Topological Structure of the Configuration Space and the Separation of Spin and Spatial Variables for *N*-Electron Systems

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The relationship between the topological structure of the multidimensional configuration space and the structure of the symmetrical permutation group S_N is analyzed. This relationship permits to separate the spin and spatial variables during the solution of the spinless stationary Schrödinger equation. It is possible to simplify the construction of wave functions for *N*-electron systems and to expand the class of trial functions in the variation method. The relation of the suggested approach to the construction of wave functions by traditional methods is demonstrated by the example of three-electron systems.

The stationary state of an atomic or molecular electron system containing N electrons is completely described by the wave function $\Psi(\mathbf{r}_1,s_1,\mathbf{r}_2,s_2,...\mathbf{r}_N,s_N)$ depending on electrons spatial coordinates $\mathbf{r}_i$ and spins s_i and satisfying (in the nonrelativistic approximation) the stationary Schrödinger equation

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

with the Hamiltonian

$$\mathbf{H} = \sum_{i=1}^{N} (-\nabla_i^2/2 + V(\mathbf{r}_i)) + \sum_{i<j}|\mathbf{r}_i-\mathbf{r}_j|^{-1}$$

where $V(\mathbf{r}_i)$ is the potential energy of the *i*th electron in the electrostatic field of nuclei.

The construction of approximate wave functions (WF) for the solution of eq 1 is one of the principal problems in quantum mechanics of atoms and molecules. In the case of one-electron approximation, there is a good enough method for the construction of approximate WF in the form of Slater determinants. Although the major part of nonempirical and semiempirical quantum chemistry methods are based on this approximation, it is insufficient for performing more or less exact calculations for multielectron systems.[1] A serious disadvantage of the one-electron approach is its disregard of correlation effects; any attempts to evaluate them by different methods (for example, using configurational interaction) result in a significant complication of the calculation scheme.

One of the greatest difficulties in the building of approximate WF is the necessity of antisymmetrization. This necessity is due to the fact that spin variables should be considered during the search for the solution of eq 1, although they are not included directly in this equation. This difficulty could be avoided if the spin and spatial variables were separated; however, it is commonly accepted that these variables cannot be separated for a system of more than two electrons.[1]

For a two-electron system, this separation is trivial.[1] The wave function is represented in the form of a product of spatial $\Phi(\mathbf{r}_1,\mathbf{r}_2)$ and spin $\chi(s_1,s_2)$ functions each of which

possesses its own symmetry. Namely, for zero total spin $S = 0$ (singlet state) spatial part is symmetrical and spin part is antisymmetrical; for $S = 1$ (triplet state), spatial part is antisymmetrical and spin part is symmetrical.

It would be natural to try to generalize this representation of the WF for systems containing more than two electrons. Unfortunately, it turns out that direct generalization is not possible. For $M > 2$, fully antisymmetric function of *M* spin variables is identically zero, so one cannot build an antisymmetric WF as a product of a symmetric spatial function and an antisymmetrical spin function. Only for the state of maximum spin there exists a representation analogous to that for two-electron system triplet state. The problem of generalizing these representations for multielectron systems does not emerge within the framework of the one-electron approach; however, any attempts to exceed the limits of one-electron approximation and to analyze the structure of exact WF inevitably return us to this problem. It turns out that the antisymmetry property of triplet-state spatial function can be generalized and used in the construction of exact WF. As to the symmetry of singlet-state spatial function, of course, the spatial function $\Phi(\mathbf{r}_1,\mathbf{r}_2)$ for $S = 0$, $N = 2$ is symmetrical from the formal point of view; however, the property which can and must be generalized is cyclic symmetry which coincides with common symmetry only for $N = 2$. The explanation can be given in terms of topological structure of the configurational space. For $N = 2$ and $S = 1$, wave function is defined in a single connected region of the configuration space; for $N = 2$ and $S = 0$, the WF is defined in two different and topologically not interconnected spaces. In the latter case, the permutation of electrons (their spins taken into account) results in the transition between these two spaces. Incomplete understanding of this problem made it impossible to separate the spin and spatial variables for electron systems with $N > 2$. The study of the topological structure of configuration space for multielectron systems leads to a new approach to the constructing of exact wave functions. In works[2−4] it was shown how the spin and spatial variables can be separated efficiently for arbitrary N-electron systems. Let us consider the scheme of this approach.

In the general case, the configuration space in which a wave function is determined can be represented by the 4*N*-

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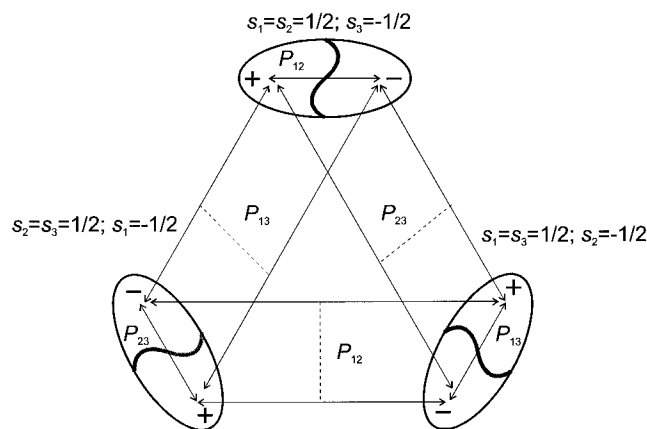
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Figure 1. Action of pairwise electron transpositions on points in the configurational space of a three-electron system.

dimensional space Q^{4N}, where the spatial coordinates of the ith electron r_i are continuous and its spin coordinates adopt two values: $s_i = +^1/_2, -^1/_2$. From our point of view, the traditional approaches consider the $\mathbf{r}$-dependent part of the WF in an oversimplified manner, as a function in a certain $3N$-dimensional space Q^{3N}. We believe that the situation will become more clear if we consider the general configuration space without such simplification,[5,6] i.e., as a $4N$-dimensional space. First, let us analyze in detail the spin space which consists of 2^N points. This space S^N can be regarded as an N-dimensional unit cube with the vertex coordinates $\{s_1,...,s_N\}$, $s_i = \pm^1/_2$. All the vertices of the cube S^N can be distributed by $(N+1)$ levels in the following way. Let the vertex $\{+^1/_2, +^1/_2, ..., +^1/_2\}$ belong to the zeroth level, N vertices with $(N-1)$ coordinates equal to $+^1/_2$ and one coordinate equal to $-^1/_2$ belong to the first level, etc.; the kth level will contain C_N^k vertices with $(N-k)$ coordinates equal to $+^1/_2$ and k coordinates equal to $-^1/_2$. At the $(N-1)$th level, there will be N vertices with one coordinate $+^1/_2$ and $(N-1)$ coordinates $-^1/_2$, and the Nth level will contain one vertex $\{-^1/_2, ..., -^1/_2\}$. Let us note that all the vertices at the kth level (they are denoted by the symbol S_k^N) are connected with vertices of the $(k-1)$th and $(k+1)$th levels by single edges (the zeroth level is connected only with the first one, and the Nth is connected with the $(N-1)$th level). The total number of vertices at all the levels is, as expected,

$$\sum_{k=0}^{N} C_N^k = 2^N$$

Thus, the $4N$-dimensional configuration space $\bar{Q}^{4N}$, where an arbitrary solution of eq 1 must be determined under the condition of the discreteness of spin variables, can be represented as a direct product of the common $3N$-dimensional space Q^{3N} and the spin space which is described by the N-dimensional unit cube S^N

$$\bar{Q}^{4N} = Q^{3N} \otimes S^N \tag{2}$$

where $\bar{Q}^{4N} \subset Q^{4N}$, that is $\bar{Q}^{4N}$ consists of 2^N $3N$-dimensional regions of the space Q^{4N} which are not topologically interconnected in Q^{4N}. These regions can also be distributed by the above-described $(N+1)$ levels, i.e., each vertex of the cube S^N corresponds to its "own" $3N$-dimensional space Q^{3N}.

The solution of eq 1 corresponding to the state with total spin S and spin projection M_s should satisfy the system of equations

$$\mathbf{S}^2 \Psi = S(S+1)\Psi$$

$$\mathbf{S}_Z \Psi = M_S \Psi \tag{3}$$

where $M_S = -S, -S+1, ..., S$; therefore, the general solution is presented in the form

$$\Psi_{S,M_S}(\mathbf{r}_1, ..., \mathbf{r}_N; s_1, ..., s_N) \tag{4}$$

i.e., it depends on S and M_S. Generally speaking, M_S can vary from $N/2$ to $-N/2$ with step 1, i.e., it can adopt $(N+1)$ values (for even N, one of the values is zero). Evidently, each function (4), which is defined in the space (2) and satisfies (1) and (3), is nonzero only within a definite set of spaces Q^{3N}; this set depends on M_S and belongs to one and the same level of $\bar{Q}^{4N}$. For $M_S = N/2$, it is a single region $Q^{3N} \in \bar{Q}^{4N} \subset Q^{4N}$ which corresponds to the zeroth level S_0^N. Let us denote this region as $\bar{Q}_0^{4N}$. There will be N such regions for $M_S = N/2 - 1$; let us denote their union as $\bar{Q}_1^{4N}$. This process can be continued: there will be $N(N-1)/2$ such regions for $M_S = N/2 - 2$ etc., up to a single region $\bar{Q}_N^{4N}$ for $M_S = -N/2$.

The topological structure of the space $\bar{Q}^{4N}$ can be related to the structure of the symmetrical permutation group S_N. Traditional method[12] for constructing the solution of eq 1 is to multiply a spatial function $\Phi(\mathbf{r}_1, ..., \mathbf{r}_N)$ which is a solution of the "spinless" equation by the spin function which satisfies the system 3

$$\Phi(\mathbf{r}_1, ..., \mathbf{r}_N)\chi_{S,M_S}(s_1, ..., s_N) \tag{5}$$

The product is subjected to the action of the antisymmetrization operator $\mathbf{A}$ in order to get an antisymmetrical solution, according to the Pauli principle

$$\Psi^\mathbf{A} = \mathbf{A}\Phi(\mathbf{r}_1, ..., \mathbf{r}_N)\chi_{S,M_S}(s_1, ..., s_N)$$

Operator $\mathbf{A}$ has the following form

$$\mathbf{A} = \sum_{P \in S_N} \epsilon_P P \tag{6}$$

the summation includes all the permutations P of the symmetrical group S_N, and ϵ_P adopts the values ± 1, depending on the evenness of the permutation P.

Let us consider the following subgroup S_k^0 of the group S_N

$$S_k^0 = S_{N-k} \otimes S_k \tag{7}$$

It can be seen from (7) that S_k^0 coincides with S_N when $k = 0$ or $k = N$. Otherwise, it is a direct product of the permutation groups which act on the two subsets which are formed after an arbitrary nontrivial partition of the set $\{1, 2, ..., N\}$. Let us denote subgroup (7) as C_k^1 and the right (or left) cosets of subgroup S_k^0 as C_k^i, $i = 2, ..., t$, where $t = N!/(N-k)!k!$ is the index of the subgroup S_k^0 in relation to the group S_N. Then, operator (6) can be rewritten in the following form

$$\mathbf{A} = \sum_{k=1}^{t}\sum_{P \in C_k} \epsilon_P P \qquad (8)$$

The antisymmetrization operator (6) in the k-dependent form (8) is naturally related to the corresponding level with the same number k in the cube S^N or in the region $\bar{Q}_k^{4N}$ of space $\bar{Q}^{4N}$. The kth level $\bar{Q}_k^{4N}$ contains C_N^k $3N$-dimensional regions $Q_{k,i}^{3N}$ ($i = 1,...,t$). One region among them corresponds to the vertex of the cube S^N with the coordinates $s = \frac{1}{2}$ in the first k positions and $s = -\frac{1}{2}$ in the remaining positions. Let us denote this region as $Q_{k,i}^{3N}$ and put it in correspondence with the subgroup S_k^0. Each of the remaining $(t-1)$ regions can be put in a one-to-one correspondence with a certain coset C_k^i of this subgroup. It can be seen that the permutations of subgroup (7), acting simultaneously on spatial and spin coordinates, do not change the spin part of function (5). Therefore, this subgroup may be called the **spin-invariant** subgroup of the group S_N. Because of the above-established correspondence between the regions $Q_{k,i}^{3N}$ and the cosets C_k^i, the permutations from C_k^i leave the corresponding spin point in the same position. Thus, after the action of operator (8) on function (5) the WF has a form

$$\Psi^{\mathbf{A}} = \sum_{i=1}^{t}\chi_{S,M_S}^{i}\{\sum_{P \in C_k^i} \epsilon_P P \varphi(\mathbf{r}_1,...,\mathbf{r}_N)\} \qquad (9)$$

Denoting

$$\Phi_i^{\mathbf{A}}(\mathbf{r}_1,...,\mathbf{r}_N) = \sum_{P \in C_k^i} \epsilon_P P \varphi(\mathbf{r}_1,...,\mathbf{r}_N) \qquad (10)$$

we can rewrite formula (9) in the following way

$$\Psi^{\mathbf{A}} = \sum_{i=1}^{t}\chi_{S,M_S}^{i}(s_1,...,s_N)\Phi_i^{\mathbf{A}}(\mathbf{r}_1,...,\mathbf{r}_N) \qquad (11)$$

As it follows from the method of its construction, function (11) is antisymmetrical as to each pairwise permutation of electrons (their spin taken into account), and the matrix elements of any operator which do not contain spin variables are equal up to a constant for function (11) and for the function

$$\Phi_1^{\mathbf{A}} = \sum_{P \in C_k^1} \epsilon_P P \varphi(\mathbf{r}_1,...,\mathbf{r}_N) \qquad (12)$$

Equation 1 and the characteristic equation of the variation method are linear and uniform; therefore, to find the coordinate part of the solution of the Schrödinger eq 1 having the form (5) it is enough to analyze and find function (12) which contains no spins, and the spin part of function (5) can be considered separately as the solution of system (3). It means exactly that the spin and spatial variables are in fact separated in our approach, because functions (10) can be obtained from function (12) with the help of simple permutational operators, i.e., it is enough to know function (10) for the construction of the complete WF (11).

To make the last paragraph more clear, let us consider an example with $N = 3$ and $M = \frac{1}{2}$ (e.g., a Li atom in the ground state). The trial WF for the lithium atom may be presented in the following form[7-9]

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3) = \mathbf{A}\sum_{\mu=1}^{N}C_{\mu}\Phi_{\mu}\chi(123) \qquad (13)$$

where $\Phi_{\mu} = \Phi_{\mu}(r_1,r_2,r_3,r_{12},r_{13},r_{23})$, $\chi(123) = \alpha(s_1)\beta(s_2)\alpha(s_3) - \beta(s_1)\alpha(s_2)\alpha(s_3)$, and $\mathbf{A}$ is an antisymmetrization operator

$$\mathbf{A} = \mathbf{1} + \mathbf{P}_{123} + \mathbf{P}_{321} - \mathbf{P}_{12} - \mathbf{P}_{13} - \mathbf{P}_{23} \qquad (14)$$

Let us consider the action of operator (14) on separate additives of the wave function

$$\Psi_{\mu}^{\mathbf{A}} = \mathbf{A}\Phi_{\mu}\chi_{\mu} =$$
$$(\mathbf{1}+\mathbf{P}_{123}+\mathbf{P}_{321}-\mathbf{P}_{12}-\mathbf{P}_{13}-\mathbf{P}_{23})\Phi_{\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\chi_{\mu}(s_1,s_2,s_3) =$$
$$\Phi_{\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)[\alpha(s_1)\beta(s_2)\alpha(s_3) - \beta(s_1)\alpha(s_2)\alpha(s_3)] +$$
$$\Phi_{\mu}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_1)[\alpha(s_1)\alpha(s_2)\beta(s_3) - \alpha(s_1)\beta(s_2)\alpha(s_3)] +$$
$$\Phi_{\mu}(\mathbf{r}_3,\mathbf{r}_1,\mathbf{r}_2)[\beta(s_1)\alpha(s_2)\alpha(s_3) - \alpha(s_1)\alpha(s_2)\beta(s_3)] -$$
$$\Phi_{\mu}(\mathbf{r}_2,\mathbf{r}_1,\mathbf{r}_3)[\beta(s_1)\alpha(s_2)\alpha(s_3) - \alpha(s_1)\beta(s_2)\alpha(s_3)] -$$
$$\Phi_{\mu}(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_1)[\alpha(s_1)\beta(s_2)\alpha(s_3) - \alpha(s_1)\alpha(s_2)\beta(s_3)] -$$
$$\Phi_{\mu}(\mathbf{r}_1,\mathbf{r}_3,\mathbf{r}_2)[\alpha(s_1)\alpha(s_2)\beta(s_3) - \beta(s_1)\alpha(s_2)\alpha(s_3)]$$

To shorten the equation, we introduced the notation

$$(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = (r_1,r_2,r_3,r_{12},r_{13},r_{23})$$

$$\mathbf{P}_{12}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = (\mathbf{r}_2,\mathbf{r}_1,\mathbf{r}_3) \equiv (r_2,r_1,r_3,r_{12},r_{23},r_{13}), \text{ etc.}$$

All spin functions in the last formula belong to one of these three types: $\alpha\alpha\beta$, $\alpha\beta\alpha$, and $\beta\alpha\alpha$. Rearranging the additives by these three spin functions, we get

$$\Psi_{\mu}^{\mathbf{A}} = \{\alpha(s_1)\alpha(s_2)\beta(s_3) \times [\Phi_{\mu}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_1) + \Phi_{\mu}(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_1) - $$
$$\Phi_{\mu}(\mathbf{r}_3,\mathbf{r}_1,\mathbf{r}_2) - \Phi_{\mu}(\mathbf{r}_1,\mathbf{r}_3,\mathbf{r}_2)]\} + \{\alpha(s_1)\beta(s_2)\alpha(s_3) \times$$
$$[\Phi_{\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) + \Phi_{\mu}(\mathbf{r}_2,\mathbf{r}_1,\mathbf{r}_3) - \Phi_{\mu}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_1) -$$
$$\Phi_{\mu}(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_1)]\} + \{\beta(s_1)\alpha(s_2)\alpha(s_3) \times [\Phi_{\mu}(\mathbf{r}_3,\mathbf{r}_1,\mathbf{r}_2) +$$
$$\Phi_{\mu}(\mathbf{r}_1,\mathbf{r}_3,\mathbf{r}_2) - \Phi_{\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) - \Phi_{\mu}(\mathbf{r}_2,\mathbf{r}_1,\mathbf{r}_3)]\} \quad (15)$$

Let us denote the components in (15) as follows

$$\Psi_{\mu}^{\mathbf{A}} = \{\chi_3[(1,2)]_{\mu}\} + \{\chi_2[(3,1)]_{\mu}\} + \{\chi_1[(2,3)]_{\mu}\} \quad (16)$$

At least two of the three braces for an arbitrary point in the configuration space $\mathbf{x}^0 \equiv \{\mathbf{r}_1^0,s_1^0;\mathbf{r}_2^0,s_2^0;\mathbf{r}_3^0,s_3^0\}$ are always equal to zero, due to the properties of spin functions. Besides, even one of them can be nonzero only for $M_S = \frac{1}{2}$, and all the three braces are zero for $M_S = \frac{3}{2}$, $-\frac{1}{2}$, and $-\frac{3}{2}$. From formula (15) one can see that the function $[(1,2)]_{\mu}$, as the spatial part of WF, is antisymmetrical in relation to the permutation (1,2) and possesses no symmetry as to the permutations (3,1) and (2,3). Similarly, the spatial functions $[(3,1)]_{\mu}$ and $[(2,3)]_{\mu}$ are antisymmetrical as to the permutations (3,1) and (2,3), respectively. The functions $[(3,1)]_{\mu}$ and $[(2,3)]$ possess no symmetry in relation to other permutations as well. It is easy to notice that the functions $[(i,j)]_{\mu}$ are interconnected by the following equations

$$[(3,1)]_{\mu} = \mathbf{P}_{321}[(1,2)]_{\mu}; [(2,3)]_{\mu} = \mathbf{P}_{123}[(1,2)]_{\mu} \quad (17)$$

and can be obtained from each other by cyclic permutations of indices (this is the generalization of symmetry property

of a two-electron system singlet state WF as the cyclic permutations coincide with the common symmetry when $N = 2$).

According to formula (2), the WF for $N = 3$ is defined for different M_S in 8 ($2^3 = 8$) nondimensional subspaces Q^9 which are parts of the space Q^{12}. When $M_S = {}^1/_2$, each of the braces in (15) and (16) is defined in one of the three Q_1^9 at the first level of cube S^N. Let us denote these spaces (for Li because of the central symmetry of the Hamiltonian one can represent the spatial part of the WF as a function of six particle-to-particle distances instead of nine Cartesian coordinates) as $Q(1,2)$, $Q(1,3)$, and $Q(2,3)$. These spaces are shown schematically in Figure 1. We assume that $\mathbf{x}^0 \in Q(1,2)$ if $s_1 = s_2 = {}^1/_2$ and $s_3 = -{}^1/_2$; in general, $\mathbf{x}^0 \in Q(i,j)$ if $s_i = s_j = {}^1/_2$ and $s_k = -{}^1/_2$.

Let us consider an arbitrary point $\mathbf{x}^0 = \{\mathbf{r}_1^0, s_1^0; \mathbf{r}_2^0, s_2^0; \mathbf{r}_3^0, s_3^0\}$ in the space $Q(1,2)$. After the electron permutation $(1,2)$, $(1,3)$, or $(2,3)$, the points $P_{(i,j)}\mathbf{x}^0$ can either stay in the same space or move into another space at the same first level. For $\mathbf{x}^0 \in Q(i,j)$ we have $P_{(i,j)}\mathbf{x}^0 \in Q(i,j)$ when and only when $s_i = s_j = {}^1/_2$; in the other case, $P_{(i,j)}\mathbf{x}^0 \in Q(i',j')$ where i' does not coincide with i and/or j' is not equal to j. The spatial functions $(1,2)$, $(2,3)$, $(3,1)$ emerged as a result of an antisymmetrization, so it is easy to see that if the configuration point remains in the same space, the value of the corresponding spatial function is multiplied by (-1). It means that the component $[(i,j)]_\mu$ of the function $\Psi_\mu^{\mathbf{A}}$ is antisymmetrical with respect to the permutation (i,j) (s_i is then equal to s_j). This antisymmetricity leads to the existence of a nodal surface in each of the spaces Q dividing these spaces into regions of different signs. These nodal surfaces are also shown in Figure 1. The antisymmetricity requirement does not arise for other permutations, because they transfer the point representing the electron configuration from a certain space into other spaces which are not topologically connected with the initial one.

This analysis leads to the idea of simplifying the antisymmetrization operator (14) and consequently extending the class of trial functions in the variation method. Matrix element of an arbitrary hermitian operator $\mathbf{F}$ containing no spin variables between functions (13) and (16) is

$$f_{mn} = \int \Psi_m^{\mathbf{A}} \cdot \mathbf{F} \cdot \Psi_n^{\mathbf{A}} \, d\tau = \int \{\chi_3[(1,2)]_m + \chi_2[(3,1)]_m +$$
$$\chi_1[(2,3)]_m\}\mathbf{F}\cdot\{\chi_3[(1,2)]_n + \chi_2[(3,1)]_n + \chi_1[(2,3)]_n\} \, d\tau$$

After summation by the spin variables, taking into account orthogonality of the spin functions and renaming the spatial variables we get

$$f_{mn} = \int [(1,2)_m \mathbf{F}\cdot(1,2)_n] \, dq + \int [(3,1)_m \mathbf{F}\cdot(3,1)_n] \, dq +$$
$$[(2,3)_m \mathbf{F}\cdot(2,3)_n] \, dq = 3\int [(1,2)_m \mathbf{F}\cdot(1,2)_n] \, dq \quad (18)$$

As functions $(1,2)_m$, $(3,1)_m$, $(2,3)_m$ are related to each other by transpositions of variables, matrix elements of spin-containing operators may be also written in terms of the functions $(1,2)$ alone. For example,

$$(\mathbf{s}_x^2)_{mn} = \frac{3}{4}\{3\int [(1,2)_m \cdot (1,2)_n] \, dq +$$
$$2\int [(1,2)_m \cdot \mathbf{P}_{321}(1,2)_n] \, dq + 2\int [(1,2)_m \cdot \mathbf{P}_{123}(1,2)_n] \, dq\}$$

Equation 1 and the characteristic equation are uniform and

linear. Therefore, as it was noted above for functions (10) and (12), eq 18 shows that the trial function can be taken not in the equivalent forms (13) or (16) but in a simpler form, according to formula (12):

$$\Psi_\mu^{\mathbf{A}} = [(1,2)]_\mu \quad (19)$$

In our case $N = 3$ and $M_S = {}^1/_2$, we can take a trial function which is antisymmetric with regard to the permutation $(1,2)$, i.e., function (19). Then we can find the coefficients C_μ of formula (13) and use eq 17 to construct the complete function (15) or (16) which is equivalent to (13). Function (13) can also be simplified, if we use a simpler operator instead of (14):

$$\mathbf{A'} = \mathbf{1} - \mathbf{P}_{12} \quad (20)$$

This operator is the part of complete antisymmetrization operator (8) corresponding to the summation by the permutations $P \in S_2^0$, because the subgroup S_2^0 coincides with the group $\{1,(1,2)\}$ in this case. Then, two terms out of twelve will remain in eq 15. Besides, each space $Q(i,j)$ is divided into two parts by a nodal surface (its dimension is equal to that of the space minus 1), dividing $Q(i,j)$ into two equivalent parts.[10] The direct use of such a nodal surface for calculations of the He atom[11] in the ^3S state improved the calculations accuracy by factor of about 10 [11].

Conclusion. The wave function of an N-electron system can be considered as a function consisting of 2^N components, each of them corresponding to a definite M_S value. For each spin state which is characterized by the spin projection M_S, these components may be regarded as defined in certain regions of the configuration space corresponding to specified levels of the cube S^N, which represents the spin space of the N-electron system. This configuration space consists of a number of components which are topologically not connected. Each component contains nodal surfaces dividing it into regions of the wave functions' constant sign. Transpositions of electrons move the point representing the electron configuration either between different components or between regions of different WF sign within the same component. Antisymmetry condition for the complete wave function may be replaced by the set of boundary conditions requiring that the WF should be zero at the nodal surfaces.

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