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Multiplicity of the Ground State of Large Alternant Organic Molecules with Conjugated Bonds

(Do Organic Ferromagnetics Exist?)

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The multiplicity and the full spin of the ground state of large alternate molecules with conjugated bonds are considered. It is strictly shown that if the numbers of starred and unstarred atoms (say, carbon) differ from each other the full spin of the molecule is more than zero. Some possible planar and linear molecules having the full spin to be proportional to their sizes are presented. Particularly, they would be ferromagnets at infinite sizes.

Key words: Organic molecules, large alternant ~

1. Introduction

It is well known that alternant hydrocarbons have a number of outstanding chemical and physical properties, particularly, high thermochemical stability. We may recall that a conjugate system is called an alternant one if its atoms can be subdivided into two groups, denoted by (A^+) and (A), respectively, so that each atom A^+ is surrounded only by A atoms, and vice versa. These properties of alternant hydrocarbons are readily apparent from a consideration of such systems within the framework of the Hückel method. In particular, the parity theorem is valid, according to which the Hückel orbital energies are symmetrical with respect to a certain energy equal to the Coulomb integral in the MO method. In alternant hydrocarbons the charge is uniformly distributed throughout the molecule, which results in a very insignificant (or zero, in case of symmetry) dipole moment. Proof of these theorems and their corollaries can be found in Dewar's book [1].

One interesting class of alternant hydrocarbons is represented by molecules in which the number of A and A^+ atoms is unequal. It is found that the ground state of these molecules displays high multiplicity, i.e. their total spin S is positive and equals:

$$S=\frac{|n_A-n_{A^+}|}{2}, \tag{1}$$

where n_A and n_{A^+} are the numbers of carbon atoms in groups A and A^+, respectively. One consequence of this is that a polymer molecule of the type shown in Fig. 1 has a total spin proportional to the number of chain links (X being some divalent atom, such as O, S, etc.), i.e. exhibits ferromagnetism.

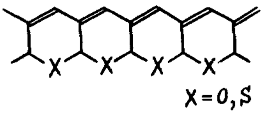

Fig. 1. Macromolecule having a resultant spin proportional to its length

It is impossible to prove the assertion expressed by Eq. (1) by any one-electron method whatsoever (including the Hückel method). For this reason, the present paper is devoted to a treatment of this case within the more realistic framework of the valence bond method. In [2] Bulaevsky has shown that the valence bond method is a very accurate means of describing conjugate hydrocarbons if the system's ground state and the lowest quasihomeopolar excited states are considered. He derived an expression for the exchange integral in terms of the parameters of the Pariser-Parr-Pople Hamiltonian [3]. Thereby, investigation of any conjugate system is reduced to a study of the corresponding Heisenberg Hamiltonian spectrum of the molecule:

$$H=\sum_{l(l')} J_{l,l'}(S_l S_{l'}-\tfrac{1}{4}), \qquad (2)$$

where S_l is a spin operator (of spin 1/2) of the carbon atom with subscript l. Summation includes only the nearest neighbours; $J_{l,l'}$ are exchange integrals, their magnitude depending on the length of the chemical bond between two adjacent atoms l and l'; non-neighbour exchange integrals are small. It is essential that all $J_{l,l'}>0$ (i.e. the bonds between atoms are antiferromagnetic).

The exchange integral $J_{l,l'}$ for two neighbour atoms can be expressed in terms of the parameters of a Pariser-Parr-Pople Hamiltonian:

$$J_{1,2}=\tfrac{1}{2}[\sqrt{(\gamma_{11}-\gamma_{12})^2+16\beta^2}-(\gamma_{11}-\gamma_{12})],$$

where β_{12} is a resonance integral; γ_{11} and γ_{12} are Coulomb integrals for a hydrocarbon molecule.

In Sect. 2 we shall prove for Hamiltonian (2) an important theorem of nondegeneracy (i.e. uniqueness) of the lowest state with respect to energy with a given S_z-projection of the total spin upon the z-axis, as well as Eq. (1). We shall then consider a few examples of determining multiplicity in simple radical molecules. And finally, in Sects. 4 and 5 we shall describe a number of possible types of planar and linear conjugate magnetic systems with heteroatoms.

2. Nondegeneracy of Ground State in Alternant Systems

We shall now demonstrate that the lowest energy state with a given S_z for Hamiltonian (2) is nondegenerate by the method suggested by Lieb, Schultz and Mattis in [4], except that the Hamiltonian is here somewhat more general, namely:

$$H'=\tfrac{1}{2}\sum_{l,l'} J^{(1)}_{l,l'}(S^+_l S^-_{l'}+S^-_l S^+_{l'})+\sum_{l,l'} J^{(2)}_{l,l'}S^z_l S^z_{l'}. \tag{3}$$

For $J^{(1)}_{l,l'}=J^{(2)}_{l,l'}=J_{l,l'}$ Eq. (3) reduces to Eq. (2). We require, however, that all $J^{(1)}_{l,l'}$ and $J^{(2)}_{l,l'}$ are positive.

$$S^+_l=S^x_l+iS^y_l, \qquad S^-_l=S^x_l-iS^y_l. \tag{4}$$

If $J^{(1)}_{l,l'}=0$, Hamiltonian (3) becomes an Ising Hamiltonian with easily determinable eigenfunctions and eigenvalues, since all S^z_l are commutable with the Hamiltonian. Therefore, S^z_l can be regarded as numbers ($\frac{1}{2}$ or $-\frac{1}{2}$), and $S^z_l S^z_{l'}=\frac{1}{4}$ if the spins of adjacent atoms are unidirectional, and equal to $-\frac{1}{4}$ if the spins are oppositely directed. To determine the lowest state energy, a spin configuration should be chosen such that:

$$\sum_{l,l'} J^{(2)}_{l,l'}S^z_l S^z_{l'} \tag{5}$$

is minimum. Since all $J^{(2)}_{l,l'}>0$, the spin distribution in an alternant molecule corresponding to the lowest energy value is when all the atoms of group A^+ have $S^z_l=\frac{1}{2}$ (upward spin), and the atoms of group A have $S^z_l=-\frac{1}{2}$ (downward spin), or vice versa. Indeed, in that case all the terms in (5) will be negative. Consequently, the ground state will correspond to a total projection S_z equal to

$$S^z=\frac{|n_A-n_{A^+}|}{2}. \tag{6}$$

If the lowest state is nondegenerate, it means that for any variation of exchange integrals $J^{(1)}_{l,l'}$ and $J^{(2)}_{l,l'}$ (but such that $J^{(1)}_{l,l'}>0$, $J^{(2)}_{l,l'}>0$), it does not intersect with other S^z. This leads to a situation when even for those values of $J^{(1)}_{l,l'}$ and $J^{(2)}_{l,l'}$ which characterize a molecule in equilibrium configuration, in the ground state we have $S^z=|n_A-n_{A^+}|/2$.

We shall give the proof of the nondegeneracy theorem in an abridged form as it is a nearly word-to-word repetition of the proof given in [4].

To begin with, we carry out the canonical transformation for the atoms of group A^+:

$$S^x_l\to -S^x_l, \qquad S^y_l\to -S^y_l, \qquad S^z_l\to -S^z_l \tag{7}$$

leaving the spin operators of A atoms unchanged. Then, the Hamiltonian (3) for alternant molecules can be rewritten in the form:

$$H'=-\tfrac{1}{2}\sum_{l,l'} J^{(1)}_{l,l'}(S^+_l S^-_{l'}+S^-_l S^+_{l'})+\sum_{l,l'} J^{(2)}_{l,l'}S^z_l S^z_{l'}. \tag{8}$$

Let amplitude c_α correspond to a certain configuration of spins in molecule α.

System energy can be rewritten in terms of amplitude c_α as

$$E' = -\tfrac{1}{2} \sum_{\alpha, \alpha'} J^{(1)}_{\alpha, \alpha'} c_\alpha c_{\alpha'(\alpha)} + \sum_{\alpha} J^{(2)}_\alpha c^2_\alpha . \tag{9}$$

Positive numbers $J^{(1)}_{\alpha, \alpha'}$ depend on the subscripts of the two configurations α and α'. Configuration α' arises from α under the action of the operator:

$$S^+_l S^-_{l'} + S^-_l S^+_{l'} .$$

Here as usual, the operator S^+_l turns the spin of the lth atom upwards and S^-_l downwards (or results in zero). Summation in (9) is carried out over all possible configurations. Besides, there is a natural normalization condition:

$$\sum_\alpha c^2_\alpha = 1. \tag{10}$$

It is clear that for the lowest state all $c_\alpha > 0$. If there were any amplitudes $c_\alpha < 0$, then there would be a certain number of positive terms in the first sum of (9), and using a set of amplitudes $|c_\alpha|$ instead of c_α we would be able to decrease the energy still further, in contradiction to the initial assumption.

There also can be no zero values of c_α, since in the equation for c_α we have:

$$E' c_\alpha = -\tfrac{1}{2} \sum_{\alpha'(\alpha)} J^{(1)}_{\alpha, \alpha'} c_{\alpha'(\alpha)} + J^{(2)}_\alpha c_\alpha \tag{11}$$

and if $c_\alpha = 0$, it would give that:

$$\sum_{\alpha'(\alpha)} J^{(1)}_{\alpha, \alpha'} c_{\alpha'(\alpha)} = 0 \tag{12}$$

again leading to negative amplitudes. Thus, for the lowest energy state, all $c_{\alpha'} > 0$. No two different states with all c_α positive can exist because of their orthogonality. This remark completes the proof.

From the above proof concerning the value of S^z in the ground state of Ising Hamiltonian configuration it follows that in the limit, when $J^{(1)}_{l, l'} = 0$ for an alternant molecule in the ground state:

$$S \geqslant \frac{|n_A - n_{A^+}|}{2} . \tag{13}$$

A consideration of special cases, particularly those of 1) open chains and cycles with an even number of atoms; 2) molecules involving symmetry with respect to substitution of unasterisked atoms by asterisked ones suggests that (13) can be written as a precise equality:

$$S = \frac{|n_A - n_{A^+}|}{2} . \tag{14}$$

3. Examples

Let us consider a few examples.

In the Ising limit, the lowest energy configuration corresponds to the spin distribution of Fig. 2b.

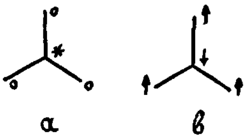

Fig. 2. Trimethylmethylene molecule: (a) atoms of two groups A^+ and A; (b) spin distribution in atoms in the ground state in the Ising limit

Hence, for this molecule $S=1$, but not $S=2$, because this molecule can be derived from the allyl radical for which $S=\frac{1}{2}$ in the ground state, by adding one carbon atoms also having $S=\frac{1}{2}$. According to the angular moment addition rule, the resultant spin can be either 0 or 1. Therefore, the only possibility is that $S=1$.

We note here without proof that the molecules shown in Figs. 3a, b have $S=\frac{1}{2}$ (Fig. 3a) and $S=0$ (Fig. 3b). The latter molecule is diamagnetic although there exists no Kekulé structure to describe it. Therefore, an alternant molecule may have a diamagnetic ground state even if there is no Kekulé structure to represent it.

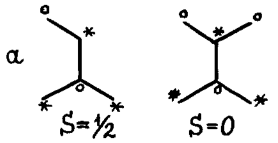

Fig. 3. Hydrocarbon molecules having $S=\frac{1}{2}$ (a) and $S=0$ (b) in the ground state

Figure 4 shows several hydrocarbons of this kind:

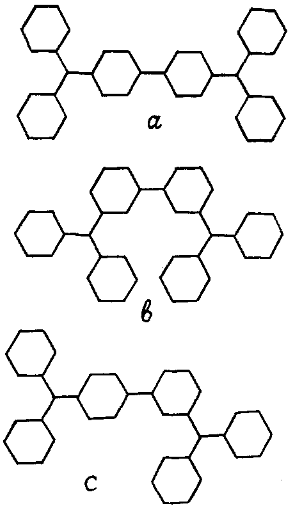

Fig. 4. Large hydrocarbon molecules: (a) Chichibabin hydrocarbon (b) Schlenk-Brauns hydrocarbon, (c) a hydrocarbon having different number of atoms in the two groups. Isomers (a) and (b) must have $S=0$ in the ground state, and isomer (c) $-S=1$

(Figure 4a): Chichibabin hydrocarbon which has been shown both experimentally and theoretically by Syrkin and Dyatkina [5] to have a very low singlet-to-triplet transition energy, even though it is diamagnetic in its ground state;

(Figure 4b): Schlenk-Brauns hydrocarbon. There is a standing opinion in the literature that this hydrocarbon is a genuine biradical (i.e. in its ground state $S=1$). This contradicts our predictions, since this hydrocarbon has a plane of symmetry with respect to substitution of unasterisked atoms for the asterisked ones. In the ground state such a molecule must always have $S=0$, i.e. exhibit diamagnetic properties at sufficiently low temperatures.

(Figure 4c): The third hydrocarbon shown in Fig. 4c does not have such a symmetry, and in its ground state $S=1$.

The Leo triradical (Fig. 5) is analogous to the above compounds but has $S=\frac{3}{2}$ in the ground state.

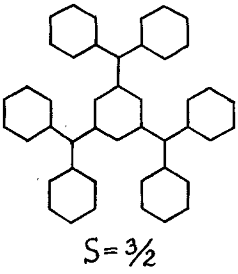

Fig. 5. Leo triradical $S=\frac{3}{2}$

Figure 6 illustrates a condensed aromatic system which, depending on its size, can have a very high total spin in the ground state. Thus, if such a system has L rows of rings (Fig. 6 shows 5 rows), the system's total spin will be $(L-1)/2$ (for the molecule shown in Fig. 6, $S=2$).

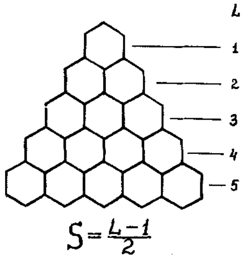

Fig. 6. Triangular condensed aromatic system comprising L rows of rings ($L=5$) and having the ground state spin $S=(L-1)/2$ ($S=2$)

Other examples of polyradicals can be found in the book by A. L. Buchachenko: "Stable radicals" [6].

4. Infinite Systems

Now we shall give a few examples of molecules having total spin proportional to their size. Figs. 7 and 8 show several possible polymer systems. R can in all cases be selected from either the divalent atoms of O and S, or some other stabilizing group.

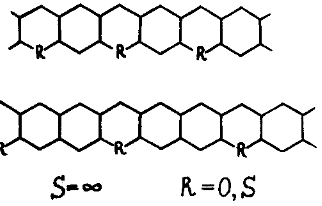

Fig. 7. Macromolecules of hydrocarbons with periodically introduced heteroatoms

What is shown in Fig. 8 is not a hydrocarbon polyradical. It should be mentioned that all the arguments set forth in Sect. 2 are easily applicable to alternant systems with heteroatoms.

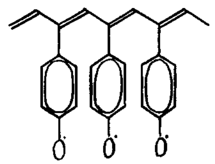

Fig. 8. A polysemiquinone acetylene macromolecule

Finally, Figs 9–11 give a few examples of planar infinite systems with infinite total spin in the ground state (i.e. ferromagnetics).

Figure 9 shows a planar system that can be constructed from graphite lattice by substituting boron atoms for certain carbon atoms in the order indicated (some other trivalent atom can be employed having suitable length of chemical bond between said atom and carbon atom). Note that irregular lattices with boron atoms are well known.

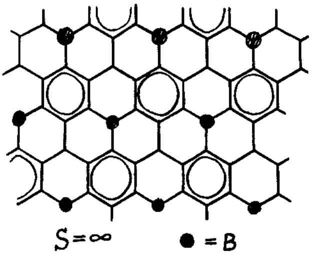

Fig. 9. Two-dimensional structure derived from graphite lattice by substituting boron atoms for certain carbon atoms

In Fig. 11 the group denoted by X can be any trivalent group or an atom of appropriate size. Thus, the question that opens the present paper, viz.: "Do organic

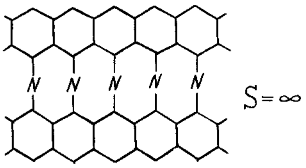

Fig. 10. Hypothetical two-dimensional system comprising polyacene macromolecules linked via nitrogen atoms

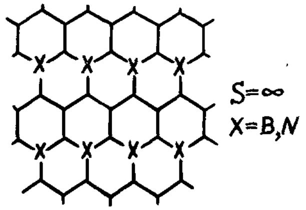

Fig. 11. Two-dimensional structure derived from graphite lattice by substituting boron or nitrogen atoms for certain carbon atoms

ferromagnetics exist?" – we can now answer in the affirmative. Quantitative evaluation of their parameters (Curie temperatures, etc.) is a matter of the nearest future.

5. Non-Alternant Systems

To conclude, we shall make a few remarks concerning non-alternant systems. For these, it is impossible to prove the theorem of nondegeneracy of the ground state, and we are therefore not in a position to determine from general considerations the system's resultant spin in the ground state. However, we can have some idea of the reactions in which non-alternant systems are converted to alternant ones. One example of such a reaction is breaking up a ring consisting of an odd number of carbon atoms.

Consider a fulvene molecule (Fig. 12a). Its ground state is characterized by $S=0$. When the cycle is broken as shown in Fig. 12b, the molecule becomes a linear alternant system with $S=0$, and when the cycle is broken in a different way, as shown in Fig. 12c, it becomes an alternant system with $S=1$ in the ground state.

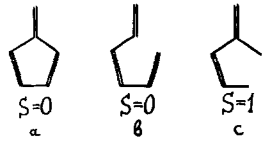

Fig. 12. A fulvene molecule (a) and two alternant molecules derived from it, with $S=0$ (b) and $S=1$ (c), by breaking different bonds of the five-member fulvene ring

It can be concluded that the reaction which breaks the ring in the manner shown in Fig. 12b can be effected under heating, and that breaking the ring as shown in Fig. 12c can be effected by exciting into the triplet state, i.e. photochemically.

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