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Valence-Bond Calculation of the Electronic Structures for $C_5H_5^+$, $C_5H_5^-$, $C_7H_7^+$, and $C_7H_7^-$ in Symmetric Configurations

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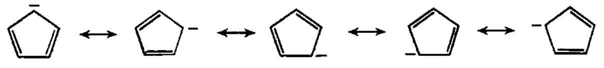
Abstract: *Ab initio* valence-bond calculations have been made of the electronic structures of $(CH)_5$ and $(CH)_7$ positive and negative ions under D_{5h} and D_{7h} symmetries, respectively. The lowest singlet and triplet energies are determined for each ion. The results indicate that the two aromatic ions have $^1A_1$ ground states and the two antiaromatic ions have $^3A_2$ ground states. The problem of interpreting VB calculations for these types of systems is also discussed.

In three recent communications the question of the structures of $C_5H_5^+$ and $C_5H_5^-$ is discussed from different theoretical points of view.[1-3] The calculation methods used varied from CNDO, MINDO/3, to *ab initio*, but were all of the SCF type with no configuration interaction included. We have examined *ab initio* VB calculations on the planar, symmetric forms of $C_5H_5^+$, $C_5H_5^-$, $C_7H_7^+$, and $C_7H_7^-$ in order to examine the question of how the VB results differ between aromatic and antiaromatic substances. Although these calculations do not provide the information of a complete geometry search, they do indicate the directions that any distortions from the symmetric configuration are likely to take. The method used for these calculations is the mixed MO–VB procedure that was applied to the benzene molecule by us and described in a previous communication.[4]

$C_5H_5^+$ and $C_5H_5^-$. The designation of aromatic and antiaromatic for cyclic $(CH)_n$ type systems follows from the importance of the $4n + 2$ rule originally discovered by Hückel,[5] implied by the fact that all but the lowest of the occupied MO's of the π system are doubly degenerate. This leads to the observation that only systems with $4n + 2$ π electrons will be closed shell types. It has been pointed out many times[6] that the VB method does not provide anything in its method that distinguishes in such a definitive way between the properties of cyclic systems with $4n$ or $4n + 2$ electrons. Thus for $C_5H_5^-$ one can write the bonding structures



A set of five resonance structures equivalent to these except for the sign of the charge can be written for $C_5H_5^+$, of course. Thus the simplest form of the resonance theory would say that the resonance stabilization of two substances is the same. This is, of course, a very naive approach.

The energies obtained for several spatial symmetries are given in Table I. The most obvious conclusion from these results is that the negative ion should be much more stable than the positive one on two counts. (a) The separation between the ground state and excited state energies is much greater in $C_5H_5^-$ than in $C_5H_5^+$. (b) The lowest energy of the positive ion is actually for a triplet state and these are notoriously reactive. These results conform to those predicted using simple MO arguments.

The VB structures and occupation numbers which comprise the total wave functions for the $^1A_1$ ground state of $C_5H_5^-$ and the lowest $^1E_2$ and $^1A_1$ states of $C_5H_5^+$ are given in Table II. The most striking fact about these numbers is the indication that the "Dewar-type" covalent structures are favored in these states in the positive ion while the "Kekule-type" structures are favored in the negative ion. If a distortion were to occur in the positive ion which shortened the distance between any two nonadjacent carbon atoms the long bond of one of the Dewar-type covalent structures would be strengthened. This distortion also lifts the degeneracy of the $^1E_2$ state and there is an allowed configuration interaction with the $^1A_1$, state. It is expected that these two effects would lead to the eventual attainment of the types of geometries discussed earlier[1-3] by other workers.

The actual calculated ground state of the positive ion, $^3A_2$, is much more difficult to discuss in terms of VB structures, since the one-to-one correspondence that exists between bond diagrams and linearly independent VB basis functions for singlet states does not apply to states of any other multiplicity. This might be thought to be a severe limitation to the VB method, and it is, as far as the present state of knowledge is concerned. However, if we look to the future it seems likely that chemists must learn how to deal qualitatively with bonding in molecules that are not in sta-

Table I. VB Energies and Symmetries of States of $C_5H_5^+$ and $C_5H_5^-$

$C_5H_5^+$ State	$C_5H_5^+$ Energy, au	$C_5H_5^-$ State	$C_5H_5^-$ Energy, au
$^1A_1$	−191.2505		
$^1E_1$	−191.2629	$^1A_1$	−191.3254
$^1E_2$	−191.3388	$^1E_1$	−191.5238
$^3E_2$	−191.3599	$^1E_2$	−191.6336
$^3E_1$	−191.4720	$^3E_2$	−191.7710
$^1A_1$	−191.5468	$^3E_1$	−191.7748
$^1E_2$	−191.5789	$^1E_1$	−191.7918
$^3A_2$	−191.6082	$^1A_1$	−192.0080

Table II. Number of Functions for Covalent and Singly Polar Structures of $C_7H_7^+$ and $C_7H_7^-$ under D_{7h} Symmetry

State	No. of Functions Singlet	No. of Functions Triplet
A_1	22	24
A_2	13	30
E_1	35	54
E_2	35	54
E_3	35	54

Table III. Energies and Symmetries of States of $C_7H_7^+$ and $C_7H_7^-$

$C_7H_7^+$ State	$C_7H_7^+$ Energy, au	$C_7H_7^-$ State	$C_7H_7^-$ Energy, au
		$^1E_1$	−268.3385
		$^3A_2$	−268.3401
$^3E_2$	−268.1851	$^3E_2$	−268.3613
$^3A_2$	−268.1919	$^1E_2$	−268.3639
$^3E_3$	−268.2277	$^3E_1$	−268.3779
$^1E_2$	−268.2766	$^1E_1$	−268.4441
$^1E_1$	−268.2798	$^3E_3$	−268.4784
$^3E_2$	−268.3094	$^3E_2$	−268.4786
$^1E_3$	−268.3437	$^3E_1$	−268.4985
$^3E_3$	−268.3814	$^1A_1$	−268.6300
$^3E_1$	−268.3821	$^1E_2$	−268.6457
$^1A_1$	−268.5392	$^3A_2$	−268.6638

ble singlet states. The rules of bonding theory developed over the years have been formulated by considering data on stable substances to a large extent, and there has been no overwhelming mass of information to guide theory in the construction of bonding diagrams for triplet states. On the more theoretical side there appears to have been little or no work on the problem of finding a method for constructing a linearly independent set of bonding functions for nonsinglet states that corresponds to the ease and simplicity of the Rumer diagrams for singlet systems.[7] It appears that the VB method will require the solution of this problem if it is to become a really useful tool in guiding the course of qualititive bonding theories in the future.

Hehre and Schleyer[3] estimated the triplet-singlet separation in D_{5h} $C_5H_5^+$ to be 17 kcal from their SCF calculations. It is seen from Table I that the $^3A_2$-$^1E_2$ separation is 18.4 kcal and the $^3A_2$-$^1A_1$ separation is 38.5 kcal. Hehre and Schleyer do not give the symmetries of their states, but presumably, the lower value given here corresponds to theirs.

$C_7H_7^+$ and $C_7H_7^-$. The total number of singlet VB structures that may be drawn for $C_7H_7^+$ and $C_7H_7^-$ (the same, of course) is 490 and the total number of triplet functions is 588. These numbers include all symmetry types, of course. We have not performed "full" π calculations with matrices of this size. Table II shows the number of functions of each of the symmetry types which arise for the heptagonal ions when we restrict the basis to covalent and singly polar functions. The energies obtained with this basis are given in Table III. Examination of this table shows that again, the antiaromatic ion has several low-lying energy states, while the ion satisfying the Hückel rule has a considerable separation between the lowest and the first excited state. Also, in conformity with the C_5H_5 case, the lowest antiaromatic state is triplet. When the most important structures in the wave functions are compared to the C_5H_5 case, some considerable difference is observed. The ten most important

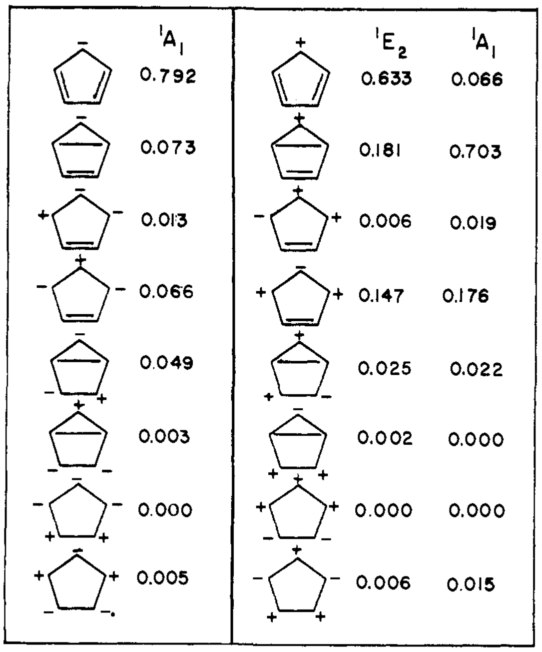


Figure 1. Valence-bond structures and occupation number for selected states of $C_5H_5^+$ and $C_5H_5^-$.

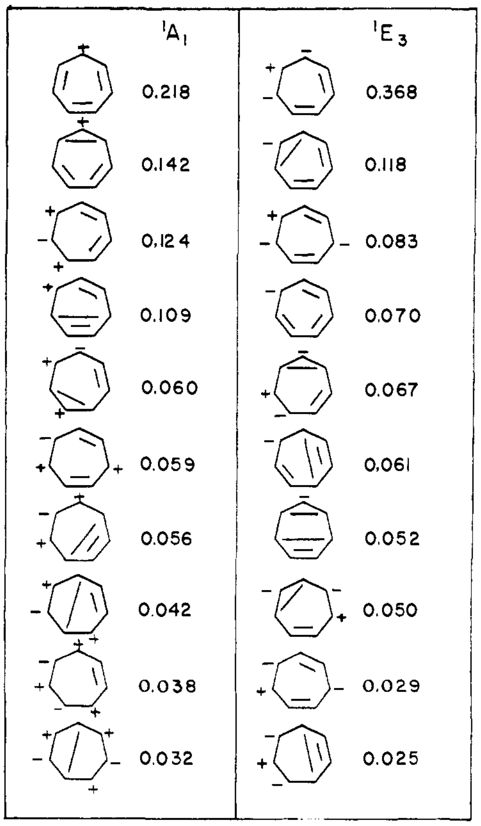


Figure 2. Valence-bond structures and occupation number for the $^1A_1$ state of $C_7H_7^+$ and the $^1E_3$ state of $C_7H_7^-$.

structures for the $^1E_3$ state of $C_7H_7^-$ and the $^1A_1$ state of $C_7H_7^+$ are given in Figure 2. The comparison of the two systems is quite difficult in this case, a circumstance due in part to the very large number of structures. The calculation reported here gives the excitation energy $^3A_2$-$^1E_3$ to be 11.4 kcal and $^3A_2$-$^1A_1$ to be 21.2 kcal for the heptagonal negative ion. As far as kinetic processes are concerned either of these is readily accessible from the ground state at normal temperatures.

These calculations on $C_7H_7^+$ and $C_7H_7^-$ show as well as those on the C_5H_5 compounds that the rules used by chemists to judge qualitatively the acceptability of VB structures were designed primarily with the data on stable, singlet substances and that they may work rather poorly when applied to more exotic states.

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Simple *ab Initio* Studies of the Isomers of N_2H_2, Li_2O, C_3H_4, and O_3

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Abstract: The results of a series of FSGO computations including geometry optimizations are reported for the isomers of N_2H_2, Li_2O, C_3H_4, and O_3, and are compared to values obtained from the semiempirical INDO and from conventional *ab initio* procedures. Reasonable FSGO structures are obtained for all of these systems, and some predictions are significantly superior to those of INDO. The FSGO descriptions of cis-trans isomers, highly polarized double bonds, ionic bonds, cumulative double bonds, a double bond in a ring, and a non-Lewis electron structure are examined. Certain kinds of "nonstandard" bonding are shown to be poorly represented, and the energy of double and triple bonds is consistently underestimated. A set of recommended exponents and locations for FSGO bond orbitals is given.

Most of the currently employed methods for determining electronic wave functions initially adopt an atomic orientation and use a linear combination of atomic orbitals to form molecular orbitals. An alternative approach which focuses directly on molecular functions, the floating spherical Gaussian orbital (FSGO) method, has been developed by Frost.[1] This method describes each pair of electrons by a spherical Gaussian orbital, ϕ_i

$$\phi_i = (2\alpha_i/\pi)^{3/4}\exp[-\alpha_i(\mathbf{r}-\mathbf{R}_i)^2] \qquad (1)$$

and approximates the electronic wave function by a Slater determinant of the FSGO's. The exponents α_i and the orbital centers $\mathbf{R}_i$ are determined variationally. Since the calculations require only integrals which can be readily evaluated, FSGO wave functions can be generated for systems of moderate size, and the method is competitive with semiempirical schemes such as CNDO or INDO[2] and with minimum basis set techniques such as STO-3G.[3] In many respects the FSGO method is the simplest *ab initio* procedure yet developed.

FSGO wave functions have the further advantage of being interpretable in terms of classical chemistry, since one can clearly distinguish the location and "size" of the core, bonding, and lone pair orbitals. In fact, the FSGO model can be regarded as a quantum mechanical equivalent of the Lewis electron dot model, and information obtained from calculations on molecules can be related to the highly successful VSEPR theory of Gillespie.[4]

Unfortunately, the FSGO procedure is at best only semiquantitative. The basis set employed is "subminimal" in comparison with conventional minimum basis set calculations; hence, only a rough approximation to the Hartree-Fock result can be obtained. While the method appears to describe simple hydrocarbons reasonably well,[5-9] bond angles and bond lengths for some systems are not predicted accurately.[10,11] It is unclear how much confidence can be placed in numerical results obtained for systems with bonding patterns that have not been previously studied, or for systems which are not adequately described by a single Lewis structure. In the following, we report the results of a series of FSGO computations of the isomers of N_2H_2, Li_2O, C_3H_4, and O_3, and evaluate these results in comparison to values obtained from semiempirical and conventional *ab initio* procedures. These molecules include examples of cis-trans isomerism, highly polarized double bonds, ionic bonds, cumulative double bonds, a double bond in a ring, and a non-Lewis electron structure; they are also species for which semiempirical analyses are often inaccurate. By comparing energies, geometries, and electronic structures of the various isomers, we seek to assess the ability of the FSGO method to deal with these species, and to determine more clearly its applicability as a structural tool in chemistry.

Computational Information

The computations were performed in double precision on an IBM-360-44 computer. The necessary integrals were calculated using formulas given by Frost;[12] the error function related integrals were evaluated using a polynomial approximation developed by Mosier and Shillady.[13] Care was taken to avoid computing integrals which were less than 10^{-13} and to avoid recomputing integrals which had not changed from the previous iteration. Molecular symmetry was not, however, employed in the evaluation of the two-electron integrals.