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The matrix theory of electron spin multiplets for atoms and molecules

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In this article a matrix method for the construction of spin multiplets (spin-configurations) is suggested in order to solve the multielectron problem for atoms and mulecules by means of configuration interaction.

A simple graphical way is given to enumerate configurations and to break their set into subsets of configurations related to the given projection of the total spin of a system S_Z. It is found that all matrices in the theory of spin multiplets are convex and in cases of two, three, and four electrons are broken into blocks of an order no higher than 3.

The model of the solution of the multielectron Schrödinger equation, in which the total spin of core electrons is zero, is considered. In this model the construction of linear combinations of configurations is reduced to the construction of those for but valence electrons.

Key words: Spin multiplets—configuration interaction—electron molecular spectra

Introduction

The calculation of electron and electron-vibration spectra of molecules by the configuration interaction method leads to the problem of the construction of spin multiplets in the basis of one-electron functions. This problem is usually solved by means of permutation group representation theory, and is reduced to the construction of irreducible representations of the electron permutation group [1]. If these irreducible representations are known, the linear combinations of Slater determinants corresponding to the given total spin S of molecular electrons and its projections S_Z may be built.

Distributing N electrons among M orbitals in accordance with the Pauli principle for the given total molecular spin an enormous number of configurations is obtained. The complete enumeration of these configurations is quite a bulky problem and the use of a large number of configurations is impossible due to limitations on the computer memory and on the time of calculations of matrix elements.

At the same time, the formal exhaustive enumeration of configurations is not really necessary to construct molecular spectra. As a rule, molecular spectra correspond to transitions between levels of multiplets with the total spin $S^2 \leq N/2(N/2+1)$, and spin projections $S_Z = 0, \pm\frac{1}{2}, \pm 1$.

Thus, there is no necessity to observe the total spin projections with a magnitude larger than one. Moreover, it is not expedient to take into account configurations with low-lying unoccupied orbitals and high-lying occupied orbitals, if the difference between them is comparable with the energy of X-ray quanta, as they are unlikely to correspond to the physical phenomenon of an optical excitation of a molecule. Therefore, we can confine ourselves to the model of the electron shell of a molecule, consisting of m low-lying doubly occupied orbitals and n singly occupied orbitals, so that $N = 2m + n$.

Here, the problem of the construction of linear combinations of configurations (LCC) will be solved by the direct matrix method, which tending to the results, got traditionally by means of permutation group representation theory. Thus, the independent method of the same problem is suggested here, what in some cases makes it possible to regard the whole problem in the scope of the matrix theory with the note that the permutation group representation theory can be realized by means of matrices of corresponding structure.

All the results are corollary of symmetry properties of matrices considered in which permutational symmetry of the electron system is reflected. Due to this property, the possibility of partial diagonalization of the Hamiltonian matrix appears, dividing the total matrix into blocks, corresponding to the particular projections of the total electron spin of a molecule. This very procedure makes the process of seeking for LCC particularly obvious.

1. The total scheme for N singly occupied orbitals

Consider a molecule with N electrons which occupy N different one-electron orbitals. The molecular Hamiltonian in the Born-Oppenheimer approximation includes one-electron operators of the interaction between the electrons and the nuclei of the molecule and of the Coulomb repulsion of the electrons.

In the configuration interaction method (CI) a wave function is constructed in LCC form

$$\Psi = \sum_k C_k \Phi_k \tag{1}$$

where Φ_k is a Slater determinant, constructed from N spin-orbitals, and the

C_k-LCC coefficients have to be determined. Determinantal functions Φ_k are orthogonal in spin. By means of a variational procedure or Bubnov-Galerkin method, a system of algebraic equations is obtained for the coefficients C_k. The matrix elements of the basis functions Φ_k can be calculated in accordance with rules, given in [2].

Basis configurations Φ_k for the given set of N spin-orbitals correspond to energetically degenerated states of the molecule neglecting interactions of the electrons. Taking into consideration two directions of spin for separated electrons on an orbital, we come to 2^N configurations. As with the increase of the number of electrons, the number of configurations is growing quite quickly, for illustration the electron configurations can be represented graphically like a tree, the method of propagation of its branches is clear from Fig. 1, given for the case $N=4$.

The graph, connected arrows in vertical directions, corresponds to the separate configuration. We shall call a tier a horizontal set of arrows on the tree. The position of an arrow on the given tier of the tree corresponds to a one-electron level, occupied by the electron with the given spin projection. Thus, all possible vertical graphs of the given tree reflect electron configurations of the system. Spins $+\frac{1}{2}$ and $-\frac{1}{2}$ are denoted by arrows, directed up and down respectively. The sum of spin projections for each graph is equal to the projection of the total spin of the system of the z-axis. Fig. 1 shows that the left and the right graphs give the only maximal magnitude of the projections of the total spin of the system.

These projections are the part of the spin multiplet with the maximal possible multiplicity. Thus, there is only one multiplet with the maximal total spin, the square of which is $S^2 = N/2(N/2+1)$ for N orbitals. It is not difficult to calculate the numbers of the remaining multiplets, for which $S^2 < N/2(N/2+1)$. So for the case $N=4$, illustrated by Fig. 1, the following numbers of configurations, related respectively to projections of the total spin $S_Z = -2, -1, 0, 1, 2$ are obtained: one configuration for $S_Z = -2$, four configurations for $S_Z = -1$, six configurations for $S_Z = 0$, four configurations for $S_Z = 1$, one configuration for $S_Z = 2$. Note, that the set of configuration numbers coincides with the binomial

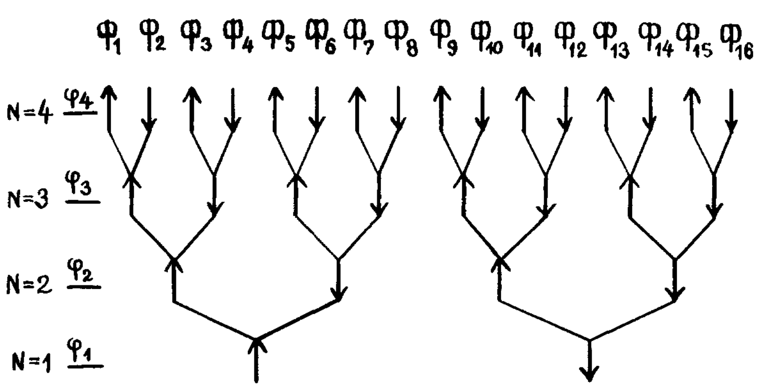

Fig. 1. The tree of electron configurations

coefficients C_4^0, C_4^1, C_4^2, C_4^3, C_4^4. There is the following distribution of configuration numbers among the total spin projections with $S^2 \leq N/2(N/2+1)$ (the number of configurations is written in brackets near spin projection S_Z)

$$-\frac{N}{2}(C_N^0),\quad -\frac{N}{2}+1(C_N^1),\quad -\frac{N}{2}+2(C_N^2),\quad \ldots,$$

$$\frac{N}{2}-2(C_N^{N-2}),\quad \frac{N}{2}-1(C_1^{N-1}),\quad \frac{N}{2}(C_N^N).$$

It is clear that multiplicities of electron states for which the maximal magnitude of the projection of the total spin along the z-axis successively is given by

$$\frac{N}{2}, \frac{N}{2}-1, \frac{N}{2}-2, \ldots,$$

are equal to differences of consecutive binomial coefficients

$$C_N^0, C_N^1 - C_N^0, C_N^2 - C_N^1, \ldots,$$

so, in the case $N=4$: 1 multiplet with max $S_Z=2$; 3 triplets with max $S_Z=1$, 2 singlets with $S_Z=0$.

For the case of N electrons we have: 1 multiplet with max $|S_Z|=N/2$, (C_N^1-1) multiplets with max $|S_Z|=N/2-1$, $(C_N^2-C_N^1)$ multiplets with max $|S_Z|=N/2-2$ and etc. The total number of multiplets is equal to the maximal binomial coefficients $C_N^{N/2}$ for even N, and $C_N^{(N+1)/2}$ for odd N. The number of configurations with the minimal spin is equal to $C_N^{N/2}-C_N^{(N/2)-1}$ for even N, and $C_N^{(N-1)/2}-C_N^{(N-1)/2-1}$ for odd N. Numbers C_N^k where $k=1,2,\ldots,N-1$, determine the order of the energy matrix in the CI method, describing electron terms of the system with the total spin projecction.

$$S_Z = -\frac{N}{2}+k.$$

So, at $N=4$ the secular equation of the 4-th order is obtained for $S_Z=-1$, the secular equation of 6-th order - at $S_Z=0$, one of 4-th order - at $S_Z=1$. After diagonalization of corresponding matrices one has to group the same eigenvalues and the LCC's related to them. By this method LCC will be gathered to multiplets with the given value S^2, that finishes the procedure of LCC calculation for electron states with the given values of the total spin values and its projection along the z-axis. So, the problem of electron multiplet construction is reduced to the diagonalization of CI matrices, taken for configurations with equal spin projections S_Z. Orders and the structure of these matrices are determined by the permutation symmetry of the electron system, and one can find them for the given basis of electron configurations Φ_k by means of the tree of electron configurations (Fig. 1). As the matrices mentioned possess a special structure, they should be considered in detail. For some particular cases the diagonalization of matrices of the CI method can be done analytically, therefore it is expedient to dwell on these cases and to yield some formulas which are important for application.

Considering all configurations with the same projection of the total spin S_Z, we see that all graphs with the same numbers of arrows "up" and "down" should be chosen from the electron configuration tree. Denote molecular orbitals by φ_i, where $i = 1, \dots, N$.

In Fig. 1 horizontal dashes to the left show orbital energy levels. For the case $N = 4$ there are 16 electron configurations Φ_k for a set of four molecular orbitals φ_1, φ_2, φ_3, φ_4, as it is seen from Fig. 1.

Now construct LCC (1) referring to the given projection of the total spin S_Z. To calculate the energy E and the LCC coefficients C_k of the electron system by the CI method, there is the system of linear equations

$$\sum_k C_k\left(\int \Phi_l \hat{\mathscr{H}} \Phi_k d\tau - E\delta_{lk}\right) = 0, \qquad l, k = 1, \dots, N, \tag{2}$$

where $\hat{\mathscr{H}}$ is the Hamiltonian of an atom or a molecule in the Born–Oppenheimer approximation, $d\tau$ is the volume element in the space of the coordinates of all electrons of the system, δ_{lk} is the Kronecker symbol.

The calculation of matrix elements of configurations is brought to the following result. Integrals of one-electron operators give the same contributions to diagonal matrix elements of configurations.

Diagonal two-electron integrals ($k = l$) of configurations are equal to the sum of Coulomb two-electron integrals J_{ij}, corresponding to all possible pairs of orbitals φ_i, φ_j, i.e. $J = \sum_{i>j=l}^{N} J_{ij}$ without exchange integrals $K_{i'j'}$, in which orbitals $\varphi_{i'}$, $\varphi_{j'}$ are chosen in accordance with the rule: in k-th configuration all possible combinations of two orbitals in subsets of orbitals, occupied by electrons with equal spins are taken. Nondiagonal matrix elements ($k \neq l$) are equal to exchange integrals, taken with "minus" sign, $-K_{ij}$ between orbitals φ_i and φ_j, numbers i, j being found by means of the rule: in k-th and l-th configuration orbitals with the same direction of spin arrows are crossed out; the remaining two orbitals give the desired numbers i and j; if the number of such pairs is larger than 2, the exchange integral is equal to 0. All mentioned rules result from the spin orthogonality of spin-orbitals.

Thus the total contribution of one-electron and two-electron Coulomb integrals to diagonal matrix elements are equal for all configurations and if they are subtracted from the energy E, the rest matrix keeps only exchange integrals, the sum of which in any row and any column of the matrix is the same. A matrix with this property is called convex.

It is known, that any convex matrix possesses the eigenvalue, which is equal to the sum of elements in a row, eigenvector $\boldsymbol{X} = \{n^{-1/2}, n^{-1/2}, \dots, n^{-1/2}\}$, where n is the matrix order. LCC for this eigenvalue is a component of the multiplet with the maximal spin value.

Thus, for any number of electrons the multiplet with maximal spin value can be constructed in an obvious way, without any matrix diagonalization.

All matrices of CI method for the given N electron configurations tree keep the same set of $N(N-1)/2$ exchange integrals. In Sect. 3 cases $N=2, 3$ and 4 will be discussed in detail and LCC will be found, which form all possible multiplets.

2. The closed core model

Consider the following model of the electron shell of an atom or a molecule. Regard n orbitals from which m low-lying orbitals φ_i are occupied by pairs of electrons with opposite spins, and $n-m$ high-lying orbitals are occupied by one electron. As the m low-lying orbitals are doubly degenerate, spins of the orbital electrons cannot have the same direction due to the Pauli principle so we can consider the closed core.

Thus, LCC of the closed core should be constructed not from the whole set of configurations with $S_Z=0$, but from those which correspond to the sum projection $S_Z=0$ for m low-lying orbitals φ_i. Moreover, the model in which the total spin of the core is 0, is realistic.

LCC, corresponding to the zero total spin of the core, can be written in an obvious form.

Now again turn to Fig. 1. For the core with $N=4$, one has $\varphi_1=\varphi_2$ and $\varphi_3=\varphi_4$. So basis configurations $\Phi_6, \Phi_7, \Phi_{10}, \Phi_{11}$ should be chosen. If LCCs are constructed in the form

$$\Psi_1=\frac{1}{\sqrt{2}}(\Phi_6-\Phi_7), \Psi_2=\frac{1}{\sqrt{2}}(\Phi_{10}-\Phi_{11}) \tag{3}$$

they shall correspond to zero total spin of pair of electrons on $\varphi_3=\varphi_4$.

It is obvious that linear combination of Ψ_1 and Ψ_2 will not change the total spin of this pair of electrons. Then for the LCC

$$\Psi=\frac{1}{\sqrt{2}}(\Psi_1-\Psi_2) \tag{4}$$

one obtains zero total spin for the remaining pair of electrons on orbitals $\varphi_1=\varphi_2$.

So, it is found the desired LCC

$$\Psi=2^{-1}(\Phi_6-\Phi_7-\Phi_{10}+\Phi_{11}) \tag{5}$$

which corresponds to $S^2=S_Z=0$.

For $2m$ core electrons, the LCC with $S^2=S_Z=0$ can be constructed, if one takes advantage of the following tree of electron configurations, given by Fig. 2.

Here the tree tiers mean, as usual, electron orbitals, however, now each orbital is occupied by two electrons with opposite spin.

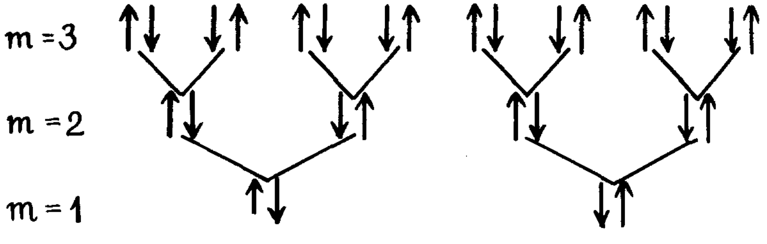

Fig. 2. The tree of electron configurations of a closed core

We begin to construct the LCC by combining configurations of the upper tier. For the pair of neighbor graphs, beginning, e.g. with the last pair on the left, we take the differences between configurations $\Phi_1-\Phi_2$, $\Phi_3-\Phi_4, \ldots, \Phi_{2^m-1}-\Phi_{2^m}$. In this case the zero total spin for the pair of electrons, occupying the m-th orbital, is obtained. Then at the $(m-1)$-th tier of the tree, we take the differences of the combinations which correspond to the neighbour graphs. We arrive at the following LCC: $\Phi_1-\Phi_2-(\Phi_3-\Phi_4)$, $\Phi_5-\Phi_6-(\Phi_7-\Phi_8), \ldots, \Phi_{2^m-3}-\Phi_{2^m-2}-(\Phi_{2^m-1}-\Phi_{2^m})$. This method is continued to the lower tier of the tree, the last action will be the substraction of the LCC corresponding to the right half of the tree from the LCC corresponding to the left half of the tree, so the LCC with zero total spin of the core will be obtained.

The general alternation of signs "+" and "−" before Φ_1, $\Phi_2, \ldots, \Phi_{2^m}$ can be obtained from the LCC, calculated consequently for $m=1,2,\ldots$. Note, that it is enough to find signs for the left (or right) half of the tree illustrated by Fig. 2. Normalized coefficients obtained in the LCC should be equal to $2^{-m/2}$.

Note, that other LCCs of the core, corresponding to $S^2=S_Z=0$ do not exist. Really, $\Phi_1+\Phi_2=0$ as orbitals for the pair of electrtons are the same and their antisymmetrical combinations are 0.

LCC for all electrons of the system, including both the core and the valent ones should be constructed beginning with LCC, obtained just now, for the zero total core spin. So, the total spin of the system will be determined by the valence electrons and for their number being no more than 4, the problem of LCC calculation corresponding to the given total spin, with the magnitude of maximal projection no more than 2, can be solved analytically.

The next problem consists in combining the LCC for given S^2 and S_Z, corresponding to the system energies, close enough to the energy of this state, that should be calculated. This problem is reduced to the numerical solution of a secular equation like (2), in which matrix elements are calculated not from configurations Φ_i, but from $(\mathrm{LCC})_i$ for the given S^2 and S_Z. Call LCC for the given S^2 and S_Z by spin-configuration (SC). Then, a wave function of an atom or a molecule, constructed by the method mentioned above is the lilnear combination of spin-configurations (LCSC). A LCSC function is transformed by a representation of S^2 and S_Z.

Solving the equation of the method of LCSC numerically, we get a series of terms, describing the states of a system with definite values of S^2 and S_Z. Transitions between terms can be classified in series in which $\Delta S = 0, \pm 1$ and etc.

Taking into consideration the system space symmetry, one can classify both terms and spectra over the irreducible representations of the corresponding group of symmetry, as a result the matrix of the LCSC method for defined S^2 and S_Z will be separated into blocks belonging to the types of the representations of the symmetry group.

3. The calculation of SC for 2, 3 and 4 electrons

$N = 2$. This case is simple, however, it is expedient to begin with the consideration of this very case of two electron, occupying different orbitals.

The electron configurations are illustrated by Fig. 3. Configurations Φ_1 and Φ_2 are components of multiplets for spin $S = 1$, with projections $S_Z = +1$ and $S_Z = -1$ correspondingly. Energies of these configurations are degenerate and equal to $E + J_{12} - K_{12}$, where E is the configuration energy without taking electron-electron interaction into account, J_{12} is the Coulomb two-electron integral, K_{12} the two-electron exchange integral. The remaining configurations Φ_3 and Φ_4 lead to a matrix of the second order like

$$\begin{bmatrix} E+J_{12} & K_{12} \\ K_{12} & E+J_{12} \end{bmatrix} \tag{6}$$

which has eigenvalues $E+J_{12}-K_{12}$ and $E+J_{12}+K_{12}$ and eigenvectors $(2^{-1/2}, 2^{-1/2})$ and $(2^{-1/2}, -2^{-1/2})$, correspondingly. These two LCCs correspond to energies $E+J_{12}-K_{12}$ and $E+J_{12}+K_{12}$. Thus, the first eigenvalue belongs to the triplet and the second one should belong to the singlet, which both have the same spin projections $S_Z = 0$.

$$E_1 = E + J_{12} - K_{12}, \Psi_1 = \Phi_1;\ S_Z = 1;$$

$$E_2 = E + J_{12} - K_{12}, \Psi_2 = \Phi_2;\ S_Z = -1;$$

$$E_3 = E + J_{12} - K_{12}, \Psi_3 = 2^{-1/2}(\Phi_3 + \Phi_4),\ S_Z = 0;$$

$$E_4 = E + J_{12} + K_{12}, \Psi_4 = 2^{-1/2}(\Phi_3 - \Phi_4),\ S_Z = 0.$$

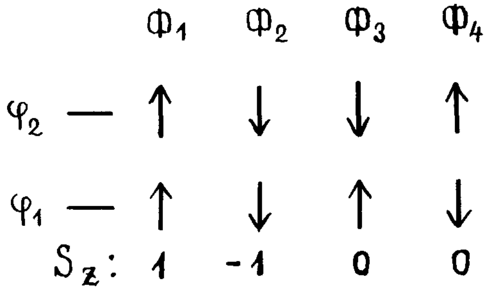

Fig. 3. Electron configurations for 2 electrons

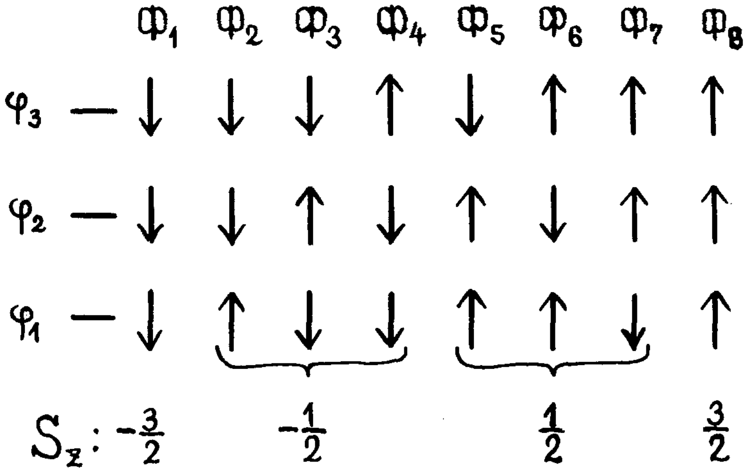

Fig. 4. Electron configurations for 3 electrons

The first three rows correspond to the components of the spin triplet, and the last row corresponds to the spin singlet. As $K_{12}>0$ hence $E_{\text{sing}}>E_{\text{tr}}$ and Hund's rule is valid, which says, that electron states with greater total spin have less energy than states with less total spin.

Hund's rule can be broken if several singlet LCC's are combined.

$N=3$. Now take the tree of configurations up to the third tier of arrows.

Fig. 4 shows that for the system of three electrons there are 1 quartet and 2 doublets.

While constructing LCC's we arrive at two secular equations of third order with identical matrices of the following type

$$A=\begin{bmatrix} J-K_{12} & -K_{23} & -K_{13} \\ -K_{23} & J-K_{13} & -K_{12} \\ -K_{13} & -K_{12} & J-K_{23} \end{bmatrix}=\begin{bmatrix} J & 0 & 0 \\ 0 & J & 0 \\ 0 & 0 & J \end{bmatrix}-\begin{bmatrix} K_{12} & K_{23} & K_{13} \\ K_{23} & K_{13} & K_{12} \\ K_{13} & K_{12} & K_{23} \end{bmatrix} \tag{8}$$

where $J=J_{12}+J_{13}+J_{23}$.

The special structure of this matrix makes it possible to find its eigenvalues in analytical form:

$$\begin{aligned} E_1&=J-K_{12}-K_{23}-K_{13} \\ E_2&=J-(K_{12}^2+K_{13}^2+K_{23}^2-K_{12}K_{13}-K_{12}K_{23}-K_{13}K_{23})^{1/2} \\ E_3&=J+(K_{12}^2+K_{13}^2+K_{23}^2-K_{12}K_{13}-K_{12}K_{23}-K_{13}K_{23})^{1/2}. \end{aligned} \tag{9}$$

The corresponding eigenvectors are $C_1=\{3^{-1/2}, 3^{-1/2}, 3^{-1/2}\}$;

$$C_2=\{2\cdot 6^{-1/2}e_1;\ -6^{-1/2}e_1+2^{-1/2}e_2;\ -6^{-1/2}e_1-2^{-1/2}e_2\},$$

$$C_3=\{2\cdot 6^{-1/2}e_3;\ -6^{-1/2}e_3+2^{-1/2}e_4;\ -6^{-1/2}e_3-2^{-1/2}e_4\}$$

where

$$e_1=(t+\lambda^{1/2})(U^2+(t+\lambda^{1/2})^2)^{-1/2}; \qquad e_2=U(U^2+(t+\lambda^{1/2})^2)^{-1/2};$$

$$e_3=(t-\lambda^{1/2})(U^2+(t-\lambda^{1/2})^2)^{-1/2}; \qquad e_4=U(U^2+(t-\lambda^{1/2})^2)^{-1/2};$$

$$t=K_{12}-0.5(K_{23}+K_{13}); \qquad U=0.5\cdot 3^{1/2}(K_{23}-K_{13}),$$

$$\lambda=K_{12}^2+K_{13}^2+K_{23}^2-K_{12}K_{13}-K_{12}K_{23}-K_{13}K_{23}.$$

The wave functions $\Psi_i^{(1/2)}$ for the projection of the total spin $S_Z=\frac{1}{2}$ can be constructed as the scalar product of the vectors C_i with the vector $\Phi=\{\Phi_2, \Phi_3, \Phi_4\}$, i.e. $\Psi_i^{(1/2)}=C_i\cdot\Phi$, $i=1, 2, 3$. The analogous result is obtained for projections of the total spin $S_Z=-\frac{1}{2}$ after replacements $\Phi_2\to\Phi_7$, $\Phi_3\to\Phi_6$ and $\Phi_4\to\Phi_5$.

Functions like $\Psi_1^{(\pm 1/2)}$ together with the configurations Φ_1 and Φ_8 belong to the quartet with the total spin $S=3/2$. Functions like $\{\Psi_2^{(1/2)}, \Psi_2^{(-1/2)}\}$, $\{\Psi_3^{(1/2)}, \Psi_3^{(-1/2)}\}$ are two doublets with the total spin $S=1/2$. Thus, all SC's for the case of three electrons are found.

$N=4$. By means of the tree, illustrated by Fig. 1, one obtains the following configurations for 4 electrons, shown in Fig. 5 (the indices of Φ's do not coincide with those in Fig. 1). There are 1 quantet, 3 triplets, 2 singlets. The configurations Φ_1 and Φ_{16} belong to the quintet. For total spin projections $S_Z=1$ and $S_Z=-1$ we arrive at the identical matrices of 4-th order

$$A_4(S_Z=1,-1) = \begin{bmatrix} J-K_{12}-K_{13}-K_{23} & -K_{34} & -K_{24} & -K_{14} \\ -K_{34} & J-K_{12}-K_{14}-K_{24} & -K_{23} & -K_{13} \\ -K_{24} & -K_{23} & J-K_{13}-K_{14}-K_{34} & -K_{12} \\ -K_{14} & -K_{13} & -K_{12} & J-K_{23}-K_{24}-K_{34} \end{bmatrix} \qquad (11)$$

where $J=\sum_{j>i=1}^{4} J_{ij}$.

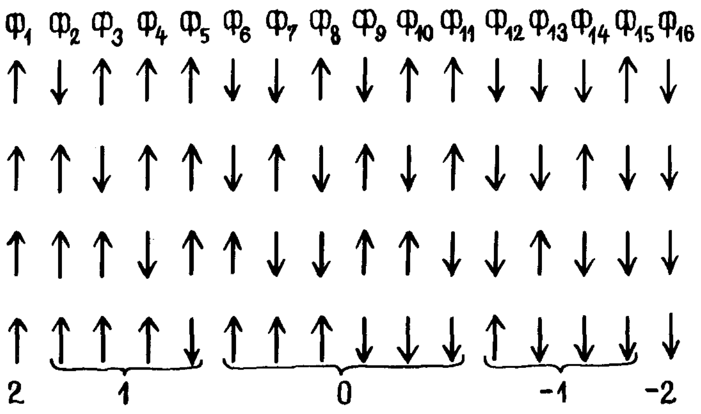

Fig. 5. Electron configurations for 4 electrons

The rows and columns of the matrix (11) correspond to configurations Φ_2, Φ_3, Φ_4, Φ_5 or Φ_{12}, Φ_{13}, Φ_{14}, Φ_{15}. By means of the orthogonal transformation

$$C_4 = \tfrac{1}{2}\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 \end{bmatrix} \tag{12}$$

the matrix (11) is reduced to the block type

$$\tilde{C}_4 A_4 C_4 = \begin{bmatrix} J-K & 0 & 0 & 0 \\ 0 & J-K_{12}-K_{34} & K_{24}-K_{13} & K_{14}-K_{23} \\ 0 & K_{24}-K_{13} & J-K_{23}-K_{14} & K_{34}-K_{12} \\ 0 & K_{14}-K_{23} & K_{34}-K_{12} & J-K_{13}-K_{24} \end{bmatrix} \tag{13}$$

where $K = \sum_{j>i=1}^{4} K_{ij}$.

Eigenvalue $(J-K)$ belongs to the quintet, corresponding eigenvector being $\{\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\}$.

After diagonalization of the rest block of 3-rd order of the matrix (13) we shall obtain eigenvectors, related to 3 triplets with different energies.

To calculate LCC's corresponding to $S_Z = 0$, we have to diagonalize the matrix of 6-th order

$$A_6(S_Z=0) = \begin{bmatrix} J-K_{12}-K_{34} & -K_{23} & -K_{24} & -K_{13} & -K_{14} & 0 \\ -K_{23} & J-K_{13}-K_{24} & -K_{34} & -K_{12} & 0 & -K_{14} \\ -K_{24} & -K_{34} & J-K_{14}-K_{23} & 0 & -K_{12} & -K_{13} \\ -K_{13} & -K_{12} & 0 & J-K_{14}-K_{23} & -K_{34} & -K_{24} \\ -K_{14} & 0 & -K_{12} & -K_{34} & J-K_{13}-K_{24} & -K_{23} \\ 0 & -K_{14} & -K_{13} & -K_{24} & -K_{23} & J-K_{12}-K_{34} \end{bmatrix}. \tag{14}$$

The rows and the columns of the matrix (4) correspond to configurations Φ_6, Φ_7, Φ_8, Φ_9, Φ_{10}, Φ_{11}.

By means of an orthogonal transformation of type

$$C_6 = (\tfrac{1}{2})^{1/2}\begin{bmatrix} 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & -1 & 0 & 0 \end{bmatrix} \tag{15}$$

the matrix (14) is reduced to the block type:

$$\tilde{C}_6 A_6 C_6 = \left[\begin{array}{cccccc} J-K_{12}-K_{34} & -K_{23}-K_{14} & -K_{24}-K_{13} & & & \\ -K_{23}-K_{14} & J-K_{13}-K_{24} & -K_{34}-K_{12} & & 0 & \\ -K_{24}-K_{13} & -K_{34}-K_{12} & J-K_{14}-K_{23} & & & \\ & & & J-K_{12}-K_{34} & K_{24}-K_{13} & K_{14}-K_{23} \\ & 0 & & K_{24}-K_{13} & J-K_{14}-K_{23} & K_{34}-K_{12} \\ & & & K_{14}-K_{23} & K_{34}-K_{12} & J-K_{13}-K_{24} \end{array}\right] \quad (16)$$

The matrix (16) is broken up into two blocks of the third order. The lower block coincides with the lower block of the matrix (13) and hence describes the components of 3 triplets, corresponding to the projection of the total spin $S_Z = 0$.

The upper block of the matrix (16) has the structure of the matrix (8), therefore it can be diagonalized by an analogous method, and formulas like (9), (10) can be obtained for eigenvalues and eigenvectors.

Eigenvalue $E_1 = J - \sum_{j>i=1}^{4} K_{ij}$ and eigenvector $C_1 = \{3^{-1/2}, 3^{-1/2}, 3^{-1/2}\}$ are a quintet component for which $S_Z = 0$. The remaining two SC's of this block describe 2 singlets with $S^2 = 0$ and $S_Z = 0$.

In the arbitrary case of N electrons it is also possible to reduce secular equations to blocks relating to the definite projections of the total spin S_Z. However, the least order of blocks is $N-1$. A further simplification of the structure of the rest matrices of large orders can be obtained neglecting small exchange integrals.

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