

# Role of Wave Functions' Nodal Surfaces in Interpretation of the Pauli Principle

Evgenii A. Smolenskii,<sup>\*,†</sup> Peter P. Aristov,<sup>‡</sup> Sergey Ya. Itshenko,<sup>‡</sup> Sergey A. Shpilkin,<sup>†</sup> and Sergey N. Maximoff

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow, 117913 Russia, and Moscow State University, Moscow, Russia

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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 by the example of calculating the energy of the Li atom in the ground state.

## NODAL SURFACES FOR TWO-ELECTRON SYSTEMS

To illustrate our approach to principles of constructing wave functions (WFs) of multielectron systems 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

$$\mathbf{H}\Psi = E\Psi \quad (1)$$

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 and the WF presented in the form

$$\Psi(r_1, s_1; r_2, s_2) = \chi(s_1, s_2)\Phi(r_1, r_2) \quad (2)$$

where  $r_i = (x_i, y_i, z_i)$ , ( $i = 1, 2$ ),  $\chi(s_1, s_2)$  is the spin function, and  $\Phi(r_1, r_2)$  is the spatial function.

According to the Pauli principle, the  $\Psi$  function should be antisymmetrical with respect to permutations of both spin and spatial coordinates of two electrons:

for  $S = 0$  (singlet state):

antisymmetrical  $\chi(s_1, s_2)$

symmetrical  $\Phi(r_1, r_2)$

for  $S = 1$  (triplet state):

symmetrical  $\chi(s_1, s_2)$

antisymmetrical  $\Phi(r_1, r_2)$

Let us consider the triplet state in more detail. The antisymmetry requirement for the WF (2) results in the condition<sup>1</sup>

$$\Phi(r_1, r_2) = -\Phi(r_2, r_1) \quad (3)$$

The function  $\Phi(r_1, r_2)$  is defined in the six-dimensional space  $Q^6$ , which is the product of two common Euclidean spaces. 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.<sup>2</sup> The form of this surface is defined by the equation

$$\Phi(r_1, r_2) = 0 \quad (4)$$

In the one-particle approximation WF is usually represented by the Slater determinant, yielding for the function  $\Phi(r_1, r_2)$

$$\Phi_{12}(r_1, r_2) = \begin{vmatrix} \varphi_1(r_1)\varphi_1(r_2) \\ \varphi_2(r_1)\varphi_2(r_2) \end{vmatrix} \quad (5)$$

The antisymmetry imposed by the Pauli principle leads to the correlation of electrons with parallel spins: usually this correlation is expressed as a requirement that the WF (5) is reduced to zero when the coordinates of electrons in the physical space are identical, *i.e.*, when  $r_1 = r_2$ .<sup>3</sup> However, evidently, the equation  $r_1 = r_2$  (that is,  $x_1 = x_2$ ,  $y_1 = y_2$ ,  $z_1 = z_2$ ) defines a three-dimensional manifold in  $Q^6$ :  $R_0^3 \subset \Omega_0^5$ .<sup>2</sup> Thus, the usual idea about 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:

$$\begin{vmatrix} \varphi_1(r_1)\varphi_1(r_2) \\ \varphi_2(r_1)\varphi_2(r_2) \end{vmatrix} = \varphi_1(r_1)\varphi_2(r_2) - \varphi_1(r_2)\varphi_2(r_1) = 0$$

Separating the variables, we get

$$\frac{\varphi_1(r_1)}{\varphi_2(r_1)} = \frac{\varphi_1(r_2)}{\varphi_2(r_2)}$$

Let us consider the function

$$g_{12}(r) = \frac{\varphi_1(r)}{\varphi_2(r)}$$

(the function

$$g_{21}(r) = \frac{\varphi_2(r)}{\varphi_1(r)}$$

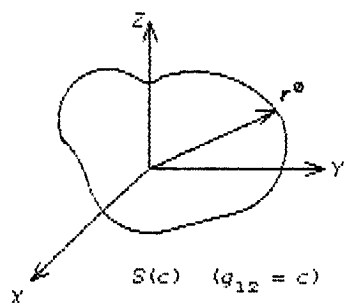
may be considered in the same way). The equations  $g_{12}(r)$

<sup>†</sup> Russian Academy of Sciences.

<sup>‡</sup> Moscow State University.

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Chart 1



$= c$  for all  $c$  values define a family of surfaces  $S(c)$  (the level surfaces of the  $g_{12}$  function) in the common physical space (Chart 1).

For any fixed position of one electron  $r_1 = r^0$ , this electron falls into one of the surfaces  $S$ , namely, into the surface  $g_{12}(r) = g_{12}(r^0)$ . The other electron may be situated neither in the point  $r_2 = r_1 = r^0$  nor in all points of the surface  $g_{12}(r) = g_{12}(r^0)$ . Thus, the Pauli principle with respect to function 5 indeed forbids not only the configuration  $r_1 = r_2$  but also 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  $g_{12}(r_1) = g_{12}(r_2)$ . Mathematically, 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

$$\varphi_1(r), \varphi_2(r), \dots, \varphi_n(r) \quad (6)$$

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

$$\Psi = \sum_{(i,j)} C_{ij} \begin{vmatrix} \varphi_i(r_1) & \varphi_i(r_2) \\ \varphi_j(r_1) & \varphi_j(r_2) \end{vmatrix} = \sum_{(i,j)} C_{ij} \Phi_{ij} \quad (7)$$

Just like function 5, each of the functions  $\Phi_{ij}$  in formula 7 has a nodal surface of the form  $g_{ij}(r_1) = g_{ij}(r_2)$ . (Evidently,  $g_{ij} = g_{ji}^{-1}$ ,  $g_{ji} = \varphi_i/\varphi_j$ .) Generally speaking, all these nodal surfaces are different. Meanwhile, eq 1 has a unique solution for any eigenvalue  $E$ ; therefore, a single nodal surface exists, corresponding to the set of the electrons' mutual positions  $(r_1, r_2)$  forbidden by the Pauli principle. It may be one of the reasons why the CI method converges so slowly: the expansion 7 containing terms with various nodal surfaces should approach the true solution of eq 1 with a single nodal surface. Naturally, superposition of a great number of functions  $\Phi_{ij}$  with a complete enough basis (6) finally may approach the true function, but this process converges slowly.

In particular cases, when the Hamiltonian of eq 1 has certain symmetry, a solution of this equation may be represented by a function 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).

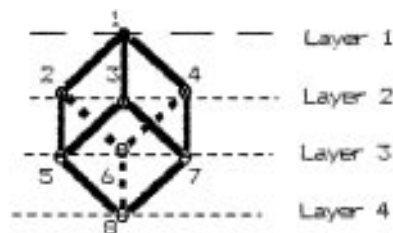


Figure 1. The distribution of the cube's vertices "by layers".

Correspondingly, the equation of nodal surface may be written in coordinates of this smaller-dimensionality space. In particular, as shown in refs 4 and 5, the 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 bans 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

The situation for a system with the number of electrons  $N > 2$  is the analogous but also complicated by the fact that the spin and spatial variables are not separated. It is easy to show that WFs always have nodal surfaces for  $N > 2$ , and the dimensionality of these surfaces is always  $3N - 1$ , whereas the traditional ideas<sup>3</sup> about correlation of electrons with parallel spins correspond to nodal manifolds of dimensionality  $3N - 3$ , as follows from analysis of the equation  $r_i = r_j$  (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 was regarded as insoluble for  $N > 2$ .<sup>1</sup> 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  $4^N$ -dimensional space, and only afterwards we introduced the limitations upon the spin coordinates. The final result is as follows. The configuration space where the WF is defined consists of a set of  $2^N$  subspaces with dimensionality  $3^N$  embedded in the  $4^N$ -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  $S_N$ .<sup>6</sup> Figure 1 is an example of how the vertices of this cube are grouped into layers in the case of three electrons.

For  $S = 3/2$  and  $M_s = 3/2$ , the WF is different from zero only in the area  $Q^9$  that corresponds to the vertex 1 (in this case,  $S(S+1) = 15/4$ ); for  $S = 3/2$  and  $M_s = -3/2$ , it is nonzero only in the  $Q^9$  that corresponds to the vertex 8. If  $M_s = 1/2$ , the subspaces  $Q^9$  correspond to vertices 2, 3, and 4 (layer 2);  $S(S+1)$  may be equal either to  $15/4$  or to  $3/4$ . For  $M_s = -1/2$ , the subspaces  $Q^9$  correspond to vertices 5, 6, and 7 (layer 3).

Each subspace  $Q^9$  is divided by a nodal surface of the WF into regions of wave function constant sign. Transpositions of the electrons move the point corresponding to the

electron configuration either between subspaces  $Q^9$  belonging to one layer or from one region of constant WF sign to another one within the same subspace. Figure 2 contains the scheme of the three nine-dimensional subspaces corresponding to  $M_s = 1/2$  and  $S(S+1) = 3/4$  for the case  $N = 3$ . Arrows represent the effects of transpositions  $P_{ij}$  (pairwise permutations from the  $S_3$  group) on the configuration point. It can be seen again from this scheme that each of the three spaces  $Q^9$  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  $(r_1^0, s_1; r_2^0, s_2; r_3^0, s_3)$  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  $3^N$ -dimensional space, whereas we regard this part as defined in different spaces, with 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<sup>9</sup> 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 refs 6 and 8, all three spatial functions that correspond to the scheme in Figure 2 are connected to each other by simple relations, and it is sufficient to consider the solution in only one of these spaces for solving (1).

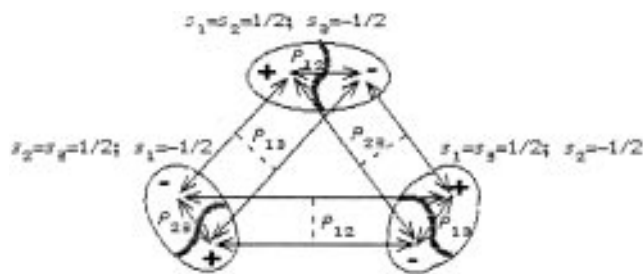
The cases of  $N = 3$  and  $N = 4$  are still simple enough to be handled by traditional approaches, that is, with the use of the Slater determinants. Let us assume that we have three functions  $\varphi_1(r)$ ,  $\varphi_2(r)$ , and  $\varphi_3(r)$ . In the general case, the WF in the form of the Slater determinant for  $N = 3$  and  $M_s = 1/2$  (as a rule, the condition  $\varphi_1 = \varphi_3$  is used) is written as

$$\Psi = \begin{vmatrix} \varphi_1(r_1)\alpha(s_1) & \varphi_1(r_2)\alpha(s_2) & \varphi_1(r_3)\alpha(s_3) \\ \varphi_2(r_1)\alpha(s_1) & \varphi_2(r_2)\alpha(s_2) & \varphi_2(r_3)\alpha(s_3) \\ \varphi_3(r_1)\beta(s_1) & \varphi_3(r_2)\beta(s_2) & \varphi_3(r_3)\beta(s_3) \end{vmatrix} \quad (8)$$

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

$$\begin{aligned} \Psi &= \varphi_3(r_1)\beta(s_1) \times \begin{vmatrix} \varphi_1(r_2)\alpha(s_2) & \varphi_1(r_3)\alpha(s_3) \\ \varphi_2(r_2)\alpha(s_2) & \varphi_2(r_3)\alpha(s_3) \end{vmatrix} - \\ &- \varphi_3(r_2)\beta(s_2) \times \begin{vmatrix} \varphi_1(r_1)\alpha(s_1) & \varphi_1(r_3)\alpha(s_3) \\ \varphi_2(r_1)\alpha(s_1) & \varphi_2(r_3)\alpha(s_3) \end{vmatrix} + \\ &+ \varphi_3(r_3)\beta(s_3) \times \begin{vmatrix} \varphi_1(r_1)\alpha(s_1) & \varphi_1(r_2)\alpha(s_2) \\ \varphi_2(r_1)\alpha(s_1) & \varphi_2(r_2)\alpha(s_2) \end{vmatrix} \\ &= \left\{ \beta(s_1)\alpha(s_2)\alpha(s_3)\varphi_3(r_1) \times \begin{vmatrix} \varphi_1(r_2) & \varphi_1(r_3) \\ \varphi_2(r_2) & \varphi_2(r_3) \end{vmatrix} \right\} + \\ &+ \left\{ \alpha(s_1)\beta(s_2)\alpha(s_3)\varphi_3(r_2) \times \begin{vmatrix} \varphi_1(r_3) & \varphi_1(r_1) \\ \varphi_2(r_3) & \varphi_2(r_1) \end{vmatrix} \right\} + \\ &+ \left\{ \alpha(s_1)\alpha(s_2)\beta(s_3)\varphi_3(r_3) \times \begin{vmatrix} \varphi_1(r_1) & \varphi_1(r_2) \\ \varphi_2(r_1) & \varphi_2(r_2) \end{vmatrix} \right\} \quad (9) \end{aligned}$$

From the last expression it can be seen that only one of the three summands in braces is nonzero for any point



**Figure 2.** The scheme of the configuration space for  $N = 3$  and  $S = 1/2$ .

$(r_1^0, s_1; r_2^0, s_2; r_3^0, s_3)$  of the configuration space, due to the properties of the spin functions  $\alpha$  and  $\beta$ . Actually, each of these three summands can be considered as defined in its own subspace, according to the scheme in Figure 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  $g_{12}(r)$  *const.* (The remaining two summands are reduced to zero according to properties of spin functions.) Just as in the case  $N = 2$ , the function  $g_{12}(r)$  is a function in the common physical space. For another distribution of spin functions in the determinant 8, as is considered in ref 1, we would get other surfaces: namely,  $g_{13}(r) = \varphi_1/\varphi_3 = \text{const}$  and  $g_{23}(r) = \varphi_2/\varphi_3 = \text{const}$ . Let us note that the function 8, as follows from the expansion 9, also may be reduced to zero when  $\varphi_3(r) = 0$ , 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  $\varphi_3$  (exactly as  $\varphi_1$  and  $\varphi_2$ ) may have no nodes at all.

For the CI method with  $N = 3$  and the base set  $\varphi_1, \varphi_2, \dots, \varphi_n$  (naturally, this set may differ from the basis 6 for  $N = 2$ ), the situation is the same 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 Schrödinger's differential equation is true for all  $N$ . This means that the CI method must converge very slowly for multi-electron systems.

Similar to function 8, let us consider the Slater determinant for  $N = 4$  and the functions  $\varphi_1, \varphi_2, \varphi_3, \varphi_4$ :

$$\Psi = \begin{vmatrix} \varphi_1(r_1)\alpha(s_1) & \varphi_1(r_2)\alpha(s_2) & \varphi_1(r_3)\alpha(s_3) & \varphi_1(r_4)\alpha(s_4) \\ \varphi_2(r_1)\alpha(s_1) & \varphi_2(r_2)\alpha(s_2) & \varphi_2(r_3)\alpha(s_3) & \varphi_2(r_4)\alpha(s_4) \\ \varphi_3(r_1)\beta(s_1) & \varphi_3(r_2)\beta(s_2) & \varphi_3(r_3)\beta(s_3) & \varphi_3(r_4)\beta(s_4) \\ \varphi_4(r_1)\beta(s_1) & \varphi_4(r_2)\beta(s_2) & \varphi_4(r_3)\beta(s_3) & \varphi_4(r_4)\beta(s_4) \end{vmatrix} \quad (10)$$

The WF (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:

$$\Psi = \sum_{(ij)} \epsilon_{p_{ij}} \alpha(s_i)\alpha(s_j)\beta(s_k)\beta(s_l) \times \begin{vmatrix} \varphi_1(r_i)\varphi_1(r_j) \\ \varphi_2(r_i)\varphi_2(r_j) \end{vmatrix} \times \begin{vmatrix} \varphi_3(r_k)\varphi_3(r_l) \\ \varphi_4(r_k)\varphi_4(r_l) \end{vmatrix} \quad (11)$$

where  $\epsilon_{p_{ij}} = \pm 1$ , depending on the evenness of the sum  $i + j$ . However, exactly as for expansion 9, we can permute

the columns of the second-order determinants in (11) so that  $\epsilon_P = 1$  for all the cases. The summation 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  $(r_1, +1/2; r_2, +1/2; r_3, -1/2; r_4, -1/2)$ , the only term not identically equal to zero is

$$\alpha(s_1)\alpha(s_2)\beta(s_3)\beta(s_4) \times \left| \begin{array}{cc} \varphi_1(r_1)\varphi_1(r_2) \\ \varphi_2(r_1)\varphi_2(r_2) \end{array} \right| \times \left| \begin{array}{cc} \varphi_3(r_3)\varphi_3(r_4) \\ \varphi_4(r_3)\varphi_4(r_4) \end{array} \right|$$

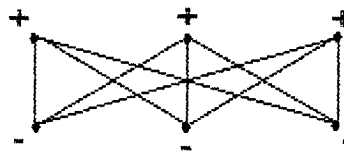
Here, similarly to the cases of  $N = 2$  and  $N = 3$ , the function (10) is reduced to zero any time when two electrons with the spin projection  $+1/2$  are situated at the surface  $g_{12}(r) = \text{const}$ , or when two electrons with the spin projection  $-1/2$  are situated at the surface  $g_{34}(r) = \text{const}$ , 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 family of surfaces (in the physical space) that determines the configurations forbidden by the Pauli principle. All that was said about the CI method in the cases of  $N = 2$  and  $N = 3$  may be repeated for  $N = 4$ .

#### INTERPRETATION OF THE PAULI PRINCIPLE AND 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  $N = 2-4$  shows that the physical sense of the Pauli principle may be interpreted for these systems in a simple way. Namely, for these systems exist certain families of surfaces in the physical space (there are already two such families for  $N = 4$ , although they may coincide, as was noted above) such that two electrons with equal spin projections "must not" be situated on the same surface simultaneously; that is, the probability density of such states is reduced to zero.

This interpretation may be generalized. Let the function  $\Phi(r_1, r_2)$  for the above-considered case  $N = 2$ ,  $S = 1$  be the exact solution of the Schroedinger eq 1 and let the coordinates of the first electron be fixed, that is,  $r_1 = r^0$ . Then, we get the function  $\Phi(r^0, r_2) = \Phi_P(r_2)$ , and the equation  $\Phi_P(r) = 0$  defines a surface in the physical space determining exactly those configurations that are forbidden by the Pauli principle. That is, if one of the electrons has the coordinates  $r^0$ , the other electron must not be situated not only in the point  $r_2 = r^0$  but also at the whole surface in the physical space. Unfortunately, there is no 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 or more electrons with parallel spins, although rigorous consideration<sup>6,8</sup> of multielectron wave functions does not imply such difficulties. Nevertheless, we may suppose that systems containing three or more electrons with parallel spins (including all systems with  $N \geq 5$ ) have much more complex wave functions than in the above-described cases  $N = 2, 3$ , and 4. For example, the wave function for  $N = 3$  and  $M_s = 3/2$  is defined in the space corresponding to the vertex 1 in the scheme of Figure 1; therefore, all three nodal surfaces

Chart 2



are contained in one and the same space  $Q^9$ , intersecting in a complex way and forming a topological structure related to the well-known Kuratowski graph<sup>9</sup> (Chart 2).

Consideration of calculation results for the triplet state of the He atom<sup>4,5</sup> lets us get the explicit equation of the surface in the physical space where electrons cannot be situated simultaneously. It is the surface  $r = \sqrt{x^2 + y^2 + z^2} = \text{const}$ . The nodal surface of the WF, accordingly, is  $r_1 - r_2 = 0$ . In refs 10 and 11 a geometrical interpretation of the physical sense of the Pauli principle for exact wave functions was suggested: the hypothetical force were considered that ensured the fulfillment of the Pauli principle and a hypothesis was formulated that permits one to construct nodal surfaces for arbitrary multielectron wave functions in the explicit form. Let us analyze this hypothesis.

One can construct for any electron a potential function having the meaning of the "local" energy depending on the Hamiltonian and taking into account interactions with nuclei and other electrons with equal spin projections. The form of this function is

$$u_i(r_i) = -\sum_{\alpha} \frac{z_{\alpha}}{r_{i\alpha}} + \sum'_{j \neq i} \frac{1}{r_{ij}} \quad (12)$$

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  $s_i = s_j$ :

$$G_{ij}(r_i, r_j) = u_i - u_j \quad (13)$$

The hypothesis consists in the assumption that zeros of 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 Figure 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 terms of families of surfaces in the three-dimensional physical space. Although there are two such families 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.<sup>10,11</sup>

Let us examine from the our hypothesis' point of view the calculations for the Li atom and corresponding ions,<sup>12-14</sup> which are presently the most accurate for these systems. The

**Table 1.** Calculations of Li Atom Energies ( $^2S$ )

max. order of functions in basis	no. of functions in basis	calcd energy, amu	
		function 14	function 16
1	5	-7.421 257	-7.444 296
2	17	-7.465 906	-7.470 491

trial functions are constructed as follows. The functions of the Hylleraas coordinates

$$\Phi_i = r_1^{n_1} r_2^{n_2} r_3^{n_3} r_{12}^{n_4} r_{13}^{n_5} r_{23}^{n_6} \exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_3) \quad (14)$$

are multiplied by the corresponding spin functions and then antisymmetrized by the standard procedure using the permutations that constitute the  $S_3$  group. Analysis of the wave functions, taking into account regions where their components are defined, shows that in the subspace where  $s_1 = s_2 = 1/2$  (the upper one in Figure 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 (13). For the remaining functions, nodal surfaces have the form

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

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 used). Using a basis set of 296 functions of the form (14), in ref 12 very good results for the energy of the Li atom were obtained, and, since a significant part of these functions have nodal surfaces of the form (13), these results confirm our hypothesis to some extent.

To check the hypothesis once more, we elaborated a program for calculating the ground state ( $^2S$ ) energy of the Li atom, using both standard antisymmetrization procedure<sup>15,16</sup> and the nodal surface obtained from (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 the product was subjected to antisymmetrization. In the second case, the WF was constructed in the form  $\Psi = \sum C_i \Psi_i$ , where

$$\Psi_i = \{(1+P_{12})[r_1^{n_1} r_2^{n_2} r_3^{n_3} r_{12}^{n_4} r_{13}^{n_5} r_{23}^{n_6}]\} \times (e^{-\alpha r_1} - e^{-\alpha r_2})e^{-\beta(r_1+r_2)-\gamma r_3} \quad (16)$$

The function 16 is defined for the region of the configuration space in Figure 2 where  $s_1 = s_2 = 1/2$  and  $s_3 = -1/2$ . The expression in braces is symmetrical with respect to permutation of the first and second electrons. The expression  $(e^{-\alpha r_1} - e^{-\alpha r_2})$  in function 16 ensures both antisymmetry of the function  $\Psi_i$  and its reduction to zero at  $r_1 = r_2$ . The  $\alpha$ ,  $\beta$ , and  $\gamma$  values were equal for all  $\Psi_i$ .

Results of energy calculations for the Li atom (IBM PC-486) are given in Table 1; the order of the  $\Psi_i$  function is defined as  $\sum_{k=1}^6 n_{ik}$ . The experimental energy value for the Li atom ( $^2S$  state) is -7.478 069 amu.<sup>12</sup>

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 wave functions of the Li atom in the ground state make it possible to obtain energy values that are closer to experiment. This effect becomes especially marked if we conduct the calculations using the first-order functions that are presented in Table 2.

**Table 2.** Base Functions up to the First Order

no. of 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 Li Atom Energies (Ground State,  $^2S$ )

functions from Table 2	no. of functions in basis	calcd energy, amu	
		functions 14	functions 16
1-3	3	-7.419 873	-7.412 465
4 and 5	2	-7.402 252	-7.441 177

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 and 5. The results of calculations are given in Table 3.

The results shown in Tables 1 and 3 leave no doubt that the choice of nodal surfaces in trial wave functions is extremely important for the construction of trial wave functions. We may hope that use of boundary conditions 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 basis functions have different nodal surfaces in this case.

As to calculations of the He atom, in our paper<sup>5</sup> we showed the possibility of implementing an essentially new approach to constructing wave functions. Namely, knowing *a priori* the form of nodal surfaces of exact wave functions, we can formulate the requirements of the Pauli principle in terms of nodal surfaces. Instead of demanding the antisymmetry of 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:  $r_1 \leq r_2$  and  $r_1 \geq r_2$ . 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<sup>5</sup> for a WF with 47 terms are more accurate than the results by Pekeris,<sup>16</sup> 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 wave functions, 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 hypothesis (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

Chart 3

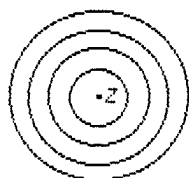
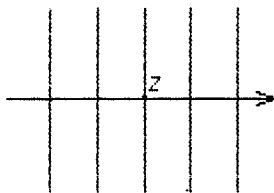


Chart 4



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

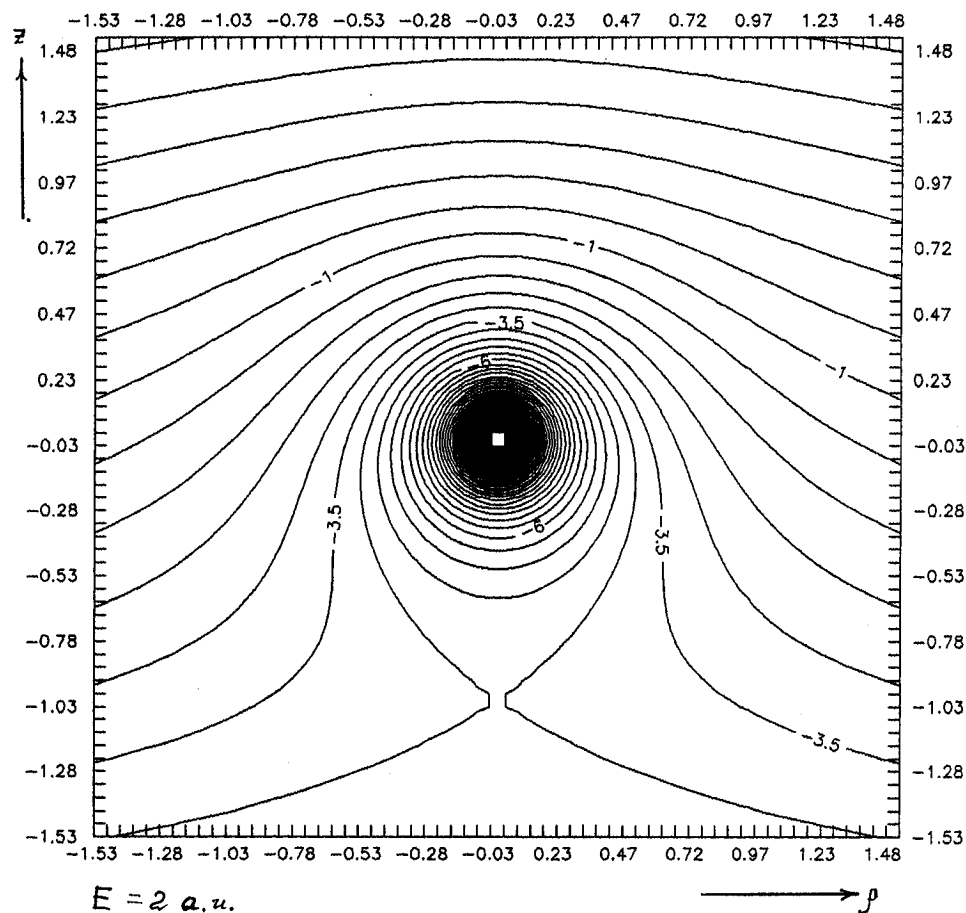
extended (as calculations for  $\text{He}^5$  show) and the convergence is accelerated.

### 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 wave functions, for example, concerning nuclear systems. Quantum chemical calculations by the Monte Carlo method already use nodal surfaces of wave functions as they are. Above all, we should mention Anderson's calculations for atoms and small molecules.<sup>18-20</sup> In his study,<sup>20</sup> Anderson noted the relationship between nodal surfaces and the Pauli principle; the study<sup>21</sup> describes the calculations for the  $\text{H}_2$  molecule in the triplet state and explicitly presents the sections of the nodal surface (of the form  $g_{12} = c$ ) in the physical space.

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.

Chart 5



The nodal surfaces of wave functions 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 wave functions 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 shown in Chart 3.

These are spheres with the center in the nucleus  $Z$ ; the Pauli principle bans the "simultaneous" positioning of two electrons with parallel spins at each of these spheres. In very strong fields, where Coulomb interactions are negligible, our hypothesis will produce the following form of nodal surfaces for these systems (for example, in the electric field  $E$ ) (Chart 4).

These planes are perpendicular to the field direction, that is, the Pauli principle forbids the positioning of two electrons with parallel spins at each of these planes. However, in fields of intermediate intensity, where Coulomb interactions are comparable to the field gradient (from the usual viewpoint, of course, these fields are very strong), the following nodal surfaces may be hypothesized (Chart 5).

These spheres are distorted along the field direction. 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.

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 the 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 deeper 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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#### REFERENCES AND NOTES

- (1) McWeeny, R.; Sutcliffe, B. T. *Methods of Molecular Quantum Mechanics*; Academic Press: London & New York, 1969.
- (2) Smolenskii, E. A. *Zh. Fiz. Khim.* **1986**, *60*, 1068–1077.
- (3) Gillespie, R. J. *Molecular Geometry*; Van Nostrand Reinhold Company: London, New York, etc., 1972.
- (4) Smolenskii, E. A. *Dokl. Akad. Nauk SSSR* **1982**, *266*, 160–164.
- (5) Smolenskii, E. A. *Teor. Eksp. Khim.* **1983**, *19*, 523–528.
- (6) Smolenskii, E. A.; Zefirov, N. S. *Dokl. Akad. Nauk* **1993**, *329*, 40–43.
- (7) Stankevich, I. V.; Smolenskii, E. A.; Zefirov, N. S. *Dokl. Akad. Nauk SSSR* **1991**, *314*, 213–216.
- (8) Smolenskii, E. A.; Stankevich, I. V. *Theor. Matem. Fiz.* **1991**, *88*, 46–58.
- (9) Smolenskii, E. A.; Stankevich, I. V.; Zefirov, N. S. *Dokl. Akad. Nauk SSSR* **1991**, *317*, 413–417.
- (10) Smolenskii, E. A. *Zh. Fiz. Khim.* **1988**, *62*, 3273–3278.
- (11) Smolenskii, E. A. *Dokl. Akad. Nauk SSSR* **1989**, *304*, 595–598.
- (12) King, F. W.; Bergsbaken, M. P. *J. Chem. Phys.* **1990**, *93*, 2570–2574.
- (13) King, F. W.; Dressel, P. R. *J. Chem. Phys.* **1989**, *90*, 6449–6462.
- (14) King, F. W. *Phys. Rev. A* **1988**, *38*, 6017–6026.
- (15) Larsson, S. *Phys. Rev.* **1968**, *169*, 49–54.
- (16) Pekeris, C. L. *Phys. Rev.* **1959**, *115*, 1216–1220.
- (17) Anderson, J. B. *J. Chem. Phys.* **1993**, *99*, 345–351.
- (18) Anderson, J. B. *J. Chem. Phys.* **1980**, *73*, 3897–3899.
- (19) Diedrich, D. L.; Anderson, J. B. *J. Chem. Phys.* **1994**, *100*, 8089–8095.
- (20) Anderson, J. B. *J. Chem. Phys.* **1975**, *63*, 1499–1503.
- (21) Anderson, J. B.; Travnor, C. A.; Boghosian, B. M. *J. Chem. Phys.* **1991**, *95*, 7418–7425.

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