

Early Stage of the Development of Quantum Chemistry Without Spin and Its Recent Applications*

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General ideas, on which the quantum chemistry without spin is based, are discussed. Three important applications of quantum chemistry without spin are presented in detail: (1) the methods for finding the molecular spin-multiplets allowed by the Pauli principle; (2) the symmetry properties of the electron density that determines the Kohn-Sham equations in the density functional theory; and (3) the foundations of the Pauli principle. In particular, it was demonstrated that, on the

one hand, the Pauli exclusion principle cannot be derived from other fundamental principles of quantum mechanics; on the other hand, it cannot be considered as a postulate, since all other symmetry options for the total wave function of identical particles, except the one-dimensional representations, are forbidden. © 2012 Wiley Periodicals, Inc.

DOI: 10.1002/qua.24223

General Idea and Constructions; Some Historical Reminiscences

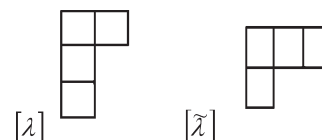
In this article, I describe the early stages of the creation of so-called quantum chemistry without spin and then discuss some recent applications to the density functional theory (DFT) and to the foundation of the Pauli exclusion principle, which lays in the base of quantum mechanics and the theory of the molecular structure.

Though the concept of 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. So, the calculations of chemical structure can be carried out without using the spin variables and this really can be done due to the separation of space and spin coordinates in the absence of spin interactions. In this case, the total spin S is a good quantum number, and the wave functions should be eigenfunctions of \hat{S}^2 (in a central field (atoms) this approximation is known as Russell-Saunders, or LS-coupling). The total wave function can be represented as a product of a coordinate wave function and a spin wave function. What is important is that for the electron system there is a unique correspondence between the permutation symmetry of the coordinate wave function and the value of total spin, see below. This explains that why in the absence of spin interactions, the energy of a system of electrons depends on the value of their total spin S .

The wave function that is antisymmetric with respect to electron permutations (obeying the Pauli principle) and describing the state with the total spin S can be constructed as linear combinations of products of coordinate and spin wave functions, symmetrized according to the irreducible representations $\Gamma^{[\lambda]}$ of the permutation group $\pi_N^{[1-3]}$

$$\Psi^{[1^N]} = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi_r^{[\lambda]} \Omega_r^{[\lambda]} \quad (1)$$

In Eq. (1), $[\lambda]$ is the Young diagram with N cells* and $\Gamma^{[\lambda]}$ denotes the representation conjugate to $\Gamma^{[\lambda]}$. Its matrix elements are $\Gamma_{\tilde{r}\tilde{r}'}^{[\lambda]}(P) = (-1)^p \Gamma_{r'r}^{[\lambda]}(P)$, where p is the parity of the permutation P . The Young diagram $[\tilde{\lambda}]$ is dual to $[\lambda]$, that is, it is obtained from the latter by replacing rows by columns. For example,



The sum in Eq. (1) is taken over all the basis functions of the representation. The factor $\sqrt{f_\lambda}$ arises from the orthogonality conditions of the total wave function. Since the electron spin $s = 1/2$ has only two projections $s_z = \pm 1/2$, the spin Young diagrams $[\tilde{\lambda}]$ cannot have more than two boxes in a column. That is, each diagram has no more than two rows. Consequently, the coordinate Young diagrams $[\lambda]$ dual to it cannot have more than two columns. If in one box of a column in a spin Young diagram, the electron spin projection is $1/2$, then in the other box of this column the electron spin projection is $-1/2$, that is, the spins of these two electrons should be coupled. It is evident that the contribution to the total spin of the system will come only from uncoupled electron spins; their

This article was published online on 18 June 2012. An error was subsequently identified. This notice is included in the online and print version to indicate that both have been corrected on 25 July 2012.

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*The number N can be always decomposed as a sum of different positive components: $\lambda^{(1)} + \lambda^{(2)} + \dots + \lambda^{(m)}$, $\lambda^{(1)} \geq \lambda^{(2)} \geq \dots \geq \lambda^{(m)}$. Each partition can be depicted graphically by means of Young diagrams, in which each number $\lambda^{(l)}$ is represented by a row of $\lambda^{(l)}$ cells. As it is proved in the theory of permutation groups, each Young diagram uniquely corresponds to a specific irreducible representation of the permutation group π_N , see Chapter 2 in Ref. [1].

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number equals to the difference between the lengths of the rows in the corresponding Young diagram, $(\tilde{\lambda}^{(1)} - \tilde{\lambda}^{(2)})$, and

$$S = \frac{1}{2}(\tilde{\lambda}^{(1)} - \tilde{\lambda}^{(2)}). \quad (2)$$

Formula (2) enables one to easily find the values of the spin, S , for each spin Young diagram. For example, for the spin Young diagram above $S = 1$. Such a one-to-one correspondence between a Young diagram and the total spin is valid only for particles with spin $1/2$. For particles with $s > 1/2$ several values of S may correspond to the permutation symmetry of given Young diagram, see Classification of Molecular States section.

Thus, the main idea of quantum chemistry without spin is to use in the calculations with a spinless Hamiltonian only the coordinate wave functions whose permutation symmetry is uniquely connected with the value of the total spin S of the state. In the case of the absence of the spin-dependent interactions, this approach is quite natural; it allows solving the problems in an explicit way for states with arbitrary S .

The first application to molecular problems of the method of coordinate wave functions symmetrized according to the irreducible representation of the permutation group and, therefore, corresponding to a definite value of S was done by Kotani and Siga^[4] to study the CH_4 molecule. Then Kotani et al.^[5,6] applied this approach to the configuration interaction calculations of diatomic molecules.

In 1940, Fock,^[7] without application of the group theory, has constructed the coordinate function corresponding to a definite value of S , which was antisymmetric in two groups of its arguments and had a special cyclic symmetry. As was shown by Demkov^[8] (see also Section 7–11 in Hamermesh text-book^[9]), Fock's symmetry corresponds to the symmetry of a coordinate two-column Young diagram; thus, it corresponds to a spin two-row Young diagram and describes the state with a definite total spin. Luzanov^[10] in a recent interesting publication revisited the Fock approach. He reformulated it using the elegant formalism of the reduced density matrices.

In 1961, the general method of calculation of the matrix elements of a Hamiltonian for nuclear and atomic multishell configurations, based on the coordinate wave functions, was elaborated in my publications.^[11,12] For this, I introduced the transformation matrices of the permutation group[†] and suggested to construct the functions in Eq. (1) using the normalized Young operators[‡]

$$\omega_{\tau}^{[\lambda]} = \sqrt{\frac{f_{\lambda}}{N!}} \sum_P \Gamma_{\tau}^{[\lambda]}(P)P \quad (3)$$

where, the summation over P runs over all the $N!$ permutations of the permutation group π_N , $\Gamma_{\tau}^{[\lambda]}(P)$ are the matrix elements and f_{λ} is the dimension of the irreducible representation $\Gamma^{[\lambda]}$. The application of operator (3) to a nonsymmetrized product of orthonormal one-particle functions $\varphi_k(k)$,

$$\Phi_0 = \varphi_1(1)\varphi_2(2)\dots\varphi_N(N) \quad (4)$$

produces a normalized function

$$\Phi_n^{[\lambda]} = \omega_n^{[\lambda]}\Phi_0 = \sqrt{\frac{f_{\lambda}}{N!}} \sum_P \Gamma_{\tau}^{[\lambda]}(P)P\Phi_0 \quad (5)$$

transforming in accordance with the representation $\Gamma^{[\lambda]}$ of the permutation group π_N .

In 1963, I applied the methodology^[11,12] to molecular systems^[15,16] and then elaborated it in a series of papers^[17–19] where this approach was named as the coordinate function method. It was systemized and generalized in a monograph,^[1] where the methods of finding of the allowed by the Pauli principle molecular spin-multiplets were also presented in detail, see next Section.

The methodology^[1] allows for obtaining the energy matrix elements for arbitrary electronic configurations in an explicit compact form. In Ref. [20], the energy matrix elements were obtained for an arbitrary configuration of nonorthogonal orbitals in the state with a definite spin S . In the case of the single-occupied and orthogonal orbitals, the expectation value of the energy is reduced to a very simple form

$$E_t^{[\lambda]} = \sum_a h_{aa} + \sum_{a<b} [g_{ab,ab} + \Gamma_{tt}^{[\lambda]}(P_{ab})g_{ab,ba}] \quad (6)$$

where h_{aa} are the one-electron integrals, $g_{ab,ab}$ and $g_{ab,ba}$ are the two-electron Coulomb and exchange integrals, respectively, and $\Gamma_{tt}^{[\lambda]}(P_{ab})$ is the diagonal matrix element of the transposition of orbitals ϕ_a and ϕ_b in the product (4). Only, the exchange terms depend on the permutation symmetry of the state, that is, on the value of S . Such kind of expression allows deriving the SCF equations for the state with a definite spin S , taking into account all f_{λ} functions in Eq. (1); the self-consistent field (SCF) equations have been also obtained for the non-orthogonal orbital case, see Chapter 8 in Ref. [1].

At the same time, in the 1960s, the conceptions of quantum chemistry without spin were independently developed by Matsen.^[21–24] Later the coordinate function approach was applied to molecular studies by Goddard,^[25,26] Gallup,^[27,28] Gerratt,^[29,30] and many others, see a comprehensive review by Klein^[31] and references therein.

The first presentation of my concepts of quantum chemistry without spin on an international forum was in 1969 at the International Symposium on Theory of Atomic and Molecular Electronic Shells (Vilnius, Lithuania). There many prominent quantum chemists participated, among them was Octay Sinoglu. As I remember, in the beginning of Symposium he

[†]As was shown by Kramer,^[13] these transformation matrices are identical to the invariants of the unitary groups and can be considered as an analog of the $3n-j$ symbols of the three-dimensional rotation group, see also Ref. [14], Section 3.9 "The Kaplan matrices and n_j symbols for group $\text{SU}(n)$."

[‡]Operator (3) should not be mixed up with the operator that symmetrizes the rows and antisymmetrizes the columns in Young diagram and which is also often referred to as the Young operator, see Ref. [9].

made a big problem for the Organizing Committee. According to the Program, the first report should be done by the Chairman of the Symposium A.P. Yutsis, second was the report by Sinanoglu. Sinanoglu refused to participate, if he was not allowed to be the first speaker. I do not know how this was arranged, but the first speaker remained Yutsis.

Classification of Molecular States

Nuclear molecular multiplets

The representation of the total wave function as a product of coordinate and spin wave functions allows for the derivation of simple and clear methods for finding the molecular spin-multiplets permitted by the Pauli principle. My first study on the application of the permutation group to the construction of the total wave function was done in 1959, see Ref. [32]. There, I developed a clear and convenient procedure for finding the values of the total nuclear spin allowed by the Pauli principle for molecular states with a given point symmetry. The total nuclear spin I is a good quantum number, if we neglect the hyperfine interactions. For nuclei with the half-integer spin i the total wave function can be presented in the same form as Eq. (1). For the integer spin i , the total wave function should be symmetric and the permutation symmetries of coordinate and spin wave functions in Eq. (1) must be the same.

In the case when the nuclear spin $i > 1/2$, there is no unique connection between the total spin I and the spin Young diagram. The product of N one-nucleus spin functions symmetrized according to the Young diagram $[\lambda]$ belongs to the irreducible representation $U_{2i+1}^{[\lambda]}$ of the group of unitary transformations \mathbf{U}_{2i+1} . Since the group \mathbf{R}_3 is a subgroup of \mathbf{U}_{2i+1} , the irreducible representations $U_{2i+1}^{[\lambda]}$ in general become reducible upon restricting the operations to those of \mathbf{R}_3 and hence $U_{2i+1}^{[\lambda]}$ splits into the irreducible representations $D^{(l)}$ of \mathbf{R}_3

$$U_{2i+1}^{[\lambda]} = \sum_l a_\lambda^{(l)} D^{(l)} \quad (7)$$

The method for finding the decomposition (7) is described in details in Ref. [1], Section 4.5; in Appendix 3 of this book Tables of possible I for all $[\lambda]$ for $N = 1-4$ and $i = 1/2 - 3$ are presented.

The permutations of N identical nuclei are generally not all realized by the operations of the corresponding point group; hence, this point group is isomorphic with a subgroup of the permutation group of identical nuclei, π_N . The irreducible representations $\Gamma^{(\alpha)}$ of the point subgroup of the group π_N contained in its representation $\Gamma^{[\lambda]}$ are given by the decomposition

$$\Gamma^{[\lambda]} = \sum_\alpha a_\lambda^{(\alpha)} \Gamma^{(\alpha)} \quad (8)$$

where coefficients $a_\lambda^{(\alpha)}$ are found with the aid of character tables for permutation and point groups. For this, it is necessary to place each operation of the point group into

correspondence with the appropriate permutation of the nuclei.

As aforementioned, the connection between the permutation symmetries of the coordinate and nuclear spin functions depends on the statistics of the nuclei. Together with the decompositions (7) and (8), it makes possible to associate with each type of point symmetry $\Gamma^{(\alpha)}$ the values of total nuclear spin I permitted by the Pauli principle. Schematically, this approach can be represented as

$$\begin{array}{cc}
 \text{a) Bose statistics} & \text{b) Fermi statistics} \\
 \Gamma^{[\lambda]} \longleftrightarrow U_{2i+1}^{[\lambda]} & \Gamma^{[\lambda]} \longleftrightarrow U_{2i+1}^{[\lambda]} \\
 \downarrow & \downarrow \\
 \Gamma^{(\alpha)} \longleftrightarrow D^{[I]} & \Gamma^{(\alpha)} \longleftrightarrow D^{[I]}
 \end{array} \quad (9)$$

Several examples of application of the scheme (9) are presented in Ref. [1], Section 6.5.

Electronic molecular multiplets

Except for the study,^[33] the methods for finding the electronic molecular multiplets were elaborated by the author in collaboration with Rodimova.^[34-37] In the first paper,^[33] the valence bond method and the case when each atom has one valence electron on a nondegenerate orbital was considered. The number of independent covalent structures in the system of N valence electrons is equal to the number of ways of coupling the electron spins to give the total spin S . Let us denote it by $n(N, S)$. On the other hand, it is equal to the dimension of the irreducible representation $\Gamma^{[\tilde{\lambda}]}$ where $[\tilde{\lambda}]$ is the spin Young diagram. Using the expression for the dimension of irreducible representations of the permutation group, Eq. (2.18) in Ref. [1], and the connection with the total spin S , Eq. (2), we obtain a useful expression for the number of the covalent structures

$$n(N, S) = \frac{N!(2S+1)}{(N/2+S+1)!(N/2-S)!} \quad (10)$$

In the case of one valence electron on a nondegenerate orbital per atom, the method of finding possible electronic multiplets is similar to the method of determining the nuclear molecular multiplets (9) for fermions. Namely:

$$\begin{array}{cc}
 \Gamma^{[\tilde{\lambda}]} \longleftrightarrow U_2^{[\tilde{\lambda}]} & \\
 \downarrow & \downarrow \\
 \Gamma^{(\alpha)} \longleftrightarrow D^{[S]} &
 \end{array} \quad (11)$$

However, for electrons there is a unique connection between $[\tilde{\lambda}]$ and S . The coefficients $a_\lambda^{(\alpha)}$ in Eq. (8) are found using the characters of the permutation and point groups. For the ionic configurations, the procedure becomes more

complicated. It is described in detail in Ref. [33], see also Section 6.10 in Ref. [1].

The method described above was applied to the problem of finding the allowed multiplets for the ring of six hydrogen atoms. This problem was solved by Mattheiss^[38] and discussed in detail by Slater.^[39] The method they used was based on the distribution of electron spins among the atoms in all possible ways and finding the characters of the reducible representations, followed by subtraction from one another of the representations corresponding to different values of the total spin projections. This method is very cumbersome even for finding the 14 multiplets arising from the covalent structures. The application of the methodology developed in Ref. [33] allowed to find all 268 multiplets which arise in this problem, without any difficulties, see Ref. [33] and Section 6.11 in Ref. [1].

The general cases were considered in Refs. [34–37]. It should be mentioned that the action of the operation R of a point group on a configuration of degenerate localized orbitals, characterized by some definite value of angular momentum l_a , is reduced to two successive operations: a permutation of the orbitals \bar{P} , corresponding to the operation R , and an operation of the point symmetry R_a in the space of each orbital. As was shown in Ref. [34], for the coordinate state with the permutation symmetry $[\lambda]$, the character of the permutation \bar{P} , which can be presented as a product of commuting cycles of lengths $n_1, n_2, \dots, n_{k'}$, is equal to

$$\chi^{[\lambda]}(R) = \chi^{[\lambda]}(\bar{P})\chi^{(l_1)}(R^{n_1})\chi^{(l_2)}(R^{n_2})\dots\chi^{(l_{k'})}(R^{n_{k'}})\tau(R) \quad (12)$$

where $\tau(R)$ denotes the number of configurations, which remains invariant under the operation R .

It should be mentioned that the problem of determining which molecular multiplets may arise for configurations of equivalent electrons was first treated by Kotani.^[40] But his method required cumbersome calculations of the spin factor. Goscinski and Ohn^[41] improved the Kotani approach using the technique of the permutation group similar to that used by us in Ref. [34].

An important problem for finding the allowed multiplets of the system containing subsystems characterized by an irreducible representation Γ_a of the local symmetry group G_a and a total spin S_a was solved in Refs. [35 and 37]. It can be atoms in molecules, complexes of impurity centers in crystals, and so forth. Depending on the value of S_a , the subsystems behave under permutations as bosons or fermions. The formulas were derived for the character of the reducible representation made up of the coordinate functions of the system with a definite symmetry with respect to permutations of the subsystems; resolution of this representation on its irreducible parts yields the allowed representations $\Gamma^{(\alpha)}$ of the point symmetry group of the system. The allowed values of the spin S of the system are obtained as was described for the nuclear-spin multiplets, see Eq. (7). The great advantage of the method^[35,37] lies in its independence of the number of particles in subsystems.

The method^[35] for finding the allowed multiplets was generalized and developed to the problem of classification of the

states of impurities in a crystal field.^[36] In this problem, the cases of weak and strong crystal field were considered separately taking into account the spin-orbit coupling.

Let us stress that the symmetry of a many-particle state and its multiplicity allowed by the Pauli principle are completely dictated by the symmetry (antisymmetry) of the total wave function; thus, they can be found only within the framework of Ψ – formalism. Therefore, they cannot be obtained by the density functional theory (DFT) approaches based on a conception of the electron density. Evidently, the problems in which the so-called Berry phase^[42,43] is important cannot be studied by DFT. The application of DFT to magnetic systems also meets with many difficulties. The reason lies in the basic impossibility of introducing the concept of the total spin into the DFT formalism. In the next section, we discuss this matter in detail.

Independence of the Electron Density from S and Its Consequence for DFT

According to the Hohenberg–Kohn theorem,^[44] all properties of the electronic system in its ground state are uniquely determined by the ground state electronic density $\rho(\mathbf{r})$. The latter is the diagonal element of the spinless one-electron reduced density matrix^[45]

$$\rho(\mathbf{r}_1) = N \sum_{\sigma_1, \dots, \sigma_N} \int |\Psi(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N)|^2 dV^{(1)} \quad (13)$$

where sum is taken over the whole spin space and integration is performed over the configuration space of all electrons except the first. The electron density is a crucial quantity for the Kohn–Sham (KS) equations,^[46] on which the DFT method is based.

The representation of the total wave function in the form (1) allows to obtain the general form of the electronic density in the state with the definite total spin S . Let us show that the following theorem is valid:^[47,48]

Theorem. *The electron density of an arbitrary N -electron system, characterized by an N -electron wave function corresponding to the total spin S and constructed on some orthonormal orbital set, does not depend upon the total spin S and always preserves the same form as it is for a single-determinantal wave function.*

Proof. Let us substitute the total wave function in the form (1) and the coordinate wave function, expressed by Eq. (5), in the definition of electron density (13). Since the spin wave functions $\Omega_r^{[\lambda]}$ are orthonormal, Eq. (13) reduces to

$$\begin{aligned} \rho_t^{[\lambda]}(\mathbf{r}) &= \frac{N}{f_\lambda} \sum_r \int |\Phi_{rt}^{[\lambda]}|^2 dV^{(1)} \\ &= \frac{1}{(N-1)!} \sum_r \sum_{P,Q} \Gamma_{rt}^{[\lambda]}(P)^* \Gamma_{rt}^{[\lambda]}(Q) \int P \Phi_0^* Q \Phi_0 dV^{(1)}. \end{aligned} \quad (14)$$

The one-particle functions in the product (4) satisfy the orthonormal conditions; therefore, the integral in Eq. (14) is equal to

$$\delta_{PQ} \int |P\Phi_0|^2 dV^{(1)}$$

and Eq. (14) becomes

$$\rho_t^{[\lambda]}(\mathbf{r}) = \frac{1}{(N-1)!} \sum_P \sum_r \Gamma_{rt}^{[\lambda]}(P) \Gamma_{rt}^{[\lambda]}(P) \int |P\Phi_0|^2 dV^{(1)}. \quad (15)$$

Taking into account that the sum over r is equal to 1 and each $P \subset \pi_N$ can be represented as $P_i P'$ where the $(N-1)!$ permutations P' belong to the permutation group π_{N-1} not including the first electron, we arrive at the final result

$$\rho_t^{[\lambda]}(\mathbf{r}) = \sum_{n=1}^N |\varphi_n|^2. \quad (16)$$

We obtained the well-known expression of the electron density for the state described by the single-occupied determinantal function. In the same manner, it is easy to show that in the case of orbital configuration with arbitrary occupation numbers, the final expression (16) will also correspond to the electron density for the one-determinantal function but with arbitrary occupation numbers.

Thus, regardless of the permutation symmetry of the coordinate wave function, which is uniquely connected with the value of the total spin S , the electron density for all S realized in a given orbital configuration has the same form as for a single Slater determinant. It can also be proved that in a more general case of the eigenfunctions of S^2 represented as a linear superposition of different electronic configurations, as one uses in the *ab initio* configuration interaction (CI) approaches, the electron density also does not depend on S , if all configurations are built on the same orthonormal orbital set.

Because of the independence of the electron density on the total spin S , the density functionals, and, consequently, the conventional KS equations are the same for all multideterminantal wave functions corresponding to different S . The necessary condition for this is the orthonormality of the orbital set, on which these determinants are built.

At the first sight, this result is rather surprising: different linear combinations of determinants, describing the states with different S , correspond to the same electron density, as it is obtained with one determinant. On the other hand, this is to be expected, because the integration in Eq. (13) leads to a loss of information about the wave function. The concept of spin came from the Ψ – formulation of quantum mechanics and it is beyond the electron density formulation. As noted by McWeeny^[49]: ‘electron spin is in a certain sense extraneous to the DFT.’

It is also worth-while to take into account that the electron density is a one-electron quantity. As it was precisely established (see, for instance, Chapter 7 in Ref. [1]), the diagonal matrix elements of one-particle operators do not depend on the symmetry of states. The same is correct for the diagonal matrix elements with operators equal to 1.

Recently, Tchougreeff and Angyan^[50] applied the unitary group technique to the problem of the states with the total

spin S in DFT. In their study, they presented the simple proof of the Kaplan theorem 1, as they named it,⁵ using the unitary group formalism. The application of the powerful unitary group formalism did not allow these authors to solve the problems arising in DFT for state with a definite spin. This can be expected, because, as we discussed above, the concept of spin is beyond the framework of electron density approaches. The possible solutions can be found using the two-electron reduced density matrix formalism, although up today there are no significant advances in this directions, see Refs. [51–53].

The problems arising in the application of DFT to magnetic systems were properly analyzed by Illas et al.^[54,55] One of their conclusions was that the DFT calculations exaggerate the ferromagnetic coupling. Our analysis of the DFT calculations of Mn_2 ^[56] also revealed that in most of Mn_2 studies, the ferromagnetic ground state with $S = 5$ was obtained; while according to precise *ab initio* calculations, see Ref. [56] and references therein, Mn_2 is antiferromagnetic with $S = 0$. The spin-symmetry conditions in the standard KS formulation of DFT and their spectroscopic performance are discussed in the comprehensive review by Ramírez-Solis et al.^[57]

In Ref. [54], it was concluded that the spin problems in DFT can be solved, if the spin-restricted KS formalism^[58] is applied. They also stressed that the multiplet-sum method (MSM) procedure developed by Ziegler et al.^[59] is very appropriate for finding the spin-multiplet structure. However, as follows from the analysis performed in our study,^[48] the MSM procedure corresponds to the first order of perturbation theory and modifies only the exchange energy, not taking into account the correlation energy. In the procedures developed in Ref. [58], the exchange and correlation functionals are treated in the same manner, while they have a different dependence on spin. Thus, at least the correlation functionals in their formalisms do not correspond to an appropriate total spin. This is the reason that, as was demonstrated in Ref. [60], the employment of approaches^[58] does not improve the agreement with experiment.

The contemporary state of the application of DFT to transition metal chemistry has been represented by Cramer and Truhlar in a recent review.^[61] They analyzed in detail different procedures developed for studying the magnetic properties of the transition metals and demonstrated the problems arising. However, they did not stress that most of the described difficulties lay at the very root of the DFT approach and in principle cannot be resolved within the framework of the electron density formalism, see Refs. [47 and 48]. As was already mentioned, a possible way to the solution can be found in the two-electron reduced density matrix formulation of DFT.

The Pauli Principle; Why Does It Exist in Nature?

The application of the permutation group allows also to make an analysis of the foundations of the Pauli principle.^[62–65]

⁵In Refs. [47] and [48] it was also presented a Theorem 2, in which was proved that the diagonal element of the density matrix is a invariant with respect to all operations of the group symmetry of the state.

Is the Pauli principle a postulate?

Pauli formulated his principle^[66] in 1924, before the creation of quantum mechanics (1925–1927), when he was trying to understand the experimental regularities in the classification of atomic spectral terms in a strong magnetic field. The Pauli principle was formulated as a prohibition of the existence of two electrons in an atom with the same four quantum numbers. Just after the creation of quantum mechanics, Heisenberg^[67] and Dirac^[68] derived the Pauli principle as a consequence of the antisymmetry of the wave function of a many-electron system. Later on, the analysis of experimental data has permitted to formulate the Pauli exclusion principle for all known elementary particles. 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

$$P_{ij}\Psi(1, \dots, i, \dots, j, \dots, N) = (-1)^{2s}\Psi(1, \dots, i, \dots, j, \dots, N) \quad (17)$$

That is, it is symmetric for integer values of s and antisymmetric for half-integer values of s .

Thus, the Pauli principle follows solely from experiment. Pauli himself was never satisfied by that. In his Nobel Prize lecture^[69] Pauli said:

"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."

The Pauli exclusion principle can be considered from two viewpoints. On the one hand, it asserts that particles with half-integer spin (fermions) are described by antisymmetric wave functions, and particles with integer spin (bosons) are described by symmetric wave functions. This is a so-called spin-statistics connection. The reasons why this connection between the value of spin and the permutation symmetry of wave function exists are still unknown; see discussion in Ref. [65], Section 1 in Refs. [70–72]. As emphasized by Berry and Robbins,^[73] the relation between spin and statistics "cries out for understanding."

On the other hand, according to the Pauli exclusion principle, the permutation symmetry of the total wave functions can be only of two types: symmetric or antisymmetric. Thus, both belong only to the one-dimensional (1D) 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,

$$[P, H]_- = 0. \quad (18)$$

From this, it follows that the solutions of the Schrödinger equation may belong to any representation of the permutation group, including the degenerate ones. The question might be asked: *whether the limitation on the solutions of the Schrödinger equation follows from the fundamental principles of quantum mechanics or it is an independent principle?*

Some physicists, including one of the founders of quantum mechanics Dirac^[74] (see also Schiff^[75] and Messiah^[76]), believe that there are no laws in Nature that forbid the existence of particles described by wave functions with more complicated permutation symmetry than those of bosons and fermions, and that the existing limitations are only due to the specific properties of the known elementary particles.

Messiah^[76] has even introduced the term "symmetry postulate" to emphasize the primary nature of the constraint on the allowed types of the wave function permutation symmetry. In fact, the existence of permutation degeneracy should not introduce additional uncertainty into characteristic of the state. From the Wigner-Eckart theorem generalized for the permutation group, see Eq. (4.60) in book in Ref. [1], it follows that the matrix element of an operator L , which is symmetric in all the particles, can be presented as

$$\langle \Psi_r^{[2]} | \hat{L} | \Psi_r^{[2]} \rangle = \delta_{rr} \langle \Gamma^{[2]} | \hat{L} | \Gamma^{[2]} \rangle \quad (19)$$

where index r labels the basic functions of the representation $\Gamma^{[2]}$ of the permutation group. The double vertical line in the right-hand side of this formula means that the matrix element is independent on the basic function index. Thus, the expectation value of operator L is the same for all functions belonging to the degenerate state.

Another point of view is that the symmetry postulate is not an independent principle and can be derived from the fundamental principles of quantum mechanics; in particular, from the principle of indistinguishability of identical particles. In some textbooks,^[77–79] including the famous textbook by Landau and Lifshitz,^[78] the following typical proof is presented.

From the requirement that the states of a system obtained by permutations of identical particles must all be physically equivalent, one concludes that the transposition of any two identical particles should multiply the wave function only on an insignificant phase factor,

$$P_{12}\Psi(x_1, x_2) = \Psi(x_2, x_1) = e^{i\alpha}\Psi(x_1, x_2) \quad (20)$$

where α is a real constant and x is the set of spatial and spin variables. One more application of the permutation operator P_{12} gives

$$\Psi(x_1, x_2) = e^{i2\alpha}\Psi(x_1, x_2) \quad (21)$$

or

$$e^{2i\alpha} = 1 \quad \text{and} \quad e^{i\alpha} = \pm 1 \quad (22)$$

Since all particles are assumed to be identical, the wave function should change in exactly the same way under transposition of any pair of particles, that is, it should be either totally symmetric or totally antisymmetric.

This proof contains two essential incorrectness's at once. The first simply follows from group theory. Namely, Eq. (20) is valid only for the 1D representations. The application of a group operation to one of the basis functions, belonging to

some multidimensional representation, transforms it in a linear combination of basis functions. Namely,

$$P_{12}\Psi_i = \sum_k \Gamma_{ki}(P_{12})\Psi_k. \quad (23)$$

The application of the permutation operator P_{12} to both sides of Eq. (23) leads to the identity:

$$\begin{aligned} P_{12}\{P_{12}\Psi_i\} &= \Psi_i = P_{12} \sum_k \Gamma_{ki}(P_{12})\Psi_k \\ &= \sum_l \left[\sum_k \Gamma_{lk}(P_{12})\Gamma_{ki}(P_{12}) \right] \Psi_l = \sum_l \Gamma_{li}(P_{12}^2 = I)\Psi_l = \Psi_i. \end{aligned} \quad (24)$$

Using this identity, we cannot arrive at any information about the symmetry of the wave function in contrary with Eq. (21). By requiring that under permutations the wave function must change by no more than a phase factor, one actually postulates that the representation of the permutation group, to which the wave function belongs, is 1D. Thus, the proof in Refs. [77–79] is based on the initial statement, which is then proved as a final result.

The second incorrectness in the proof above follows from physical considerations. This proof is directly related to the behavior of the wave function. However, as the wave function is not an observable, the indistinguishability principle is related to it only indirectly via the expressions of measurable quantities. As in quantum mechanics, the physical quantities are expressed as bilinear forms of wave functions, the indistinguishability principle requires the invariance of these bilinear forms and can be formulated as^[62]:

$$P\langle\Psi|\hat{L}|\Psi\rangle = \langle\Psi|\hat{L}|\Psi\rangle. \quad (25)$$

Often, one limits oneself to the requirement that the probability of a given configuration of a system of identical particles must be invariant under permutations,^[80,81]

$$P|\Psi(x_1, \dots, x_N)|^2 = |\Psi(x_1, \dots, x_N)|^2. \quad (26)$$

For a function to satisfy Eq. (26), it is sufficient that under permutations it would change as

$$P\Psi(x_1, \dots, x_N) = e^{i\alpha_P(x_1, \dots, x_N)}\Psi(x_1, \dots, x_N), \quad (27)$$

That is, unlike the case of the requirement of condition (20), in the general case the phase is a function of the coordinates and the permutation and Eq. (21) evidently does not hold.

Most other proofs of the symmetry postulate contain unjustified constraints. A critical survey of such proofs can be found in Refs. [62] and [80]. Proofs of the symmetry postulate without imposing additional constraints have been given by Girardeau^[80,81] and in my paper.^[62] As was noted later by the author (see Refs. [63] and [82]), these proofs, basing on the indistinguishability principle in the forms (25) and (26), are incorrect, because Eqs. (25) and (26) are correct only for the non-degenerate states. In a degenerate state, the system can be described with equal probability by any one of the basis

vectors of the degenerate state. As a result, we can no longer select a pure state (the one that is described by the wave function) and should regard a degenerate state as a mixed one, where each basis vector enters with the same probability. Thus, we must sum both sides of Eqs. (25) and (26) over all wave functions that belong to the degenerate state. For instance, the probability density, which described via the diagonal element of the density matrix, in the case of a degenerate state has the form

$$D(x_1, \dots, x_N; x_1, \dots, x_N) = \frac{1}{f_\lambda} \sum_{r=1}^{f_\lambda} \Psi_r^{[\lambda]}(x_1, \dots, x_N) \Psi_r^{[\lambda]*}(x_1, \dots, x_N), \quad (28)$$

where the expression (28) is written for the case of the f_λ -dimensional representation $\Gamma^{[\lambda]}$ of the permutation group π_N . The possibility of expressing the density matrix through only one of the functions implies that the degeneracy with respect to permutations has been eliminated. However, the latter cannot be achieved without violating the identity of the particles.

It is not difficult to check that for every representation $\Gamma^{[\lambda]}$ of the permutation group π_N , the probability density, Eq. (28), is a group invariant according to any permutation of the permutation group π_N :

$$PDP^{-1} = D \quad \text{for all } P \in \pi_N, \quad (29)$$

From this, it follows that the probability density obeys the indistinguishability principle even in the case of the multidimensional representations of the permutation group. Hence, the indistinguishability principle is insensitive to the symmetry of wave function and cannot be used as a criterion for selecting the correct symmetry.

Thus, we demonstrated that the Pauli exclusion principle cannot be proved, that is, it cannot be derived from other quantum-mechanical postulates. Nevertheless, as will be discussed in the following section, we may not expect that some unknown elementary particles can be described by multidimensional representations of the permutation group. The realization of only two types of permutation symmetry in nature (symmetric and antisymmetric) is by no means accidental; there are significant reasons, why it is so.

Contradictions with the concept of particle identity and their independence in the degenerate permutation states

In this section, we discuss the properties of a quantum mechanical system of identical particles that does not obey the symmetry postulate and can be in states with all possible permutation symmetries and base our study on the Hartree–Fock approximation. In this case, the states of a system of identical particles with the number of particles not conserved can be presented as vectors in the Fock space \mathbf{F} .^[83] The latter is a direct sum of spaces $\mathbf{F}^{(N)}$ corresponding to a fixed number of particles N

$$\mathbf{F} \doteq \sum_{N=0}^{\infty} \mathbf{F}^{(N)}. \quad (30)$$

Each of the space $\mathbf{F}^{(N)}$ can be presented as a direct product of one-particle spaces \mathbf{f} :

$$\mathbf{F}^{(N)} = \underbrace{\mathbf{f} \otimes \mathbf{f} \otimes \dots \otimes \mathbf{f}}_N \quad (31)$$

The basis vectors of $\mathbf{F}^{(N)}$ are the product of one-particle vectors $|v_k(k)\rangle$ belonging to spaces \mathbf{f} ; k in the parenthesis denotes the set of particle spin and space coordinates,

$$|\xi^{(N)}\rangle = |v_1(1)\rangle |v_2(2)\rangle \dots |v_N(N)\rangle. \quad (32)$$

For simplicity, let us consider the case where all one-particle vectors in Eq. (32) are different. There will be no qualitative changes in the results, if some of the vectors coincide. It is useful to mention that, $\varphi_k(k)$ in Eq. (4) are orbitals depending on the space coordinates, while $|v_k(k)\rangle$ are spin-orbitals, on which the total wave function is constructed.

One can produce $N!$ new many-particle vectors by applying to the vector (32) $N!$ permutations of the particle coordinates. These new vectors also belong to $\mathbf{F}^{(N)}$ and form in it a certain invariant subspace which is reducible. The $N!$ basis vectors of the latter, $P|\xi^{(N)}\rangle$, make up the regular representation of the permutation group π_N . As is known, the regular representation is decomposed into irreducible representations, each of which appears a number of times equal to its dimension. The space $\varepsilon^{(N)}$ falls into the direct sum

$$\varepsilon^{(N)} \doteq \sum_{\lambda_N} f_{\lambda_N} \varepsilon_{\xi}^{[\lambda_N]}. \quad (33)$$

where $\varepsilon_{\xi}^{[\lambda_N]}$ is an irreducible subspace of dimension f_{λ_N} drawn over the basis vectors $[[\lambda_N]r]$, and $[\lambda_N]$ is a Young diagram with N boxes. The basis vectors $[[\lambda_N]r]$ can be constructed from the non-symmetrized basis vector $|\xi^{(N)}\rangle$ by using the Young operators $\omega_{rt}^{[\lambda_N]}$ similar to Eq. (5),

$$[[\lambda_N]rt] = \omega_{rt}^{[\lambda_N]} |\xi^{(N)}\rangle = \left(\frac{f_{\lambda}}{N!}\right)^{1/2} \sum_P \Gamma_{rt}^{[\lambda_N]}(P) P |\xi^{(N)}\rangle \quad (34)$$

where $\Gamma_{rt}^{[\lambda_N]}(P)$ are the matrix elements of representation $\Gamma^{[\lambda_N]}$ and index t distinguishes between the bases in accordance with the decomposition of $\varepsilon_{\xi}^{(N)}$ into f_{λ} invariant subspaces and describes the symmetry under permutations of the particle vector indices.

Thus, a space with a fixed number of particles can always be divided into irreducible subspaces $\varepsilon_{\xi}^{[\lambda_N]}$, each of which is characterized by a certain permutation symmetry given by a Young diagram with N boxes. The symmetry postulate demands that the basis vectors of a system of N identical particles belong to one of the two subspaces characterized by irreducible 1D representations, either $[N]$ or $[1^N]$. All other subspaces are 'empty.' Let us examine the situation that arises when no symmetry constraints are imposed and consider the system of N identical particles described by basis vectors belonging to some irreducible subspace $\varepsilon_{\xi}^{[\lambda_N]}$.

One of the consequences of the different permutation symmetry of state vectors for bosons and fermions is the dependence of the energy of system on the particle statistics. For the same law of dynamic interaction, the so-called exchange terms enter the expression for the energy of fermion and boson system with opposite signs. The expression for the energy of a system of particles belonging to an irreducible subspace $\varepsilon_{\xi}^{[\lambda_N]}$ with an arbitrary Young diagram $[\lambda_N]$ has the form presented in Eq. (6). Namely,

$$E_t^{[\lambda]} = \sum_a \langle v_a | h | v_a \rangle + \sum_{a < b} [\langle v_a v_b | g | v_a v_b \rangle + \Gamma_{tt}^{[\lambda]}(P_{ab}) \langle v_a v_b | g | v_b v_a \rangle] \quad (35)$$

Only exchange terms in Eq. (35) depend on the symmetry of the state. For the 1D representations, $\Gamma_{tt}^{[\lambda]}(P_{ab})$ do not depend on the number of particles and permutations P_{ab} : $\Gamma^{[N]}(P_{ab}) = 1$ and $\Gamma^{[1^N]}(P_{ab}) = -1$ for all P_{ab} and N . For multidimensional representations, the matrix elements $\Gamma_{tt}^{[\lambda]}(P_{ab})$ depend on $[\lambda]$ and P_{ab} ; in general, they are different for different pairs of identical particles.[¶]

Taking into account that the transitions between states with different symmetry $[\lambda_N]$ are strictly forbidden and each state of N particle system with different $[\lambda_N]$ has a different analytical formula for its energy, we must conclude that each type of symmetry $[\lambda_N]$ corresponds to a certain kind of particles with statistics determined by this permutation symmetry. On the other hand, the classification of state with respect to the Young diagrams $[\lambda_N]$ is connected exclusively with the identity of particles. Therefore, it must be some additional inherent particle characteristics, which establishes for the N particle system to be in a state with a definite permutation symmetry, like integer and half-integer values of particle spin for bosons and fermions, and this inherent characteristic has to be different for different $[\lambda_N]$. So, the particles belonging to the different types of permutation symmetry $[\lambda_N]$ are not identical.

Let us trace down the genealogy of irreducible subspaces $\varepsilon_{\xi}^{[\lambda_N]}$. In Figure 1, the genealogy for all irreducible subspaces with $N = 2-4$ is presented.

We call the hypothetical particles characterized by the multidimensional representations of the permutation group as "intermediations" implying that they obey some intermediate between fermion and boson statistics. For bosons and fermions, there are two non-intersecting chains of irreducible representations: $[N] \rightarrow [N+1]$ and $[1^N] \rightarrow [1^{N+1}]$, respectively; and the energy expression for each type of particles has the same analytical form that does not depend on the number of particles in a system. The situation changes drastically, if we put into consideration the multidimensional representations. The number of different statistics depends on the number of particles in a system and rapidly increases with N . For the

[¶]The matrices of transpositions for all irreducible representations of groups $\pi_2-\pi_6$ are presented in Appendix 5 of Ref. [1].

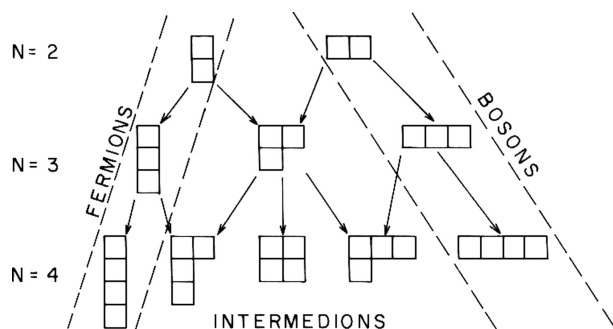


Figure 1. Symmetry of the irreducible representations of the permutation groups for $N = 2-4$ and their genealogy.

multidimensional representations we cannot select any non-intersecting chains, as in the fermion and boson cases. According to Figure 1, the intermedion particles with a definite $[\lambda_N]$ in the N th generation can originate from particles of different kinds $[\lambda_{N-1}]$ in the $(N-1)$ th generation, even from fermions or bosons (in the special case $[\lambda_3] = [21]$, it originates from both $[1^2]$ and $[2]$). The physical picture in which adding one particle changes properties of all particles cannot correspond to a system of independent identical particles (although, it cannot be excluded for some quasiparticle systems where we have not an independency of quasiparticles (see Section 2.2 in Ref. [65]).

Thus, the scenario, in which all symmetry types $[\lambda_N]$ are allowed and each of them corresponds to a definite particles statistics, contradicts the concept of particle identity and their independency from each other. The same conclusion follows from other scenarios considered in Refs. [64] and [65].

From the discussion above it follows that, although the Pauli exclusion principle cannot be derived from other fundamental principles of quantum mechanics, it cannot be considered as a postulate, since all symmetry options for the total wave function of identical particles, except the 1D representations, are forbidden. Hence, in addition to the formulation of the Pauli exclusion principle presented on p. 13, it can be also formulated as a *prohibition for identical particles to be in the degenerate permutation states*.

Keywords: quantum chemistry without spin · classification of molecular states · electron density · density functional theory · Pauli principle

How to cite this article: I. G. Kaplan, *Int. J. Quantum Chem.* **2012**, *112*, 2858–2867. DOI: 10.1002/qua.24223

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Received: 17 February 2012

Accepted: 23 April 2012

Published online on 18 June 2012