New approach to principles of constructing wave functions for multielectron systems*

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Analysis of the relationship between the structure of the symmetrical permutation group and the topological structure of the configuration space makes it possible to perform complete separation of spin and spatial variables for multielectron wave functions. This separation of variables allows one to explain the role of nodal surfaces in interpreting and understanding the physical sense of the Pauli principle for systems of fermions. The suggested hypothesis about the form of the nodal surfaces permits one to find these surfaces *a priori* for arbitrary multielectron systems. The use of nodal surfaces for constructing trial wave functions is demonstrated with the example of calculating the energy of the Li atom in the ground state.

Key words: Schroedinger equation, wave functions, symmetrical group; separation of variables, Pauli principle, nodal surfaces, graph theory; Slater determinant.

Nodal surfaces for two-electron systems. To get an idea about the essence of our new approach to principles of constructing wave functions (WFs), let us first consider two-electron systems in the stationary state. In this case, the behavior of the system is described by the wave function that is found as the solution of the Schroedinger equation

$$\mathrm{H}\,\Psi = E\,\Psi, \tag{1}$$

where the WF is the function $\Psi(x_1, y_1, z_1, s_1; x_2, y_2, z_2, s_2)$. The spin and spatial variables can be separated for this function, and the WF may be presented in the form

$$\Psi\,(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \chi(s_1, s_2)\,\Phi(\mathbf{r}_1, \mathbf{r}_2), \tag{2}$$

where $\mathbf{r}_i \equiv (x_i, y_i, z_i)$, $i = 1, 2$; $\chi(s_1, s_2)$ is the spin function, $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is the spatial function.

According to the Pauli principle, the Ψ function should be antisymmetrical with respect to permutations of both spin and spatial coordinates of two electrons; that is, in the case of Eq. (2), we have an antisymmetrical function $\chi(s_1, s_2)$ and a symmetrical function $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ for $S = 0$ (singlet state) and, *vice versa*, a symmetrical function $\chi(s_1, s_2)$ and an antisymmetrical function $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ for $S = 1$ (triplet state).[1] Let us consider the triplet state in more detail. The antisymmetry requirement for the WF (2) results in the condition

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = -\Phi(\mathbf{r}_2, \mathbf{r}_1). \tag{3}$$

Generally speaking, the function $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is defined in the six-dimensional space Q^6, which is the product of two common Euclidean spaces. The author of Ref. 2 showed that condition (3) for the WF ensures the existence of a five-dimensional nodal surface $\Omega_0{}^5$, which separates the whole Q^6 into two symmetrical parts. The form of this surface is defined by the equation

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = 0. \tag{4}$$

The WF in the one-particle approximation is usually represented by the Slater determinant, which has the following form for the function $\Phi(\mathbf{r}_1, \mathbf{r}_2)$:

$$\Phi_{1,2}(\mathbf{r}_1, \mathbf{r}_2) = \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_1(\mathbf{r}_2) \\ \varphi_2(\mathbf{r}_1) & \varphi_2(\mathbf{r}_2) \end{vmatrix}\,. \tag{5}$$

The present-day formulation of the Pauli principle as the requirement of wave function antisymmetry leads the majority of specialists to the conclusion that the WF (5) is reduced to zero when the coordinates of electrons in the physical space are identical; *i.e.*, when $\mathbf{r}_1 = \mathbf{r}_2$ (see Ref. 3). According to McWeeny,[1] this so-called correlation of parallel-spin electrons is the most important corollary of the Pauli principle. However, it is quite evident that the equation $\mathbf{r}_1 = \mathbf{r}_2$ (that is, $x_1 = x_2$, $y_1 = y_2$, $z_1 = z_2$) defines a three-dimensional manifold in Q^6: $R_0{}^3 \in \Omega_0{}^5$ (see Ref. 2). Thus, the usual idea about

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correlation of parallel-spin electrons represents only a small fraction of the situations that are actually forbidden by the Pauli principle. Indeed, let us analyze Eq. (4) for function (5):

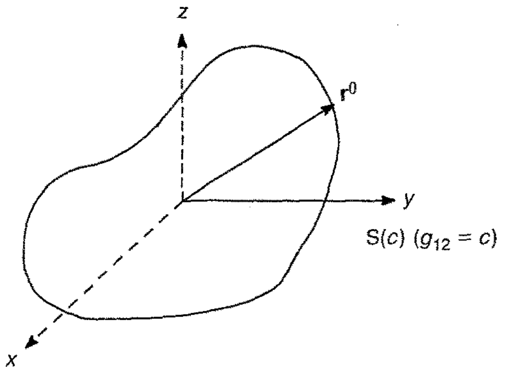
$$\begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_1(\mathbf{r}_2) \\ \varphi_2(\mathbf{r}_1) & \varphi_2(\mathbf{r}_2) \end{vmatrix} = \varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) - \varphi_1(\mathbf{r}_2)\varphi_2(\mathbf{r}_1) = 0.$$

Separating the variables, we get

$$\frac{\varphi_1(\mathbf{r}_1)}{\varphi_2(\mathbf{r}_1)} = \frac{\varphi_1(\mathbf{r}_2)}{\varphi_2(\mathbf{r}_2)}.$$

Let us consider the function $g_{12}(\mathbf{r}) = \varphi_1(\mathbf{r})/\varphi_2(\mathbf{r})$ (the function $g_{21}(\mathbf{r}) = \varphi_2(\mathbf{r})/\varphi_1(\mathbf{r})$ may be considered in the same way). Naturally, the case when φ_1 or φ_2 have zeros has to be considered separately, but this peculiarity does not change the general picture, all the more so because φ_1 and φ_2 may have no zeros at all. The equations $g_{12}(\mathbf{r}) = c$ for all c values define a family of surfaces $S(c)$ (the level of the g_{12} function) in the common physical space (Sheme 1).

Scheme 1



For any fixed position of one electron $\mathbf{r}_1 = \mathbf{r}^0$, this electron falls into one of the surfaces $S(c)$, namely, into the surface $c = g_{12}(\mathbf{r}^0)$. The other electron may not be situated not only in the point $\mathbf{r}_2 = \mathbf{r}_1 = \mathbf{r}^0$ but also in all points of the surface $g_{12}(\mathbf{r}) = g_{12}(\mathbf{r}^0)$. Thus, the Pauli principle with respect to function (5) indeed forbids not only the configuration $\mathbf{r}_1 = \mathbf{r}_2$ but immeasurably more (namely, by two dimensions) configurations. That is, figuratively speaking, the whole surface is forbidden together with one point. The union of all these forbidden configurations forms a five-dimensional surface in Q^6, defined by the equation $g_{12}(\mathbf{r}_1) = g_{12}(\mathbf{r}_2)$. From the mathematical viewpoint, this statement corresponds to the fact that the determinant (5) is reduced to zero not only when its lines (or columns) are identical but also when these lines (or columns) are proportional.

Let us consider the method of configurational interaction (CI) for our case. Let the functions

$$\{1, 2, \ldots, n\} = \{\varphi_1(\mathbf{r}), \varphi_2(\mathbf{r}), \ldots, \varphi_n(\mathbf{r})\} \qquad (6)$$

form a base set of functions, and let us assume (for simpler discussion) that all these functions may be united into configurations by their symmetry properties; that is, we may present the WF in the form

$$\Psi = \sum_{i,j} C_{ij} \begin{vmatrix} \varphi_i(\mathbf{r}_1) & \varphi_i(\mathbf{r}_2) \\ \varphi_j(\mathbf{r}_1) & \varphi_j(\mathbf{r}_2) \end{vmatrix} = \sum_{i,j} C_{ij}\Phi_{ij}. \qquad (7)$$

Just like function (5), each of the functions Φ_{ij} in formula (7) has a nodal surface of the form $g_{ij}(\mathbf{r}_1) = g_{ij}(\mathbf{r}_2)$. (Evidently, $g_{ij} = g_{ji}^{-1}$, $g_{ij} = \varphi_i/\varphi_j$.) Generally speaking, all these nodal surfaces are different. Meanwhile, as is known from the theory of differential equations, each solution of Eq. (1) is unique for any fixed E; therefore, it has a single nodal surface, which corresponds to the set of the electrons' mutual positions $(\mathbf{r}_1, \mathbf{r}_2)$ that is forbidden by the Pauli principle. It becomes evident why the CI method converges so slowly: the expansion (7) should approach the true solution of Eq. (1) with a single nodal surface.

Naturally, superposition of a great number of functions Φ_{ij} with a complete enough basis (6) finally may approach the true function, but this process converges slowly. At the same time, it is also obvious that the present-day quantum chemistry has nothing better in its disposal than the method of CI. In particular cases, when the hamiltonian of Eq. (1) has certain symmetry, this equation has a solution not in Q^6 but in a space of smaller dimensionality. For example, the H_2 molecule (in the triplet state as well) is described by a WF in the five-dimensional space (cylindrical symmetry); the He atom, in the space of dimensionality 3 (spherical symmetry). As is shown,[4,5] equation of the nodal surface for the He atom in the triplet state has the form $r_1 = r_2$ in the coordinates r_1, r_2, r_{12}; that is, the dimensionality of the nodal surface is equal to 2 in the three-dimensional space. Thus, the Pauli principle forbids the position of the two electrons at one and the same sphere with the center in the nucleus, no matter what the interelectron distance r_{12} may be.

Nodal surfaces for multielectron systems and the separation of spin and spatial variables. If we consider the WF for a system with the number of electrons $N > 2$, we will encounter the same problem, but complicated by the fact that the spin and spatial variables are not separated. It is easy to show that WFs without nodal surfaces cannot be constructed for $N > 2$, and the dimensionality of these surfaces is always $3N - 1$ in the general case, whereas the traditional ideas[3] about correlation of electrons with parallel spins always produce nodal manifolds of dimensionality $3N - 3$, as follows from analysis of the equation $\mathbf{r}_i = \mathbf{r}_j$ (that is, $x_i = x_j$, $y_i = y_j$, $z_i = z_j$ for $s_i = s_j$).

The problem of separating the spin and spatial variables for a WF in the general case is solved in Ref. 6, although this problem had been regarded as insoluble for $N > 2$.[1] The situation is complicated by the following fact: although the spin coordinates are not directly in-

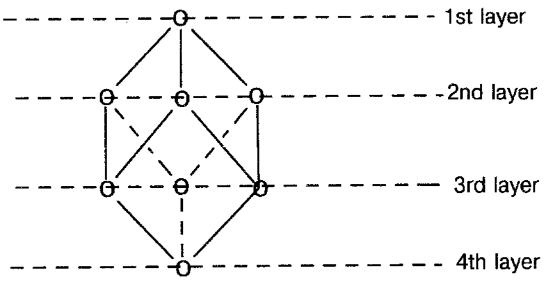


Fig. 1. "Layer" ($N = 3$) distribution of vertices of an N-dimensional cube.

cluded into the Schroedinger equation, we have to construct the solution of this equation in the form with the spin coordinates s_i; otherwise, we cannot ensure the fulfillment of the Pauli principle. To solve this problem, we first assumed the continuity of the spin coordinates (actually, they can have only two values for each electron); that is, we considered the N-electron problem in the general $4N$-dimensional space, and only afterwards we introduced the limitations upon the spin coordinates. Omitting the mathematical details, let us present the final result.

The configuration space where the WF is defined forms a set of 2^N subspaces with dimensionality $3N$ in the $4N$-dimensional space. Each of these subspaces may be put in correspondence with a vertex of the N-dimensional unit cube. These subspaces are not topologically connected in the general space, and their structure is defined by the structure of the symmetrical group S_N. For each of the spin states, the WF is different from zero only in some set of subspaces, depending on the total spin S and its projection M_S. This set belongs to one "layer" of vertices in the N-dimensional cube, related to a definite subgroup of the group S_N (see Ref. 6). Figure 1 shows the layers by which the vertices of this cube are grouped for the case $N = 3$.

For $S = 3/2$ and $M_S = 3/2$, the WF is different from zero only in the area of Q^9 that corresponds to the vertex of the"first layer" (in this case, $S(S+1) = 15/4$); for $S = 3/2$ and $M_S = -3/2$, it is nonzero only in the area of Q^9 that corresponds to the vertex of the "forth layer". If $M_S = 1/2$, the subspaces Q^9 correspond to vertices of the "second layer" ($S(S+1)$ may be equal either to 15/4 or to 3/4). For $M_S = -1/2$, the subspaces Q^9 correspond to vertices of the "third layer".

Examining the case when $M_S = 1/2$ and $S(S+1) = 3/4$, we may present the scheme (Fig. 2) of the three subspaces with the dimensionality 9 and visualize the effect of transpositions P_{ij} (pairwise permutations from the S_3 group).

It can be seen from this scheme that each of the three subspaces Q^9 has its own nodal surface (curving line), which separates this space into areas where the WF has a constant sign. Any point of the configuration space ($\mathbf{r}_1{}^0$, s_1; $\mathbf{r}_2{}^0$, s_2; $\mathbf{r}_3{}^0$, s_3) falls into one of these three subspaces; therefore, it can be shown (as was done in the previous section) that each subspace has a nodal surface with the same properties as for $N = 2$ and $S = 1$. Probably, the idea about inseparability of coordinates for $N > 2$ [1] appeared because the "spatial" part of the WF was considered in one $3N$-dimensional space, whereas we regard this part as defined in different spaces, although with one and the same dimensionality $3N$. The properties of these nodal surfaces for arbitrary N were considered rigorously from the mathematical viewpoint in Refs. 7 and 8, and the paper[9] describes the topological structure of multielectron configuration spaces (including the situation of excited states) with the help of the graph theory. As also follows from Ref. 8, all three spatial functions that correspond to the scheme in Fig. 2 are interrelated, and it is sufficient to consider the solution in only one of these spaces for solving Eq. (1).

Still, the cases when $N = 3$ and $N = 4$ are simple enough to be handled by traditional approaches, that is, with the use of the Slater determinants. Let us assume

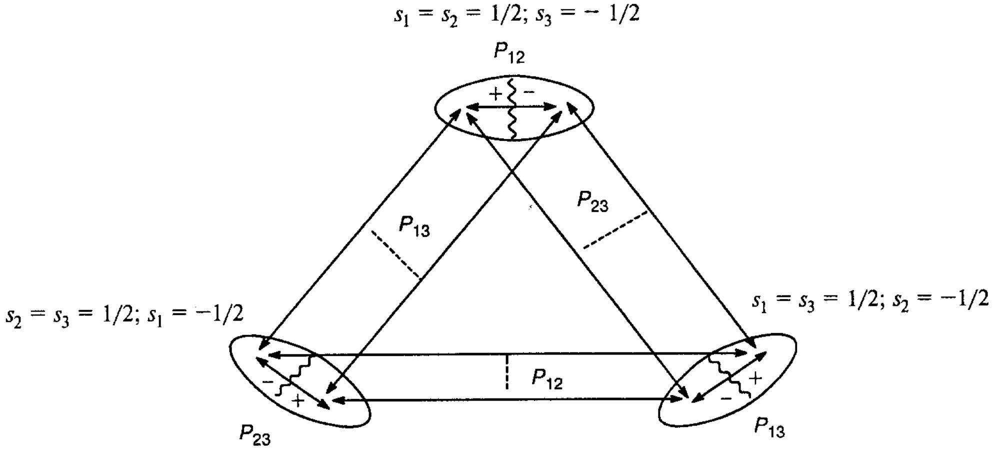


Fig. 2. Scheme of the structure of configuration space for $N = 3$ and $S = 1/2$.

that we have three functions $\varphi_1(\mathbf{r})$, $\varphi_2(\mathbf{r})$, and $\varphi_3(\mathbf{r})$. In the general case, the WF in the form of the Slater determinant for $N = 3$ and $M_S = 1/2$ (as a rule, the condition $\varphi_1 = \varphi_3$ is used) is written as

$$\Psi = \begin{vmatrix} \varphi_1(\mathbf{r}_1)\alpha(s_1) & \varphi_1(\mathbf{r}_2)\alpha(s_2) & \varphi_1(\mathbf{r}_3)\alpha(s_3) \\ \varphi_2(\mathbf{r}_1)\alpha(s_1) & \varphi_2(\mathbf{r}_2)\alpha(s_2) & \varphi_2(\mathbf{r}_3)\alpha(s_3) \\ \varphi_3(\mathbf{r}_1)\beta(s_1) & \varphi_3(\mathbf{r}_2)\beta(s_2) & \varphi_3(\mathbf{r}_3)\beta(s_3) \end{vmatrix}. \tag{8}$$

Let us expand determinant (8) by its third line:

$$\begin{aligned} \Psi &= \varphi_3(\mathbf{r}_1)\beta(s_1)\cdot\begin{vmatrix} \varphi_1(\mathbf{r}_2)\alpha(s_2) & \varphi_1(\mathbf{r}_3)\alpha(s_3) \\ \varphi_2(\mathbf{r}_2)\alpha(s_2) & \varphi_2(\mathbf{r}_3)\alpha(s_3) \end{vmatrix} - \\ &- \varphi_3(\mathbf{r}_2)\beta(s_2)\cdot\begin{vmatrix} \varphi_1(\mathbf{r}_1)\alpha(s_1) & \varphi_1(\mathbf{r}_3)\alpha(s_3) \\ \varphi_2(\mathbf{r}_1)\alpha(s_1) & \varphi_2(\mathbf{r}_3)\alpha(s_3) \end{vmatrix} + \\ &+ \varphi_3(\mathbf{r}_3)\beta(s_3)\cdot\begin{vmatrix} \varphi_1(\mathbf{r}_1)\alpha(s_1) & \varphi_1(\mathbf{r}_2)\alpha(s_2) \\ \varphi_2(\mathbf{r}_1)\alpha(s_1) & \varphi_2(\mathbf{r}_2)\alpha(s_2) \end{vmatrix} = \\ &= \left\{\beta(s_1)\alpha(s_2)\alpha(s_3)\varphi_3(\mathbf{r}_1)\cdot\begin{vmatrix} \varphi_1(\mathbf{r}_2)\varphi_1(\mathbf{r}_3) \\ \varphi_2(\mathbf{r}_2)\varphi_2(\mathbf{r}_3) \end{vmatrix}\right\} + \\ &+ \left\{\alpha(s_1)\beta(s_2)\alpha(s_3)\varphi_3(\mathbf{r}_2)\cdot\begin{vmatrix} \varphi_1(\mathbf{r}_3)\varphi_1(\mathbf{r}_1) \\ \varphi_2(\mathbf{r}_3)\varphi_2(\mathbf{r}_1) \end{vmatrix}\right\} + \\ &+ \left\{\alpha(s_1)\alpha(s_2)\beta(s_3)\varphi_3(\mathbf{r}_3)\cdot\begin{vmatrix} \varphi_1(\mathbf{r}_1)\varphi_1(\mathbf{r}_2) \\ \varphi_2(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \end{vmatrix}\right\}. \end{aligned} \tag{9}$$

If we look at the last expression attentively, we see that only one of the three summands in braces is nonzero for any point ($\mathbf{r}_1{}^0$, s_1; $\mathbf{r}_2{}^0$, s_2; $\mathbf{r}_3{}^0$, s_3) of the configuration space, due to the properties of the spin functions α and β. Actually, each of these three summands is defined in a different subspace, according to the scheme in Fig. 2. As follows from the Pauli principle, *i.e.*, from antisymmetry of function (8), the summand of expansion (9) that corresponds to equal spin coordinates of two electrons is zero in the case when these electrons "simultaneously" fall into one and the same surface $g_{12}(\mathbf{r})$ = const. (The remaining two summands are reduced to zero according to properties of spin functions.) Just as in the case $N = 2$, the function $g_{12}(\mathbf{r})$ is a function in the common physical space. For another distribution of spin functions in determinant (8), as is considered in Ref. 1, we would get other surfaces: namely, $g_{13}(\mathbf{r}) = \varphi_1/\varphi_3$ = const and $g_{23}(\mathbf{r}) = \varphi_2/\varphi_3$ = const.

Let us note that function (8), as follows from the expansion (9), also may be reduced to zero when $\varphi_3(\mathbf{r}) = 0$, but these nodes have dimensionality not greater than $3N - 3$ and are not related to the Pauli principle, all the more so because the function φ_3 (exactly as φ_1 and φ_2) may have no nodes at all.

For the CI method with $N = 3$ and the base set φ_1, φ_2,..., φ_n (naturally, this set may differ from the basis (6) for $N = 2$), we have the same situation as for $N = 2$; that is, all functions in the expansion of the type (7) have different nodal surfaces, whereas the theorem about the unique solution of Schroedinger's differential equation is true for all N. This fact means that the CI method must converge very slowly for multielectron systems, and we indeed observe this effect in quantum chemistry.[1] Similar to function (8), let us consider the Slater determinant for $N = 4$ and the functions φ_1, φ_2, φ_3, φ_4.

$$\Psi = \begin{vmatrix} \varphi_1(\mathbf{r}_1)\alpha(s_1) & \varphi_1(\mathbf{r}_2)\alpha(s_2) & \varphi_1(\mathbf{r}_3)\alpha(s_3) & \varphi_1(\mathbf{r}_4)\alpha(s_4) \\ \varphi_2(\mathbf{r}_1)\alpha(s_1) & \varphi_2(\mathbf{r}_2)\alpha(s_2) & \varphi_2(\mathbf{r}_3)\alpha(s_3) & \varphi_2(\mathbf{r}_4)\alpha(s_4) \\ \varphi_3(\mathbf{r}_1)\beta(s_1) & \varphi_3(\mathbf{r}_2)\beta(s_2) & \varphi_3(\mathbf{r}_3)\beta(s_3) & \varphi_3(\mathbf{r}_4)\beta(s_4) \\ \varphi_4(\mathbf{r}_1)\beta(s_1) & \varphi_4(\mathbf{r}_2)\beta(s_2) & \varphi_4(\mathbf{r}_3)\beta(s_3) & \varphi_4(\mathbf{r}_4)\beta(s_4) \end{vmatrix} \tag{10}$$

Wave function (10) corresponds to $N = 4$, $S = 0$, and $M_S = 0$. Expanding this determinant by the first two lines, we get the sum of six terms, in accordance with the theory,[6]

$$\Psi = \sum_{ij} \varepsilon_{p_{ij}} \alpha(s_i)\alpha(s_j)\beta(s_k)\beta(s_l)\cdot\begin{vmatrix} \varphi_1(\mathbf{r}_i) & \varphi_1(\mathbf{r}_j) \\ \varphi_2(\mathbf{r}_i) & \varphi_2(\mathbf{r}_j) \end{vmatrix}\cdot\begin{vmatrix} \varphi_3(\mathbf{r}_k) & \varphi_3(\mathbf{r}_l) \\ \varphi_4(\mathbf{r}_k) & \varphi_4(\mathbf{r}_l) \end{vmatrix}, \tag{11}$$

where $\varepsilon_{p_{ij}} = \pm 1$ depending on the evenness of the sum $(i + j)$. However, exactly as for expansion (9), we can permutate the columns of the second-order determinants in (11) so that all terms of the expansion would have equal signs. The summing is performed by (i, j) pairs, considering $i < j$, because all the numbers i, j, k, l acquire values from 1 to 4 without repetition; that is, the selection of (i, j) unambiguously defines the (k, l) pair, provided $k < l$.

For any point of the configuration space, only one of the six terms in expansion (11) is not identically equal to zero. For example, if we consider the point ($\mathbf{r}_1$, +1/2; $\mathbf{r}_2$, +1/2; $\mathbf{r}_3$, −1/2; $\mathbf{r}_4$, −1/2), the only term not identically equal to zero is

$$\alpha(s_1)\alpha(s_2)\beta(s_3)\beta(s_4)\cdot\begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_1(\mathbf{r}_2) \\ \varphi_2(\mathbf{r}_1) & \varphi_2(\mathbf{r}_2) \end{vmatrix}\cdot\begin{vmatrix} \varphi_3(\mathbf{r}_3) & \varphi_3(\mathbf{r}_4) \\ \varphi_4(\mathbf{r}_3) & \varphi_4(\mathbf{r}_4) \end{vmatrix}.$$

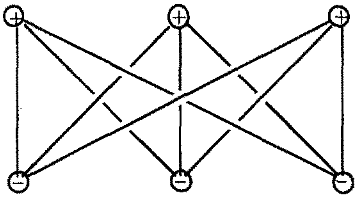
If we analyze the situation, similarly to the cases of $N = 2$ and $N = 3$, we see that the function (10) is reduced to zero any time when two electrons with the spin projection +1/2 are situated at the surface $g_{12}(\mathbf{r})$ = const, or when two electrons with the spin projection −1/2 are situated at the surface $g_{34}(\mathbf{r})$ = const, or when these cases take place simultaneously. Besides, usually $\varphi_3 = \varphi_1$, $\varphi_4 = \varphi_2$; therefore, $g_{12} = g_{34}$, and we have a single surface (in the physical space) that determines the essence of the Pauli principle. The same statements that were formulated for the CI method in the cases of $N = 2$ and $N = 3$ may be repeated for $N = 4$.

Hypothesis about the form of nodal surfaces for wave functions of multielectron systems. The above consideration of wave functions in the form of Slater's determinants for N = 2, 3, and 4 shows that the physical sense of the Pauli principle may be interpreted for these systems in a simple way. Namely, these systems have certain corresponding surfaces in the physical space (there are already two such surfaces for $N = 4$, although they most probably coincide, as was noted above) such that two electrons with equal spin projections "must not" be situated on these surfaces simultaneously; that is, the probability density of such states is reduced to zero. This interpretation is also true for the general form of the

WF. Let the function $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ for the above-considered case $N = 2$, $S = 1$ be the exact solution of the Schroedinger equation (1) and let the coordinates of the 1st electron be fixed, that is, $\mathbf{r}_1 = \mathbf{r}^0$. Then, we get the function $\Phi(\mathbf{r}^0, \mathbf{r}_2) = \Phi_0(\mathbf{r}_2)$, and the equation $\Phi_0(\mathbf{r}) = 0$ defines a surface in the physical space determining what exactly the Pauli principle forbids. That is, if one of the electrons has the coordinates $\mathbf{r}^0$, the other electron must not be situated not only in the point $\mathbf{r}_2 = \mathbf{r}^0$ but also at the whole surface in the physical space.

Unfortunately, we did not succeed in obtaining such simple interpretation for $N \geq 5$. Besides, it is also inaccessible for $N = 3$ and $N = 4$ if the spin state of the system includes three of more electrons with parallel spins, although rigorous consideration[6,8] of multielectron WF does not imply such difficulties. Nevertheless, we may state that systems containing three or more electrons with parallel spins (including all systems with $N \geq 5$) have much more complex WF than in the above-described cases $N = 2, 3, 4$. This statement is explained by the fact that wave functions for $N = 3$ and $M_S = 3/2$ are defined in the space corresponding to the vertex of the "first layer" in the scheme of Fig. 1; therefore, all the three nodal surfaces are contained in one and the same space Q^9. The three nodal surfaces presented in Fig. 2 intersect in a complex way within one and the same space, with the topological structure defined by the well-known Kuratowski graph[9] (Scheme 2).

Scheme 2



Consideration of calculations for the triplet state of the He atom[4,5] lets us arrive at the explicit equation of the surface in the physical space where electrons cannot be situated simultaneously. It is the surface $r = (x^2 + y^2 + z^2)^{1/2} = \text{const}$. The nodal surface of the WF, accordingly, is $r_1 - r_2 = 0$. The papers[10,11] suggest a geometrical interpretation of the physical sense of the Pauli principle for exact wave functions; they consider the existence of hypothetical forces that ensure the fulfillment of the Pauli principle and formulate a hypothesis that permits one to construct nodal surfaces for arbitrary multielectron wave functions in the explicit form. Let us analyze this hypothesis.

We can construct the potential function (that is, the "local" energy depending on the hamiltonian) for any electron. This statement means that interactions with nuclei and other electrons are taken into account. Evidently, this potential function should consider interactions between electrons with equal spin projections (the papers[10,11] did not specially mention this necessity). The form of this function is

$$u_i(\mathbf{r}_i) = -\sum_{\alpha} \frac{z_\alpha}{r_{i\alpha}} + {\sum_{j \neq i}}' \frac{1}{r_{ij}}, \tag{12}$$

where the prime at the second sum means that summation is carried out only for $s_i = s_j$. Then, functions are constructed for all i and j for which $s_i = s_j$

$$G_{ij}(\mathbf{r}_i, \mathbf{r}_j) = u_i - u_j. \tag{13}$$

The essence of the hypothesis consists in the assumption that the functions G_{ij} define the nodal surfaces that correspond to the Pauli principle. For the He atom, $G_{12} = (1/r_1 - 1/r_2)$ and the validity of the hypothesis is beyond doubt. For the Li atom in the ground state, the functions (13) are of the form

$$G_{ij} = \frac{3}{r_i} - \frac{3}{r_j},$$

that is, the nodal surfaces are $r_i - r_j = 0$. According to the scheme in Fig. 2, these nodal surfaces for each of the three spaces are $r_1 - r_2 = 0$, $r_1 - r_3 = 0$, and $r_2 - r_3 = 0$.

For the above-considered systems with $N = 2$, 3, and 4, the functions (12) depend on the coordinates of only one electron; therefore, the Pauli principle may be interpreted in the form of surfaces in the three-dimensional physical space. Although there are two such surfaces for $N = 4$, the hypothesis states that they coincide (this statement is true for the Be atom and for the LiH molecule). However, there will be no such simple interpretation for $N > 4$, and the Pauli principle may be interpreted only by nodal surfaces in multidimensional configuration space.[10,11]

Let us examine King's calculations for the Li atom and corresponding ions,[12–14] which are presently the most accurate for these systems. The trial functions are constructed as follows. Using the Hilleraas coordinates, we should take the functions in the form

$$\Phi_i = r_1^{n_{i1}} r_2^{n_{i2}} r_3^{n_{i3}} r_{12}^{n_{i4}} r_{13}^{n_{i5}} r_{23}^{n_{i6}} \cdot \exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_3) \tag{14}$$

multiply them by the corresponding spin functions, and perform antisymmetrization by the standard procedure with the use of the permutations that constitute the S_3 group. We analyzed King's functions, taking into account the distribution of their different parts by the spaces of the scheme in Fig. 2. In the area where $s_1 = s_2 = 1/2$ (the upper area in Fig. 2), all functions of the form (14) with $n_4 = n_5 = n_6 = 0$ have nodal surfaces of the form $r_1 - r_2 = 0$, in complete agreement with our hypothesis (see Eq. (13)). For the remaining functions, we get nodal surfaces of the form

$$r_1 - r_2 = f_i(r_{12}, r_{13}, r_{23}), \tag{15}$$

which is, generally speaking, close to the surface $r_1 - r_2 = 0$ (at the expense of averaging during integration, the right part of this expression is close to zero for the functions that we use). Basing on King's calculations with 296 functions of the form (14), the authors of Ref. 12 got very good results for the energy of the Li atom, and, since a significant part of these functions have nodal surfaces of the form (13), King's results confirm our hypothesis to some degree of reliability.

To check our hypothesis, we elaborated a program for calculating the ground state (^{2}S) of the Li atom, using both the standard antisymmetrization procedure[16,12] and the nodal surface obtained from Eqs. (12) and (13). In the first case, we took the spin function $\chi = \alpha(s_1)\beta(s_2)\alpha(s_3) - \beta(s_1)\alpha(s_2)\alpha(s_3)$, multiplied it by function (14), and then subjected the product to antisymmetrization. In the second case, the WF was constructed in the form $\Psi = \Sigma c_i\Psi_i$, where

$$\Psi_i = \left\{(1+P_{12})[r_1^{n_{i1}}r_2^{n_{i2}}r_3^{n_{i3}}r_{12}^{n_{i4}}r_{13}^{n_{i5}}r_{23}^{n_{i6}}]\right\} \times \\ \times\ [\exp(-\alpha r_1) - \exp(-\alpha r_2)]\cdot\exp[-\beta(r_1+r_2) - \gamma r_3] \qquad (16)$$

The function (16) is defined for the region of the configuration space in Fig. 2 where $s_1 = s_2 = 1/2$, $s_3 = -1/2$. The expression in braces is symmetrical with respect to permutation of the 1st and 2nd electrons. The expression $[\exp(-\alpha r_1) - \exp(-\alpha r_2)]$ in function (16) ensures both antisymmetry of the function Ψ_i and its reduction to zero at $r_1 = r_2$. The α, β, and γ values were equal for all Ψ_i.

Results of energy calculations for the Li atom (IBM PC-486) are given in Table 1; the order of the Ψ_i function is defined as $\sum\limits_{k=1}^{6} n_{ij}$. The experimental energy value for the Li atom (^{2}S state) is −7.478069 au.[12]

Comparing the results in Table 1, we can conclude that the boundary conditions $r_i = r_j$ that are provided by the suggested hypothesis for the WF of the Li atom in the ground state make it possible to obtain energy values that are closer to experimental results. This effect becomes especially marked if we conduct the calculations using the first-order functions that are presented in Table 2.

We performed separate calculations for the basis that consisted of the three functions *1—3* in Table 2 and for the basis of the two functions *4* and *5*. Let us note once more that nodal surfaces of functions *1—3* for standard antisymmetrization (that is, in the form (14)) and for our approach (that is, in the form (16)) coincide. At the same time, these nodal surfaces are different for functions (4), (5). The results of calculations are given in Table 3.

Table 1. Calculated energies ($E_{\rm calc}$) of Li (^{2}S) atom

Maximum order of functions in the basis	Number of functions in the basis	$-E_{\rm calc}$/au function (14)	$-E_{\rm calc}$/au function (16)
1	5	7.421257	7.444296
2	17	7.465906	7.470490

Table 2. Zero- and first-order basic functions

Function	n_1	n_2	n_3	n_4	n_5	n_6
1	0	0	0	0	0	0
2	1	0	0	0	0	0
3	0	0	1	0	0	0
4	0	0	0	1	0	0
5	0	0	0	0	1	0

Table 3. Calculations of energies ($E_{\rm calc}$) of the ground stste of Li (^{2}S) atom

Functions from Table 2	Number of functions in the basis	$-E_{\rm calc}$/au function (14)	$-E_{\rm calc}$/au function (16)
1—3	3	7.419873	7.412465
4, 5	2	7.402252	7.441177

The results shown in Tables 1 and 3 leave no doubt that the choice of nodal surfaces in trial WF plays a very great role and is extremely important for the construction of trial WF. We may hope that the use of the boundary conditions that are derived from the suggested hypothesis also will be useful for calculations with a more extended basis. Correct selection of nodal surfaces should appear even more important in calculations of molecules, because almost all base functions have different nodal surfaces in this case.

As to calculations of the He atom, in our paper[5] we showed the possibility of implementing an essentially new approach to constructing WFs. Namely, knowing *a priori* the form of nodal surfaces of an exact WF, we can formulate the requirements of the Pauli principle in terms of nodal surfaces. Instead of demanding the antisymmetry of a WF, we may require that the WF should be reduced to zero at nodal surfaces. For example, let us consider the case of the He atom. The definition range of the WF is divided into two parts: $r_1 \le r_2$ and $r_1 \ge r_2$. We may take a function of arbitrary symmetry as the trial function, considering that it should be zero at the dividing surface, that is, at $r_1 = r_2$. Calculations are conducted by the variation method for any of these parts of the space, and the complete function is restored by the antisymmetrical reflection with respect to the plane $r_1 = r_2$; this procedure is possible only when the WF is reduced to zero at this plane. Results of calculations show that the convergence increases approximately by an order of magnitude if this method is used. For example, our calculated energy values[5] for a WF with 47 terms are more accurate than the results of Pekeris,[16] who used a WF with 715 terms.

Generalizing these results, we may state that, although the antisymmetry requirement ensures the fulfillment of the Pauli principle for WF, yet it may be more convenient to use another requirement in the cases when the form of nodal surfaces is known *a priori* (and this will be the case if the our hypothesis (see Eq. (13)) is confirmed). This another requirement is reduction of the WF to zero at the nodal surfaces; that is, a system of boundary conditions may be used instead of antisymmetrization. This statement means that the whole configuration space may be divided into $N!$ isomorphic regions, and, instead of requiring the antisymmetry of wave functions, we may search for the wave functions (*i.e.*, solve the Schroedinger equation) in any of these regions without any limitations upon WF symmetry. The only limitation is the reduction of the WF to zero at the boundaries of these regions. This condition ensures the fulfillment of the Pauli principle by itself, because it permits to restore the complete antisymmetrical function (if necessary) by simple operations of permutation. Evidently, the two formulations of the Pauli principle are mathematically equivalent, although antisymmetry remains the only formulation if the form of nodal surfaces is unknown *a priori*. However, if the nodal surfaces are known, our formulation appears more convenient, if only because the class of trial functions may be significantly extended (as calculations for He show[5]) and the convergence is accelerated.

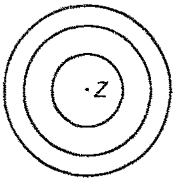
Some prospects. All the above-considered results for multielectron systems remain true for arbitrary fermion systems, which obey the Pauli principle. The use of these procedures may increase the accuracy and efficiency of calculations with the use of a WF, for example, concerning nuclear systems. Quantum chemical calculations by the Monte Carlo method already use nodal surfaces of WFs as they are. Above all, we should mention Anderson's calculations for atoms and small molecules.[18–20] In his study, Anderson noted the relationship between nodal surfaces and the Pauli principle; the study[21] describes the calculations for the H_2 molecule in the triplet state and explicitly presents the sections of the nodal surface (of the form $g_{12} = c$) in the physical space.

The authors of the very interesting paper[22] approached the same problem more closely. Unfortunately, two small inaccuracies may be noted. Firstly, the authors of that research could not overcome the accepted stereotype: they state that, although the dimensionality of the nodal surface is $(3N - 1)$, only the $(3N - 3)$-dimensional nodal surface directly derived from the antisymmetry requirement is related to the Pauli principle. In addition, their "relationship between nodal regions and permutation cells" simulates the actual situation too primitively without the separation of spin and spatial variables.

Our hypothesis about the form of nodal surfaces is surely just a hypothesis so far. It may turn out to be incorrect for more complex cases, it may be improved or changed later, but, in any case, the formulation of this problem remains a pressing question. If its solution is found some time, then new prospects must surely open for exact calculations of more complex atomic and molecular systems. Figuratively speaking, given the whole vast set of antisymmetrical wave functions that may be regarded as the possible basis for finding approximate solutions of the Schroedinger equation, we may hope to separate a significantly smaller class of functions out of this set for solving each specific problem. The nodal surfaces of WF also may be considered in traditional quantum chemical calculations of atoms and molecules, for example, with the use of Gaussian functions.

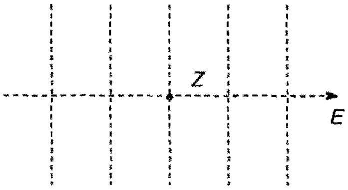
The true nodal surfaces of exact WFs depend on the problem's hamiltonian, and this fact is not related to the correctness of the suggested hypothesis. As an example, let us consider the interaction of multielectron systems with strong electric and magnetic fields. In the case of weak fields, this interaction is represented by the Stark and Zeeman effects. The forbidden surfaces for the He atom (triplet state) and for the Li and Be atoms (ground states) in the absence of fields are spheres with the center in the nucleus Z (Scheme 3); the Pauli principle bans the "simultaneous" positioning of two electrons with parallel spins at each of these spheres.

Scheme 3



In very strong fields, where Coulomb interactions are negligible, our hypothesis will produce the planar form of nodal surfaces for these systems (for example, in the electric field E). These planes are perpendicular to the field direction (Sheme 4); that is, the Pauli principle forbids the positioning of two electrons with parallel spins at each of these planes. However, in fields of intermediate intensities, where Coulomb interactions are comparable to the field gradient (from the usual viewpoint, of course, these fields are very strong), the nodal surfaces that are presented in Fig. 3 may be hypothesized.

Scheme 4



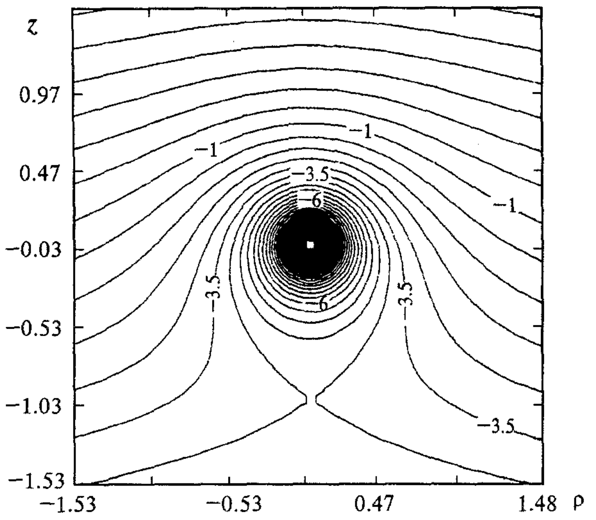


Fig. 3. Nodal surfaces of a triplet He atom in an electric field with an intensity $E = 2$ au.

These spheres are distorted along the field direction. Here two cases are possible. The energy levels of the states with these nodal surfaces may be higher than the "ground" level (then these states will be "metastable") or lower (in this case, they will be "superstable", *i.e.*, the transition into these states will involve a release of energy). In the first case, atoms will "store" the energy of the external field, and this energy may be released again after the field is "switched off". In the second case, the field may serve as a sort of catalyst for this process, and the atoms will not spontaneously return into the initial states. It is also possible that these cases may take place independently from each other. Thus, this process may be hypothetically considered as an essentially new source of energy.

Of course, if we begin to raise the field intensity under normal conditions, the nuclei and electrons will fly away in different directions long before these critical values are reached. However, these conditions quite probably may be fulfilled in some unusual cases: for example, in some cosmological systems (stellar nuclei, "black holes", and so on). There is a possibility that gravitation may play the role of such fields (for example, in black holes). In principle, the corresponding calculations might help the interpretation of some observed frequencies in cosmic radiation. We may suppose that atoms in these hypothesized superstable states have significant magnetic moments, and the matter constructed of these atoms may have abnormally high density. As a hypothesis, we may suppose the possible existence of these states in Earth's core. However, all this discussion of new atomic states is no more than just a single illustration of the prospects opened by our consideration of the Pauli principle (only somewhat more profound than the accepted antisymmetry concept) and the role of this principle in the behavior of multielectron systems and in the structure of matter.

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