Permutation Symmetry Control: Higher-order Permutations in the Valence Bond Method

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Summary The application of the Valence Bond method to the theoretical description of concerted reactions furnishes an example of the importance of higher-order permutations.

WHEN applying Valence Bond theory to chemical problems, two main approaches may be considered. The first one is to use a basis of orthogonalized atomic orbitals.[1] It has the advantage of yielding simple matrix elements but necessitates the inclusion of a great number of ionic structures because chemical binding is now dependent on the interaction of structures which differ from each other by electron shifts between neighbouring atoms. In the analysis of the mechanism of concerted reactions by this method, van der Lugt and Oosterhoff[2] found that even the completely ionic structures were needed to obtain the correct selection rules for these processes. The second approach utilizes a basis of non-orthogonal atomic orbitals where one might expect that highly ionic structures are less important and that even a restriction to covalent structures should offer a reasonable description of chemical phenomena. Now it becomes a difficult problem, however, to estimate the importance of the many higher-order permutations which yield non-zero matrix elements. In the treatment of concerted reactions with this second method, using only covalent structures, we have obtained the surprising result that indeed only the inclusion of the highest-order permutations enables to differentiate between the two modes of reaction.

As has been discussed in the preceding communication,[3] one uses the hypothesis that the transition state in a concerted reaction can be described by a wave-function which is a linear combination of two covalent Kekulé-type structure functions ψ_A and ψ_B, that participate equally:

$$\psi^+ = (\psi_A + \psi_B)/N^+ \qquad (1)$$

A second function pertains to an excited state belonging to the transition state configuration:

$$\psi^- = (\psi_A - \psi_B)/N^- \qquad (2)$$

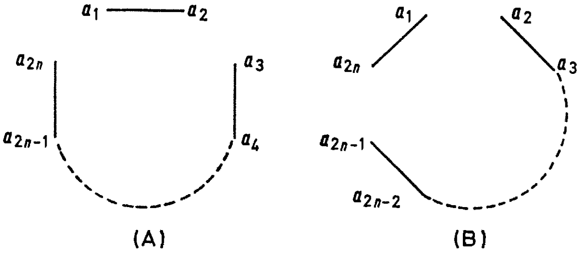
Using a set of non-orthogonal atomic orbitals $a_1, a_2, \cdots \cdot a_{2n}$

the Valence Bond functions corresponding to the structures A and B (Figure) are constructed in the standard fashion:

$$\psi_{\mathrm{A}} = \sum_P \epsilon_P P a_1(1)a_2(2) \cdots\cdots a_{2n}(2n) \quad [12][34]\cdots\cdots[2n-1\ 2n] \tag{3}$$

$$\psi_{\mathrm{B}} = \sum_P \epsilon_P P a_1(1)a_2(2) \cdots\cdots a_{2n}(2n) \quad [1\ 2n][2n-1\ 2n-2]\cdots\cdots[32] \tag{4}$$

The summations include all $2n!$ permutations P each with parity $\epsilon_P = \pm 1$, depending on whether P is even or odd. The spin functions are denoted as products of bond singlets $[ij] = 2^{-\frac{1}{2}}\,[\alpha(i)\beta(j) - \beta(i)\alpha(j)]$.



FIGURE

Continuing the analysis we write:

$$\psi^{\mp} = \sum_P \epsilon_P P u \chi^{\mp} \tag{5}$$

In this shorthand notation, u stands for the orbital product which is the same for ψ^+ and ψ^- and $\chi^{\mp}$ is an appropriate spin-function—taken to be normalised—which we will consider later. For the moment we suppress the $\mp$ index. The expectation value of the Hamiltonian becomes:

$$U = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_P \langle Pu|H|u\rangle \epsilon_P \langle P\chi|\chi\rangle}{\sum_P \langle Pu|u\rangle \epsilon_P \langle P\chi|\chi\rangle} \tag{6}$$

The influence of the permutations in the matrix elements is most conveniently discussed first starting from a consideration of the element $\langle Pu|u\rangle$, which can be represented by the following scheme:

$$\begin{pmatrix} Pa_1(1)a_2(2)\cdots\cdots a_{2n}(2n) \\ a_1(1)a_2(2)\cdots\cdots a_{2n}(2n)\end{pmatrix} = \begin{pmatrix} a_1(i)a_2(j)\cdots\cdots a_{2n}(r) \\ a_1(1)a_2(2)\cdots\cdots a_{2n}(2n)\end{pmatrix} = S_{1i}S_{2j}\cdots\cdots S_{2n,r} \tag{7}$$

where S_{pq} = atomic orbital overlap integral and $S_{kk} = 1$. If the usual approximation of neglect of non-neighbour overlap integrals is invoked, systematic inspection of the possible permutations shows that three types of permutations give non-zero matrix elements:

(i) the identity: $\langle Pu|u\rangle = \langle u|u\rangle = 1$

(ii) permutations that are simple transpositions of electron numbers on neighbouring orbitals or products of these transpositions having no numbers in common:

$$\langle Pu|u\rangle = S_{12}^2, \cdots, S_{12n}^2, S_{12}^2S_{34}^2, \cdots\cdots, \cdots\cdots, S_{23}^2S_{45}^2S_{67}^2\cdots\cdots S_{12n}^2$$

(iii) two cyclic permutations of order $2n$, in cycle notation $(1\ 2\ 3\cdots\cdots 2n)$ and $(2n\ 2n-1\cdots\cdots 1)$:

$$\langle Pu|u\rangle = S_{12}S_{23}S_{34}\cdots\cdots S_{2n-12n}S_{12n}$$

In the study of the reaction modes in concerted reactions the essential difference between two modes is the number of negative overlap integrals, odd in one mode and even in the other. Clearly only the two cyclic permutations (iii) differentiate between the modes. Regarding the elements $\langle Pu|H|u\rangle$ the same distinction is obtained, provided that a positive element $\langle a_p(i)|h_i|a_q(i)\rangle$ is associated with a negative S_{pq} and,—in agreement with the Mulliken approximation—the matrix element $\langle a_p(i)a_r(j)|e^2/r_{ij}|a_q(i)a_s(j)\rangle$ has the same sign as the overlap integral product $S_{pq}S_{rs}$.† To implement these arguments in the total energy expression (6) the summation over all the permutations is split up into two parts, the sum Σ' which pertains to the permutations (i) and (ii) and the sum over the two cyclic permutations. We substitute:

$$U_i = \sum_P{}' \langle Pu|H|u\rangle \epsilon_P \langle P\chi|\chi\rangle \tag{8}$$

$$S_i = \sum_P{}' \langle Pu|u\rangle \epsilon_P \langle P\chi|\chi\rangle \tag{9}$$

The index i refers to the fact that these expressions are *independent* of the occurrence of negative overlap integrals. We denote the *cyclic* permutations by C and we assume that there are ν negative overlap integrals.

$$\langle Cu|H|u\rangle = (-1)^{\nu} U_c \tag{10}$$

$$\langle Cu|u\rangle = (-1)^{\nu} S_c \tag{11}$$

Here $U_c < 0$ and $S_c > 0$ are introduced as the result of the application of either one or the other *cyclic* permutation. With these substitutions the energy becomes:

$$U = \frac{U_i + (-1)^{\nu}\cdot 2U_c\cdot\epsilon_C\langle C\chi|\chi\rangle}{S_i + (-1)^{\nu}\cdot 2S_c\cdot\epsilon_C\langle C\chi|\chi\rangle} \tag{12}$$

We now examine the effect of the cyclic permutations on the spin functions.

$$\chi_{\mathrm{A}} = [12][34]\cdots\cdots[2n-1\ 2n] \tag{13}$$

$$\chi_{\mathrm{B}} = [12n][2n-1\ 2n-2]\cdots\cdots[32] \tag{14}$$

Evidently:

$$C\chi_{\mathrm{A}} = (-1)^n\chi_{\mathrm{B}} \text{ and } C\chi_{\mathrm{B}} = (-1)^n\chi_{\mathrm{A}} \tag{15}$$

This yields:

$$C\chi^+ = C\chi_{\mathrm{A+B}} = (-1)^n\chi^+ \text{ and } C\chi^- = C\chi_{\mathrm{A-B}} = -(-1)^n\chi^- \tag{16}$$

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† A general discussion of matrix elements between antisymmetrized products of non-orthogonal basis orbitals has been given by Prossor and Hagstrom.[4]

For a cyclic permutation of order $2n$ one has $\epsilon_C = -1$ and thus one obtains the final energy expression:

$$U^{\mp} = \frac{U_i^{\mp} \pm (-1)^{n+\nu} \cdot 2U_c^{\mp}}{S_i^{\mp} \pm (-1)^{n+\nu} \cdot 2S_c^{\mp}} \tag{17}$$

It may be of interest to remark that χ_{A+B} and χ_{A-B} are eigenfunctions of the operator C, which commutes with H. Therefore if the spinfunctions χ_A and χ_B would not suffice to describe the transition state but other spin functions should be added—like Dewar structures in benzene—these can only combine if they belong to the same eigenvalue of $C: \pm 1$. The form of (17) would in that case not be changed.

As has been discussed in the preceding communication,[3] equation (17) demonstrates the combined influence of the number n of electron pairs and the number ν of negative overlap integrals on the energy of the transition state in a concerted reaction. From the point of view of the application of the VB method it is most interesting that this result could only be obtained including permutations of the highest order.

Concerning the neglect of ionic structures, their effect can be included to a large extent in the covalent structures by means of a transformation of the atomic orbitals before the construction of the structure wave-functions. The transformation should be such as to cause a heavier non-orthogonality between neighbouring orbitals without increasing the non-orthogonality between non-neighbours. One possibility is a basis $\boldsymbol{\alpha}'$ obtained by operating with the matrix $\mathbf{S}^{+\frac{1}{2}}$ on the original atomic orbital basis.[1b]

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[3] J. J. C. Mulder and L. J. Oosterhoff, preceding communication.

[4] F. Prosser and S. Hagstrom, *Internat. J. Quantum Chem.*, 1968, **2**, 89.