# THE PAULI EXCLUSION PRINCIPLE

## ORIGIN, VERIFICATIONS, AND APPLICATIONS


ILYA G. KAPLAN

WILEY

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**Ilya G. Kaplan**

*Materials Research Institute,*
*National Autonomous University of Mexico,*
*Mexico*

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*To my wife*
*Larisa*

# Contents

# Preface

This book is devoted to the Pauli exclusion principle, which is a fundamental principle of quantum mechanics and has been naturally kept in mind in all its numerous applications in physics, chemistry, molecular biology, and even in astronomy, see Chapter 1. Nevertheless, to the best of my knowledge, it is the first scientific (not philosophical) book devoted to the Pauli exclusion principle. Although Wolfgang Pauli formulated his principle more than 90 years ago, its rigorous theoretical foundations are still absent. In the historical survey (Chapter 1) and in other chapters of the book, I discuss in detail still existing unsolved problems connected with the Pauli exclusion principle and for some of them suggest possible solutions.

From the beginning of my scientific activity I have been interested in the issues of symmetry in quantum mechanics and in the mathematical description of it, that is, in the group theory and, particularly, in the permutation group theory. I was impressed by the simplicity and clearness of Young's mathematical language (about Young diagrams and Young tableaux, see Appendix B), especially if one takes into account Young's individuality: most of Young's papers on the permutation group were written when he was a country parish priest. For many years I was occupied with the following question: why, according to the Pauli exclusion principle, in our Nature only the antisymmetric or symmetric permutation symmetries for identical particles are realized, while the Schrödinger equation is satisfied by functions with any permutation symmetry. The possible answers on this question I discuss in Chapter 3.

I was always impressed by the Pauli deep physical intuition, which several times struck physical community. In fact, the formulation by Pauli of his principle was to a great extent based on his intuition (it was done before the creation of modern quantum mechanics), and it gave rise to the discovery of such important quantum mechanical conception as *spin* (I describe this dramatic story in Chapter 1). Another well-known example is the Pauli prediction of neutrino. Pauli made this prediction without any experimental and theoretical indications that this chargeless

and, as thought at that time, massless particle can exist. He tried to save the energy conservation law in the β-decay, because he did not agree with Niels Bohr who at that time was sure that the energy conservation law is not valid for microparticles. It turns out that Pauli was right.

The construction of functions with a given permutation symmetry is discussed in detail in Chapter 2. All necessary mathematical apparatus is given in Appendices A and B. If the total wave function of $N$ identical particle system is represented as a product of the spatial and spin wave functions symmetrized according to the appropriate irreducible representations of the permutation group, it automatically satisfies the Pauli exclusion principle and describes the state with a definite value of the total electronic or nuclear spin.

The application of the permutation group theory for the construction of molecular wave functions makes possible elaborating effective and elegant methods for finding the Pauli-allowed states in atomic, molecular, and nuclear spectroscopy (Chapter 4). In the elaborated methods the linear groups and their interconnection with the permutation group are applied. The necessary mathematical apparatus is represented in Appendix C. The classification of the Pauli-allowed states is represented for all types of many-atom molecules with the explicit formulae for the characters of reducible representations formed by a given set of atomic states. In last sections of this chapter the methods of finding the Pauli-allowed states for an arbitrary many-particle system, containing subsystems characterized by their local symmetry, are described. These methods do not depend on the number of particles in subsystems.

Chapter 5 is devoted to exotic statistics: parastatistics and fractional statistics. Although the elementary particles obeying the parastatistics are not detected, I demonstrate that the quasiparticles (collective excitations) in a periodical lattice are obeying the modified parafermi statistics; among them are the hole pairs, which are analogue of Cooper's pairs in the high $T_c$ superconductivity, and such well-known quasiparticles as excitons and magnons. The fractional statistics is also realized in our Nature for excitations in the fractional quantum Hall effect; these excitations can be considered as quasiparticles with fractional charge. However, the theoretical suggestions that the fractional statistics is realized in the high $T_c$ superconductivity have not been confirmed by experiment.

I tried to write the book for a broad audience from academic researchers to graduate students connected in their work or study with quantum mechanics. Significant efforts were made to present the book so as it will be self-sufficient for readers, since all necessary apparatus of the group theory is described in the appendices.

I would like to acknowledge Lucien Piela, Lev Pitaevsky, Olga Rodimova, Oleg Vasyutinsky, Vladimir Yurovsky, and Serge Zagoulaev for useful discussions of different problems connected with the topic of the book. Special acknowledgment goes to Ulises Miranda and Alberto Lopez who helped me to correct the book.

Mexico
February 2016

# 1

# 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

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> 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

[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.

[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.

* *
*

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 $\delta_k$ 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.

[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 $\boldsymbol{s}$ with components $s_x$, $s_y$, and $s_z$ with commutations relations the same as for the components of the orbital angular moment $\boldsymbol{l}$. The spin–orbit interaction was taken as proportional to $\boldsymbol{l}\cdot\boldsymbol{s}$. 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 $\boldsymbol{s_x}, \boldsymbol{s_y}, \boldsymbol{s_z}$ 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 $\boldsymbol{s_x} = 1/2\boldsymbol{\sigma}_x$, $\boldsymbol{s_y} = 1/2\boldsymbol{\sigma}_y$, and $\boldsymbol{s_z} = 1/2\boldsymbol{\sigma}_z$, where $\boldsymbol{\sigma}_\tau$ 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

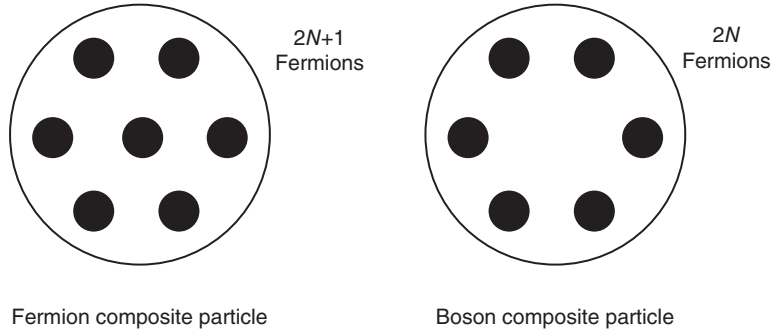


**Fig. 1.1** The statistics of composite particles

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, $\Psi_{el}$, and nuclear, $\Phi_n$, wave functions. At the equilibrium distances the nuclear wave function, in its turn, can be represented as a product of the vibrational, $\Phi_{vib}$, and rotational, $\Phi_{rot}$, 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)

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

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

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

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 $\psi$-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 $\psi$-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 $\tau$. The value $\tau = -1$ was assigned to the proton state, and the value $\tau = 1$ to the neutron state. Wigner [40] called $\tau$ 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

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