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Alternant and Non-Alternant Systems; Valence Bond Analysis

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The properties of the complete CI-matrix in a VB-formalism based on orthogonal(ized) orbitals allow for a direct demonstration of the difference between alternant and non-alternant systems, including the radical ions, carbenions and carbanions derived from them.

Key word: Alternant and non-alternant systems, VB analysis of ~

1. Introduction

After its introduction by McWeeny [1–3], the valence-bond method based on orthogonal(ized) orbitals has been used i.a. by Amos [4] and by van der Lugt and Oosterhoff [5]. The extreme simplicity of the energy matrix in this formalism has been noted, but this advantage can only be exploited if the ZDO-approximation is employed and a full CI-treatment is performed.

Here we propose to use the structural characteristics of the full CI-matrix based on all possible Slater-determinants of a specified S_z eigenvalue, that can be formed from the available orbitals, to elucidate in a direct way the consequences of the difference between alternant and non-alternant systems. Although proofs have been given previously, notably by Weyland [6] and McLachlan [7], the attractive feature of the VB-analysis is its demonstration that the signs of matrix elements control the situation. This may help to explain the fact that the alternant properties, which on first sight seem to be dependent on a particular approximation, are to a remarkable degree verified experimentally.

Although Cooper [8] has shown that the VB-method based on orthogonal (ized) orbitals can be used to prove the correspondence between the positive and negative radical ions of alternant hydrocarbons, his objective was different from ours. His analysis was directed at the integral approximations and the modifications necessary to obtain different results for the positive and negative ions. We wanted to show in a direct way the consequences of the structural difference between alternant and non-alternant hydrocarbons.

2. Construction of the Slater Determinants

We consider N atomic centers, each contributing one atomic orbital. Regarding the number of electrons we will investigate two cases: $N-a$ electrons and $N+a$ electrons. The eigenvalues of S_z will be denoted by $\pm s$, and we are lead to:

Case I: $\dfrac{N-a}{2}+s$ α-spins and $\dfrac{N-a}{2}-s$ β-spins.

Case II: $\dfrac{N+a}{2}-s$ α-spins and $\dfrac{N+a}{2}+s$ β-spins.

The number of possible Slater determinants becomes [9]:

$$\binom{N}{\dfrac{N-a}{2}+s}\binom{N}{\dfrac{N-a}{2}-s} \equiv \binom{N}{\dfrac{N+a}{2}-s}\binom{N}{\dfrac{N+a}{2}+s}.$$

The orbitals in the Slater determinants will be ordered according to increasing index and the α-spinorbitals preceding the β-spinorbitals. The order of the determinants follows from taking successive combinations for the β-spinorbitals for each possible combination of the α-spinorbitals.

It follows from inspection of Table 1 that the first determinant of Case I is complemented by the last determinant of Case II in such a way that the two determinants have no orbitals in common and together fully exhaust the available orbital basis, once in the α-spin sets and once in the β-spinsets. This will be true for each pair of determinants going down the table for Case I and going up for Case II. We will consider the matrix elements between these sets of Slater determinants (within Cases I and II) in the next section.

3. Matrix Elements

If two determinants have the property that they contain mutually exclusive sets of orbitals they will describe exactly opposite charge distributions. Taking the diagonal elements of one pair of such determinants (preferably the least polar ones) as reference we will assume that each other pair will have an equal spacing in energy from these reference diagonal elements. This means then that the diagonal elements in Case I going down in Table 1 and in Case II going up will all be equally spaced.

Invoking the ZDO approximation we immediately verify that the off-diagonal elements will either be zero or equal to a single one-electron integral (β) in the case of one spinorbital difference. When considering these matrix elements we need only look at either the α-spinset or the β-spinset because the other set must be identical in the two determinants whose matrix element we are calculating.

Case I: $abc\ldots i\ldots \underset{j}{\bigcirc}\ldots stu$ with $abc\ldots \underset{i}{\bigcirc}\ldots j\ldots stu$.

The one-spinorbital difference is in the orbitals i and j; if we assume p orbitals present between i and j the matrix element will be $(-1)^{p+1}\beta_{ij}$.

Case II: $a'b'c'\ldots \underset{i}{\bigcirc}\ldots j\ldots s't'u'$ with $a'b'c'\ldots i\ldots \underset{j}{\bigcirc}\ldots s't'u'$.

We now meet two possibilities; the total number of orbitals between i and j may be $2r$ or $2r+1$ and therefore the matrix element is either $(-1)^{2r-p+1}\beta_{ij}$ or $(-1)^{2r-p+2}\beta_{ij}$. Thus the matrix elements between two determinants in Case I and between their complementary determinants in Case II are either equal or equal with opposite sign. Summarizing, we have obtained:

Table 1.

Case I α	β
$1\ 2\ 3\ \cdots\cdots\ \frac{N-a}{2}+s-1,\ \frac{N-a}{2}+s$	$1\ 2\ \cdots\cdots\ \frac{N-a}{2}-s-1,\ \frac{N-a}{2}-s$
$1\ 2\ 3\ \cdots\cdots\ \frac{N-a}{2}+s-1,\ \frac{N-a}{2}+s$	$1\ 2\ \cdots\cdots\ \frac{N-a}{2}-s-1,\ \frac{N-a}{2}-s+1$
$\vdots$	$\vdots$
$\frac{N+a}{2}-s+1,\ \frac{N+a}{2}-s+2,\ \cdots\cdots\ N-1,\ N$	$\frac{N+a}{2}+s,\ \frac{N+a}{2}+s+2,\ \cdots\cdots\ N-1,\ N$
$\frac{N+a}{2}-s+1,\ \frac{N+a}{2}-s+2,\ \cdots\cdots\ N-1,\ N$	$\frac{N+a}{2}+s+1,\ \frac{N+a}{2}+s+2,\ \cdots\cdots\ N-1,\ N$
Case II α	β
$1\ 2\ 3\ \cdots\cdots\ \frac{N+a}{2}-s-1,\ \frac{N+a}{2}-s$	$1\ 2\ \cdots\cdots\ \frac{N+a}{2}+s-1,\ \frac{N+a}{2}+s$
$1\ 2\ 3\ \cdots\cdots\ \frac{N+a}{2}-s-1,\ \frac{N+a}{2}-s$	$1\ 2\ \cdots\cdots\ \frac{N+a}{2}+s-1,\ \frac{N+a}{2}+s+1$
$\vdots$	$\vdots$
$\frac{N-a}{2}+s+1,\ \frac{N-a}{2}+s+2,\ \cdots\cdots\ N-1,\ N$	$\frac{N-a}{2}-s,\ \frac{N-a}{2}-s+2,\ \cdots\cdots\ N-1,\ N$
$\frac{N-a}{2}+s+1,\ \frac{N-a}{2}+s+2,\ \cdots\cdots\ N-1,\ N$	$\frac{N-a}{2}-s+1,\ \frac{N-a}{2}-s+2,\ \cdots\cdots\ N-1,\ N$

a) $2r$ orbitals between i and j; this means the orbital indices of i and j are of opposite parity, one is even and the other odd:

$$\text{Matrixelement (I)} = \text{Matrixelement (II)}.$$

b) $2r+1$ orbitals between i and j; this means the orbital indices of i and j are of equal parity, both even or both odd:

$$\text{Matrixelement (I)} = -\text{Matrixelement (II)}.$$

From the foregoing it will be clear that for an alternant system (only odd-even interactions) the matrices for Cases I and II are equal but for a constant difference in the diagonal elements. In a non-alternant system we have at least one odd-odd or even-even interaction and we get an off-diagonal sign difference.

4. Exemplification of Cases I and II

(1) $a \neq 0$: Case I represents a positive ion and Case II the corresponding negative ion. If the parent molecule was alternant we obtain equal energy differences for all the states of the two systems, exactly opposite charge distributions and equal spindistributions if the number of electrons is odd.

(2) $a = 0$: The two cases become identical and we have a neutral system. If this system is alternant the energy matrix will be symmetric around the secondary diagonal. The result will be a uniform charge distribution and the occurrence of states in pairs form the complementary determinants. The odd-odd and even-even interactions present in a non-alternant molecule will manifest themselves in matrixelements with opposite sign on positions symmetrical with respect to the secondary diagonal and special properties will disappear.

5. Conclusion

Once again [10] a valence-bond analysis shows the signproducing property characteristic of permutations. In this case it is the so-called "line up" permutation that controls the situation. The elegant – admittedly qualitative – way in which valence-bond arguments can be made operative, leads us to believe that further exploration of the method, possibly in different versions, is fully warranted.

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