example, in which the validity of the Pauli exclusion principle for composite particles can be precisely checked in experiment, is the $^{16}O_2$ molecule. The nucleus ^{16}O is a boson composite particle, so the total wave function of the $^{16}O_2$ molecule must be symmetric under the permutations of nuclei. At the Born–Oppenheimer approximation [33] a molecular wave function can be represented as a product of the electronic, Ψ_{el}, and nuclear, Φ_n, wave functions. At the equilibrium distances the nuclear wave function, in its turn, can be represented as a product of the vibrational, Φ_{vib}, and rotational, Φ_{rot}, wave functions. Thus,

$$\Psi\left(^{16}O_a - {}^{16}O_b\right) = \Psi_{el}(ab)\Phi_{vib}(ab)\Phi_{rot}(ab). \tag{1.5}$$

The vibrational wave function, $\Phi_{vib}(ab)$, depends only on the magnitude of the interatomic distance and remains unaltered under the interchange of the nuclei. The ground state electronic wave, $\Psi_{el}(ab)$, is antisymmetric under the interchange of the nuclei. Hence, for fulfilling the boson symmetry of the total wave function (1.5), the rotational wave function, $\Phi_{rot}(ab)$, must be also antisymmetric under the interchange of the nuclei. The symmetry of the rotational wave function in the state with the rotational angular momentum K is determined by the factor $(-1)^K$. Therefore, in the ground electronic state the even values of K are forbidden and only odd values of K are allowed. Exactly this was revealed in 1927 in spectroscopic measurements [34] made before the theoretical studies [31, 32].

I presented above the general formulation of the Pauli exclusion principle in the terms of the permutation symmetry of the total wave function. There is also a formulation of the Pauli exclusion principle in the second quantization formalism. The second quantization for the electromagnetic field, that is, for bosons, was created by Dirac [35]; the commutations relations for fermion and boson operators in the explicit modern form were formulated by Jordan and Wigner [36], see also references therein.

For bosons, which are described by the symmetric wave functions and satisfy the Bose–Einstein statistics, the commutation relations for the creation b_k^+ and annihilation b_k operators in the quantum state k are (see Appendix E)

$$\left[b_k, b_{k'}^+\right]_- = b_k b_{k'}^+ - b_{k'}^+ b_k = \delta_{kk'},$$
$$\left[b_k, b_{k'}\right]_- = \left[b_k^+, b_{k'}^+\right]_- = 0, \tag{1.6}$$

while for fermions, which correspond to the Fermi–Dirac statistics with the antisymmetric wave functions, the commutation relations for the creation c_k^+ and annihilation c_k operators (in the fermion case they are transformed to the anticommutation relations) are

$$\left[c_k, c_{k'}^+\right]_+ = c_k c_{k'}^+ + c_{k'}^+ c_k = \delta_{kk'},$$
$$\left[c_k, c_{k'}\right]_+ = \left[c_k^+, c_{k'}^+\right]_+ = 0. \tag{1.7}$$

As follows from the second line of the fermion anticommutation relations (1.7),

$$\left(c_k^+\right)^2 = 0, \tag{1.8}$$

or no more than one fermion particle can be created in one quantum state, which is exactly the primary formulation of the Pauli principle. A more detailed description of the second quantization formalism is presented in Appendix E.

Some of the field theory specialists claimed that the second quantization formulation of the Pauli exclusion principle is the most general; see, for instance, Ref. [37]. I do not think so, these formulations are quite different. On the one hand, the second quantization formalism is developed for N-particle system in the case when each particle is characterized by its own wave function (so-called one-particle approximation),[8] while the ψ-formalism considers the permutation symmetry of the total wave function in any approximation, even for an exact solution when the particles lost their individualities. Thus, in this sense the ψ-formulation of the Pauli exclusion principle is more general than the formulation in the second quantization formalism. On the other hand, for the composite particles the formulation in the second quantization formalism allows to take into account the internal structure of the composite particle. The symmetry of the wave functions of N-particle system does not change when we go from elementary to composite particles satisfying the same statistics, while for the commutation relations of the second quantization operators it is not true; in the case of composite particles they are changed. We will discuss this problem and the reasons for this in the next subsection.

1.2   Further Developments and Still Existing Problems

In 1932, Chadwick [38] discovered neutron. In the same year, Heisenberg [39] considered consequences of the model, in which the nuclei are built from protons and neutrons, assuming that the forces between all pairs of particles are equal and in this sense the proton and neutron can be considered as different states of one particle. Heisenberg [39] introduced a variable τ. The value $\tau = -1$ was assigned to the proton state, and the value $\tau = 1$ to the neutron state. Wigner [40] called τ as *isotopic spin* (at present named also as *isobaric spin*). Taking into account for protons and neutrons their nuclear spin $s = 1/2$ too, Wigner studied the nuclear charge-spin supermultiplets for Hamiltonian not involving the isotope spin and the ordinary spin as well, see also Refs. [41, 42].

In the 1940s, Giulio Racah published a series of four papers [43–46], in which he considerably improved methods of classification and calculation of atomic spectra. At that time the calculations of atomic spectra were performed by the diagonal-sum

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[8] It is natural in the relativistic theory where the number of particles in the system can be changed.

procedure elaborated in 1929 by Slater [15]; its generalized version extended to electron shells up to f electrons was represented in the widely used Condon and Shortley book [47]. The calculations by the diagonal-sum method were very lengthy and did not give general formulas, but only numerical tables.

Racah [43–46] developed new elegant and effective methods introducing in the atomic spectroscopy the tensor operator techniques and the concept of the *fractional parentage coefficients*. The latter permitted a genealogical construction of the N-electron wave function from the parent $(N–1)$-electron states. The antisymmetric wave function for the configuration ℓ^N was presented as a linear combination of the wave functions obtained by the addition of an electron with the angular momentum ℓ to the possible states of the configuration ℓ^{N-1}. Racah studied the transformation matrices for the three-dimensional rotation group $\mathbf{R}_3$ connecting different coupling schemes for three angular momenta and introduced so-called Racah's W coefficients, see Appendix C, Section C.2. In the last paper [46] he applied the theory of continuous group to the problem of classification of the Pauli-allowed states for configurations of equivalent electrons. These publications made a great impact on the atomic spectroscopy as well as on the nuclear physics.

In 1950, Jahn [48] used the Racah approach for a classification, in the Russell–Saunders (LS) coupling scheme, of the states for the nuclear d-shell according to their transformation properties under the group of rotations in the five-dimensional space of the orbital states of the d-particle. He determined the charge–spin structure of all Wigner's supermultiplets [40]. Then Jahn with coauthors calculated the energy of nuclear d- and p-shells at the Hartree–Fock approximation using the method of the fractional parentage coefficients [49–52]. The new point in these studies was the presentation of the total wave function as a linear combination of the products of orbital and charge–spin wave functions symmetrized according to the mutually conjugate representations $\Gamma^{[\lambda]}$ and $\Gamma^{[\tilde{\lambda}]}$ of the permutation group that provides the antisymmetry of the total wave function. The Young diagram $[\tilde{\lambda}]$ is dual to $[\lambda]$, that is, it is obtained from the latter by replacing rows by columns, see Appendix A. For jj-coupling in nuclear shell model this approach was elaborated in Refs. [53, 54]. In many problems, in particular for the classification of the Pauli-allowed states, an employment of the permutation group proved to be more effective than the original Racah approach. This was demonstrated in the nuclear studies cited above and in our studies [55–57] devoted to the application of the permutation group apparatus to molecular spectroscopy for finding nuclear and electronic multiplets allowed by the Pauli exclusion principle.

In 1961, Kaplan [58] introduced the transformation matrices for the permutation group connecting representations with different types of reduction on subgroups, which can be considered as an analog of the transformation matrices connecting different angular momentum couplings for the rotation group. The symmetry properties of the transformation matrices for the permutation group were studied by Kramer [59, 60] who showed that these matrices are identical with the invariants

of the unitary groups. In the case of electrons the transformation matrices for the permutation group can be expressed in terms of the invariants of the group SU_2, which are just the $3nj$-symbols of the three-dimensional rotation group; these connections are also discussed in a special section "The Kaplan matrices and nj-symbols for group $SU(n)$" in review by Neudachin et al. [61]. Employment of Kaplan's matrices allowed obtaining the general expressions for the spatial-coordinate fractional parentage coefficients of an arbitrary multishell nuclear (or atomic) configuration [62].

The first application of the permutation group to molecular problems was done by Kotani and Siga [63] to study the CH_4 molecule. Then Kotani and coworkers [64, 65] applied this approach to the configuration interaction calculations of diatomic molecules. In 1963, Kaplan [66, 67] applied his methodology [58, 62] developed for the spherical symmetry case to molecular systems and then elaborated it in a series of papers [68], where this approach was named as the coordinate (that meant spatial coordinate) function method. Later on it was named as *spin-free quantum chemistry*. These studies were systemized and generalized in a monograph [69].

Though the concept of the spin has enabled to explain the nature of the chemical bond, electron spins are not involved directly in the formation of the latter. The interactions responsible for chemical bonding have a purely electrostatic nature. The main idea of the spin-free quantum chemistry is to use in the calculations with a nonrelativistic Hamiltonian only the spatial wave functions $\Phi_r^{[\lambda]}$, which entered the total wave function as products with the spin wave functions $\Omega_{\tilde{r}}^{[\tilde{\lambda}]}$. The Young diagram $[\tilde{\lambda}]$ is dual to $[\lambda]$, which provides the antisymmetry of the total wave function. For the spin $s = 1/2$, the spin Young diagram $[\tilde{\lambda}]$ is uniquely connected with the value of the total spin S. Thus, the spatial wave functions $\Phi_r^{[\lambda]}$ describe the antisymmetric state with the definite total spin S. In the case of the Hamiltonian not containing spin-dependent interactions, this approach is more natural than the employment of the Slater determinants; it allows obtaining the energy matrix elements in an explicit compact form for arbitrary electronic configurations in the state with a definite spin S [69, 70].

At the same time the concepts of the spin-free quantum chemistry were independently developed by Matsen [71–74]. Later this approach was applied to molecular calculations by Goddard [75, 76], Gallup [77, 78], Gerratt [79, 80], and many others.

As we mentioned in the end of the previous subsection, despite the fact that the wave function of composite particles can be characterized only by the boson or fermion permutation symmetry, its second quantization operators do not obey the pure boson or fermion commutation relations. This was studied in detail by Girardeau [81, 82] and Gilbert [83], see also recent publications [84, 85]. When the internal structure of the composite particle is taken into account, the deviations from the purely bosonic or fermionic properties usually appear. For two fermions it

was revealed earlier, in 1957, in the Bardeen–Cooper–Schrieffe (BCS) theory of superconductivity [86] based on the conception of the Cooper pairs [87], see an excellent description of their theory by Schrieffer [88].

The operators of creation, $b_{\mathbf{k}}^{+}$, and annihilation, $b_{\mathbf{k}}$, of Cooper's pair in a state $(\mathbf{k}\alpha, -\mathbf{k}\beta)$, where $\mathbf{k}$ is the electron momentum and α and β are the spin projections, are defined as products of the electron creation, $c_{\mathbf{k}\alpha}^{+}$, and annihilation, $c_{\mathbf{k}\alpha}$, operators

$$b_{\mathbf{k}}^{+} = c_{\mathbf{k}a}^{+} c_{-\mathbf{k}\beta}^{+}, \quad b_{\mathbf{k}} = c_{-\mathbf{k}\beta} c_{\mathbf{k}\alpha}. \tag{1.9}$$

The Cooper pairs have spin $S = 0$, so the permutation symmetry of their wave functions is bosonic. But their operators do not obey the boson commutation relations. Direct calculation results in

$$\left[b_{\mathbf{k}}, b_{\mathbf{k}'}^{+} \right]_{-} = \delta_{\mathbf{k}\mathbf{k}'} \left(1 - c_{\mathbf{k}\alpha}^{+} c_{\mathbf{k}\alpha} - c_{\mathbf{k}\beta}^{+} c_{\mathbf{k}\beta} \right). \tag{1.10}$$

Only in the case $\mathbf{k} \neq \mathbf{k}'$

$$[b_{\mathbf{k}}, b_{\mathbf{k}'}]_{-} = 0 \tag{1.11}$$

and Cooper's pairs obey the boson commutation relations. For $\mathbf{k} = \mathbf{k}'$

$$[b_{\mathbf{k}}, b_{\mathbf{k}}]_{-} = 1 - c_{\mathbf{k}\alpha}^{+} c_{\mathbf{k}\alpha} - c_{\mathbf{k}\beta}^{+} c_{\mathbf{k}\beta}. \tag{1.12}$$

Due to the fermion nature of electrons, the commutation relations for Cooper's pair operators are not bosonic and even more, they have the fermion occupation numbers for one-particle states, since

$$\left(b_{\mathbf{k}}^{+} \right)^{2} = (b_{\mathbf{k}})^{2} = 0. \tag{1.13}$$

Thus, Cooper's pair operators may not be considered as the Bose, or as the Fermi operators [89, 90], see Section 5.3.

One of the first studies of the effective repulsion between identical elementary particles was performed by Zeldovich [91] who considered the repulsion between elementary barions (neutrons, protons, and others) and showed that the Pauli repulsion arises when the overlap of wave functions become appreciable. This corresponds to the well known in atomic and molecular physics *exchange interaction* stipulated by the requirement of the antisymmetry of many-electron wave functions. The exchange interaction is a direct consequence of the Pauli exclusion principle. For taking into account the Pauli repulsion, different computational schemes were elaborated. We mention two methods: the Pauli repulsion operator [92], see recent application in Ref. [93], and the so-called Pauli blockade method [94], see recent application in Ref. [95].

However, the first application of the Pauli repulsion was performed by Fowler [96] in astrophysics already in the next year after Pauli suggested his principle. Fowler applied the Pauli exclusion principle for an explanation of the white-dwarf structure. The radius of the white dwarfs is comparable with the earth's radius, while their mass is comparable with the solar mass. Therefore, the average density of the white dwarfs is 10^6 times greater than the average density of the sun; it is approximately 10^6 g/cm^3. The white dwarfs are composed from plasma of bare nuclei and electrons. Fowler [96] had resolved a paradox: why such dense objects, as the white dwarfs, are not collapsed at low temperature? He applied to the electron gas in the white dwarfs the Fermi–Dirac statistics, introduced in the same 1926, and showed that even at very low temperatures the electron gas, called at this conditions as degenerate, still possesses a high energy; compressing of a white dwarf leads to increase of the inner electron pressure. Fowler concluded his paper in the following manner: "…the origin of this important part of interatomic forces (*repulsion*, *IK*) is … in the quasi-thermodynamic consequences of the existence of the quantum constraints embodied in Pauli's principle." Thus, the Pauli repulsion prevents the white dwarfs from the gravitational collapse.

In Refs. [85, 97] the Pauli exclusion principle was connected with such interesting and mysterious quantum phenomenon as entanglement [98], which at present is broadly implemented in quantum information theory [99]. The term "entanglement" was introduced by Schrödinger [100] when he analyzed the so-called Einstein–Podolsky–Rosen paradox [101], see also discussions in Refs. [102–104].

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All experimental data known to date agree with the Pauli exclusion principle. Some theoretical ideas and experimental searches for possible violations of the Pauli exclusion principle were discussed by Okun [105] and recently by Ignatiev [37]; the published experimental tests of the validity of the Pauli exclusion principle were classified in the review report by Gillaspy [106]. Below I discuss a widespread spectroscopic approach.

The systematic spectroscopic study of the validity of the Pauli exclusion principle for electrons has been recently carried out by the Violation Pauli (VIP) collaboration. In their experiments they performed a search of X-rays from the Pauli-forbidden atomic transition from the $2p$ shell to the closed $1s^2$ shell of Cu atoms, forming the non-Pauli $1s^3$ shell, see Fig. 1.2.[9] The obtained probability that the Pauli exclusion principle is violated, according to their last measurements [108, 109], was

$$\frac{1}{2}\beta^2 < 6 \times 10^{-29}. \tag{1.14}$$

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[9] It should be mentioned that it is a quite widespread approach, which at present is usually used in the experimental verification of the Pauli exclusion principle after the Ramberg and Snow experiment [107].
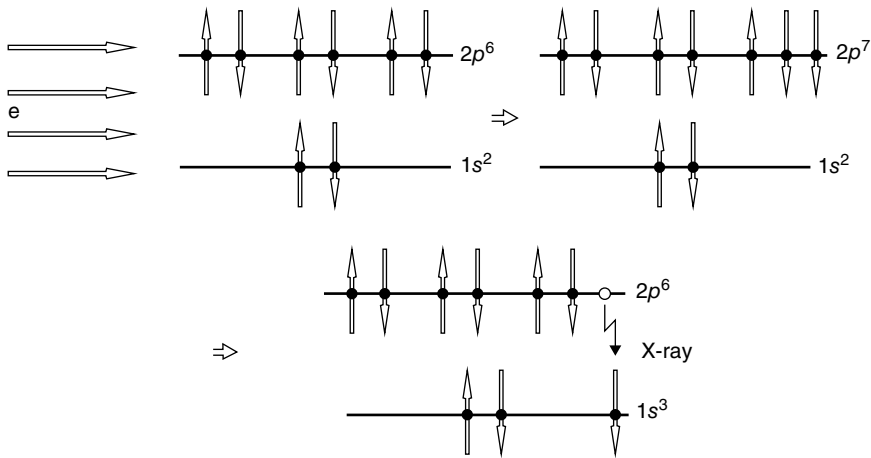
Fig. 1.2 The schematic representation of the formation of the Pauli-forbidden atomic inner-shell populations in the experimental search of the non-Pauli electrons

In the experiments performed in the Los Alamos laboratory by Elliott et al. [110] Pb instead of Cu was used. They reported a much stronger limit on the violation of the Pauli exclusion principle for electrons. Namely:

$$\frac{1}{2}\beta^2 < 2.6 \times 10^{-39}. \tag{1.15}$$

It must be mentioned that this limit was obtained by a modified method of the processing of the experimental data. As noted in Ref. [110], in the conductor there are two kinds of electrons: the current electrons that have no previous contacts with the target and the electrons within the target, which are "less new." The authors [110] took into account *all* free electrons. The application of this approach to the VIP data also changes their limit on 10 orders. On the other hand, it seems that the processing method used in Ref. [110] cannot be rigorously based. In any case, as follows from experimental data, the probability of formation of the non-Pauli states is practically zero.

It is worthwhile to make several comments in connection with the described above experimental verifications of the Pauli exclusion principle. First, usually experimenters consider the violation of the Pauli exclusion principle as a small admixture of the symmetric wave functions to the antisymmetric ones. They start from the Ignatiev–Kuzmin [111] and Greenberg–Mohapatra [112] theoretical suggestions, last years from the quon theory [113]. These theories are based on the second quantization formalism, in which only the symmetric and antisymmetric states are defined. In general, this limitation on the permutation symmetry of

the possible states is not valid, because the solutions of the Schrödinger equation may belong to any representation of the permutation group, see below Eq. (1.16) and its discussion. If the Pauli exclusion principle is violated, it means that there are some electrons described by wave functions with an arbitrary permutation symmetry, not necessarily the symmetric one, see also discussion in Chapter 3.

The electrons not satisfying the Pauli exclusion principle are not described by the antisymmetric wave functions; therefore, they may not be mixed with the normal electrons that are the fermions. The transitions between states with different permutation symmetry are strictly forbidden (superselection rule). Thus, the transitions may take place only inside this group of probable non-Pauli electrons and these electrons are not identical to the "normal" Pauli electrons; in the other case they must be characterized by the antisymmetric wave functions, compare in this connection the comments by Amado and Primakoff [114]. It is also important to stress that every system of identical particles is characterized by one of the irreducible representations of the permutation group, but not by its superposition. If particles are characterized by some superposition of irreducible representations of the permutation group, they are not satisfied by the indistinguishability principle and are not identical; whereas the Pauli exclusion principle was formulated for systems of identical particles.

And last but not the least: Since the Pauli and probable non-Pauli electrons may not possess the same permutation symmetries, it is quite doubtful that the non-Pauli electrons can be located on the filled fermionic shells. We must take into account that the energy of identical particle system depends upon its permutation symmetry. The energy level separation for non-Pauli electrons can be in another energy region than measured X-ray transitions in experiments. Thus, even if really a small part of electrons exists that does not obey the Pauli exclusion principle, these non-Pauli electrons cannot be detected in the experiments described above.

The history of creation of the Pauli exclusion principle and consequent studies clearly indicate that it was not derived from the concepts of quantum mechanics, but was based on the analysis of experimental data. Pauli himself was never satisfied by this. In his Nobel Prize lecture Pauli said [5]:

> Already in my initial paper, I especially emphasized the fact that I could not find a logical substantiation for the exclusion principle nor derive it from more general assumptions. I always had a feeling, which remains until this day, that this is the fault of some flaw in the theory.

Let us stress that this was said in 1946, or after the famous Pauli theorem [115] of the relation between spin and statistics. In this theorem, Pauli did not give a direct proof. He showed that due to some physical contradictions, the second quantization operators for particles with integral spins cannot obey the fermion commutation relations; while for particles with half-integral spins their second quantization operators cannot obey the boson commutation relations. Thus, according to the

Pauli theorem, the connection between the value of spin and the permutation symmetry of many-particle wave function, Eq. (1.1), follows if we assume that particles can obey only two types of commutation relations: boson or fermion relations. At that time it was believed that it is really so. However, Pauli was not satisfied by such kind of negative proof. Very soon it became clear that he was right.

In 1953, Green [116] (then independently Volkov [117]) showed that more general paraboson and parafermion trilinear commutation relations, satisfying all physical requirements and containing the boson and fermion commutation relations as particular cases, can be introduced. A corresponding parastatistics is classified by its rank p. For the parafermi statistics p is the maximum occupation number. For $p = 1$ the parafermi statistics becomes identical to the Fermi–Dirac statistics. For the parabose statistics there are no restrictions in the occupation numbers; for $p = 1$ the parabose statistics is reduced to the Bose–Einstein statistics (for more details, see the book by Ohnuki and Kamefuchi [118] and Chapter 5).

So far the elementary particles obeying the parastatistics are not detected. Although, as discussed in Refs. [119–121], the ordinary fermions, which differ by some intrinsic properties (e.g., charge or color), but are similar dynamically, can be described by the parafermi statistics. In this case, fermions with *different* internal quantum numbers are considered as *different*, or as different states of dynamically equivalent particles. So, *quarks* with three colors obey the parafermi statistics of rank $p = 3$; *nucleons* in nuclei (isotope spin 1/2) obey the parafermi statistics of rank $p = 2$. It is important to stress that the parafermi statistics of rank p describes systems with p different types of fermions. The total wave function for such parafermions always can be constructed as an antisymmetric function in full accordance with the Pauli exclusion principle.

In 1976, Kaplan [122] revealed that the parafermi statistics is realized for quasiparticles in a crystal lattice, for example, the Frenkel excitons or magnons, but due to a periodical crystal field, the Green trilinear commutation relations are modified by the quasi-impulse conservation law, see also Ref. [123]. Later on, it was shown that the modified parafermi statistics [122] introduced by Kaplan is valid for different types of quasiparticles in a periodical lattice: polaritons [124, 125], defectons [126], the Wannier–Mott excitons [127], delocalized holes in crystals [128], delocalized coupled hole pairs [129], and some others, see also Ref. [130].

The study of properties of the quasiparticles in a periodical lattice revealed [122, 128] that even in the absence of dynamical interactions, the quasiparticle system is characterized by some kinematic interaction depending on the deviation of their statistics from the Bose (Fermi) statistics. This kinematic interaction mixes all states of the quasiparticle band. One cannot define an independent quasiparticle in a definite state. The ideal gas of such quasiparticles does not exist fundamentally. There are also no direct connection between the commutation relations for quasiparticle operators and the permutation symmetry of many-quasiparticle wave functions.

Let us return to the Pauli theorem [115]. Since there are no prohibitions on the existence of elementary particles obeying the parastatistics commutation relations, the proof [115] loses its base. After 1940, numerous proofs of the spin–statistics connection were published; see, for instance, Refs. [131–134] and the Pauli criticism [135] on the Feynman [136] and Schwinger [137] approaches. In the comprehensive book by Duck and Sudarshan [138] and in their review [139] they criticized all proofs of the spin–statistics connection published at that time except the Sudarshan proof [140]. Only this proof they assumed as correct and elementary understandable. However, in his critical review on the Duck–Sudarshan book [138], Wightman [141] noted that none of the authors criticized in the Duck–Sudarshan book will find the proof [140] satisfactory.

In his famous lectures [142] Feynman asked:

> Why is it that particles with half-integral spin are Fermi particles whose amplitudes add with the minus sign, whereas particles with integral spin are Bose particles whose amplitudes add with the positive sign? We apologize for the fact that we cannot give you an elementary explanation. An explanation has been worked out by Pauli from complicated arguments of quantum field theory and relativity. He has shown that two must necessarily go together, but we have not been able to find a way of reproducing his arguments on an elementary level. It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one found a simple and easy explanation. The explanation is deep down in relativistic quantum mechanics. This probably means that we do not have a complete understanding of the fundamental principle involve.

Unfortunately, after that time there has not been any progress in this direction. Most proofs of the spin–statistics connection contain negative statements; they demonstrate that abnormal cases cannot exist, but they did not answer why the normal case exists. We still have no answer what are the physical reasons that identical particles with half-integer spin are described by antisymmetric functions and identical particles with integer spin are described by completely symmetric functions. As Berry and Robbins [143] emphasized, the relation between spin and statistics "cries out for understanding."[10]

It is worthwhile to stress that the Pauli exclusion principle is not reduced only to the spin–statistics connection. It can be considered from the point of the restrictions on the allowed symmetry types of many-particle wave functions. Namely, only two types of permutation symmetry are allowed: symmetric and antisymmetric. Both

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[10] After this Feynman comment, many studies were published, in which authors claimed that they fulfilled the Feynman requirement and proposed a simple explanation of the spin–statistics connection. However, none of these proofs can be considered rigorous, including recent publications by Jabs [144] and based on it a relativistic proof by Bennett [145].

belong to the one-dimensional representations of the permutation group; all other types of permutation symmetry are forbidden. However, the Schrödinger equation is invariant under any permutation of identical particles. The Hamiltonian of an identical particle system commutes with the permutation operators,

$$[P,H]_- = 0. \tag{1.16}$$

From this it follows that the solutions of the Schrödinger equation may belong to any representation of the permutation group, including multidimensional representations.

The following question might be asked:

whether this limitation on the solutions of the Schrödinger equation follows from the fundamental principles of quantum mechanics or it is an independent principle?

In Chapter 3 I discuss possible answers to this question. Here I only would like to mention that in my publications [146–148] it was rigorously proved that the indistinguishability principle is insensitive to the permutation symmetry of the wave function and cannot be used as a criterion for the verification of the Pauli exclusion principle. All published up-to-date proofs that only two types of the permutation symmetry can exist are incorrect, including the proof in the famous book by Landau and Lifshitz *Quantum Mechanics*, translated in many languages, see section 61 in English translation [149] of this book.

Thus, quantum mechanics allows all types of the permutation symmetry. In this aspect in a rigorous proof of the spin–statistics connection the possibility of the multidimensional representations of the permutation group must also be considered. However, the second quantization formalism is developed only for the symmetric and antisymmetric representations. This makes the proof of the spin–statistics connection even more improbable.

It should be mentioned that in our studies [146–148] of different scenarios following from the allowance of multidimensional representations of the permutation group, it was demonstrated that the latter leads to some contradictions with the concepts of particle identity and their independency from each other, see discussion in Section 3.2. Thus, the existence in Nature of only the one-dimensional permutation symmetries is not occasional.

It seems that at this point it makes sense to conclude this historical survey, because many of problems mentioned above will be discussed in detail in the following chapters of this book. As we saw, the Pauli exclusion principle plays the decisive role in a very wide range of phenomena: from the structure of nuclei, atoms, molecules, and solids to the formation of stars, for instance, the white dwarfs.

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