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HuLiS, a program to teach mesomerism and more

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Abstract. The HuLiS program is presented as a tool to decompose a delocalized wave function as a linear combination of localized electronic structures. The principles of the energy based HL-CI and the overlap based schemes HL-P are developed. The results obtained for a set of 10 relevant organic molecules are shown to compare very well with high level quantum chemistry calculations. A trust factor τ is introduced and its use is shown on the allyl radical case where symmetry must be taken into account.

1. Introduction

The HuLiS program[1] deals with topological methods applied to chemistry. [1] It is a tool, which originally was devoted to teaching, but recent features make it very useful for research especially in the understanding of Valence Bond view of the chemical bond.[2, 3, 4]

The most commonly used topological method in chemistry was develop by Heinrich Hückel[5] in the late 1950's when computer time was not at reach for academic use. It deals with π electrons only and gives insights into mesomerism and aromaticity. The reader unfamiliar with this method should refer to ref. [6]. Nowadays, it is a great way to introduce computational chemistry as it requires simple math and gives access to meaningful results. As we use the initial formulation of the Hückel method, we restrict ourselves to the π part of the wave function. Furthermore, this method implies the following:

- one $2p_{z_A}$ orbital per atom A is used of energy α_A;
- orbitals of adjacent atoms are orthogonal;
- the off diagonal term of the Hamiltonian matrix for two adjacent atoms A and B has a negative value β_{AB};
- the molecular orbitals are eigenfunctions of the Hamiltonian matrix and their energies are their eigenvalues.

The values of α_A and β_{AB} are tabulated elsewhere.[7] It is sufficient here to remind that the original method was built for carbon atoms, thus $\alpha_C = \alpha$ and $\beta_{CC} = \beta$ both values being lower than zero. The Hückel method leads to delocalized molecular orbitals.

In the other hand, the Valence Bond approach of the chemical bond defines the bond as a local property: as in a Lewis picture, the bond is seen as an electron pair between two atoms, which leads to three structures, one neutral (one electron on each atom) and two ionic (two

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[1] http://www.hulis.free.fr

electrons on one atom and zero on the other and the other way around). This local view of the bond is a very natural way for chemists to rationalize properties and reactivity.

The HuLiS programs takes the best of both worlds: the delocalized wave function is written as a weighted combination of localized structures, which are meaningful. This is achieved by two methods presented in this contribution.

2. The Hückel derived VB methods

In HuLiS, the Hückel delocalized wave function Ψ of energy E is computed for the system under study. In a Valence Bond vision of the chemical bond, it is then written as a linear combination of localized electronic structures ψ_i of energies ϵ_i:

$$\Psi = \sum_i^N c_i \psi_i. \tag{1}$$

Two different schemes were developed to determine the c_i values. One is based on the energy of the delocalized structure whereas the other one is based on the overlap between the delocalized and the localized structures. Both use simple linear algebra and are described in the following section. As an illustration, calculations were performed on the set of molecules given in Figure **??**, which results are summarized in Table **??**.

2.1. The energy-based scheme: Hückel Lewis Configuration Interaction (HL-CI)
The HL-CI scheme aims at building a linear combination of localized structures

$$\tilde{\Psi} = \sum_i^N c_i \psi_i \tag{2}$$

which energy $\tilde{E}$ approaches the energy of the Hückel solution E. This schemes was built as an analogy of the Hückel method in a localized structures basis (when the Hückel method is built in an atomic orbital basis). For this analogy to be followed, one sets up the overlap between two different localized structures to zero.

$$S_{HLCI} = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix} \tag{3}$$

An effective Hamiltonian is written in the basis of the localized structures :

$$\hat{H}_{HLCI} = \begin{pmatrix} \epsilon_1 & B & \cdots & B \\ B & \epsilon_2 & \cdots & B \\ \vdots & \vdots & \ddots & \vdots \\ B & B & \cdots & \epsilon_N \end{pmatrix} \tag{4}$$

The diagonal terms are the energies of each localized structure and, by analogy with the Hückel method, the interaction term is set to a negative value B. It is very important to understand that the unlike in the Hückel method, it is not possible here to define adjacent localized structures. As a consequence, one cannot determine which off diagonal terms are zero, thus all off diagonal terms are set to B. A unique negative value of $B = B_0$ can be computed, which ensures that the eigenfunction it is associated with is such that $\tilde{E} = E$.[8] By construction, the eigenfunction associated to B_0 has all c_i coefficients positive. This scheme gives c_i values which are very close

to advanced quantum chemistry methods such as Natural Resonance Theory (NRT) based on the Natural Bond Orbitals approach.[8, 9, 10, 11] However, it lacks of physics and does not account for out of phase interaction between localized structures if imposed by symmetry as all c_i are positive by construction.[12] This point is adressed in section 3.

2.2. The space-based scheme: Hückel Lewis Projection (HL-P)
To overcome the lack of physics of the HL-CI scheme the HL-P space based scheme was developed. In this scheme, energy is not used as a criterion, only overlap between structures is used. One uses the overlap between the localized structures and the Hückel solution:

$$S_\forall = \begin{pmatrix} \langle \Psi | \Psi_1 \rangle \\ \langle \Psi | \Psi_2 \rangle \\ \vdots \\ \langle \Psi | \Psi_N \rangle \end{pmatrix} \tag{5}$$

and the overlap among the localized structures:

$$S = \begin{pmatrix} 1 & \langle \Psi_1 | \Psi_2 \rangle & \langle \Psi_1 | \Psi_3 \rangle & \cdots & \langle \Psi_1 | \Psi_N \rangle \\ \langle \Psi_2 | \Psi_1 \rangle & 1 & \langle \Psi_2 | \Psi_3 \rangle & \cdots & \langle \Psi_2 | \Psi_N \rangle \\ \langle \Psi_3 | \Psi_1 \rangle & \langle \Psi_3 | \Psi_2 \rangle & 1 & \cdots & \langle \Psi_3 | \Psi_N \rangle \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \langle \Psi_N | \Psi_1 \rangle & \langle \Psi_N | \Psi_2 \rangle & \langle \Psi_N | \Psi_3 \rangle & \cdots & 1 \end{pmatrix}. \tag{6}$$

The c_i coefficients are obtained by solving the following system:

$$S_\forall = SC \tag{7}$$

with C the vector of all c_i coefficients.[12] In this scheme, a measure of the match between Ψ and $\tilde{\Psi}$ can be computed as the overlap between the two functions. It can be shown that this overlap that we call τ is the sum of the Coulson Chirgwin weights defined as:[12, 13]

$$w_i = c_i \sum_{j}^{N} c_j S_{ij}. \tag{8}$$

3. Comparison of the schemes
In order to compare the schemes among each other and to a more advanced quantum chemistry method, one computes the weights of each localized structure in $\tilde{\Psi}$. For the set of molecules presented in Figure 1 the weights and τ are given in Table 1. Both schemes give very similar results and compare very well to the *ab-initio* NRT method. A problem occurs with HL-CI when the symmetry of the total wave function imposes a c_i to be negative. As discussed in 2.1, HL-CI gives by construction only positive values for the c_i coefficients. In the case of allyl radical, the ground state wave function is of A_2 symmetry. In this case, it is the out of phase combination of the two localized structures, which is the appropriate VB solution (Figure 2). The calculation of τ for the HL-CI solution shows this failure (it drops to zero). Thus, despite the fact that τ was introduced in the HL-P framework, it is important to compute it for the HL-CI results.
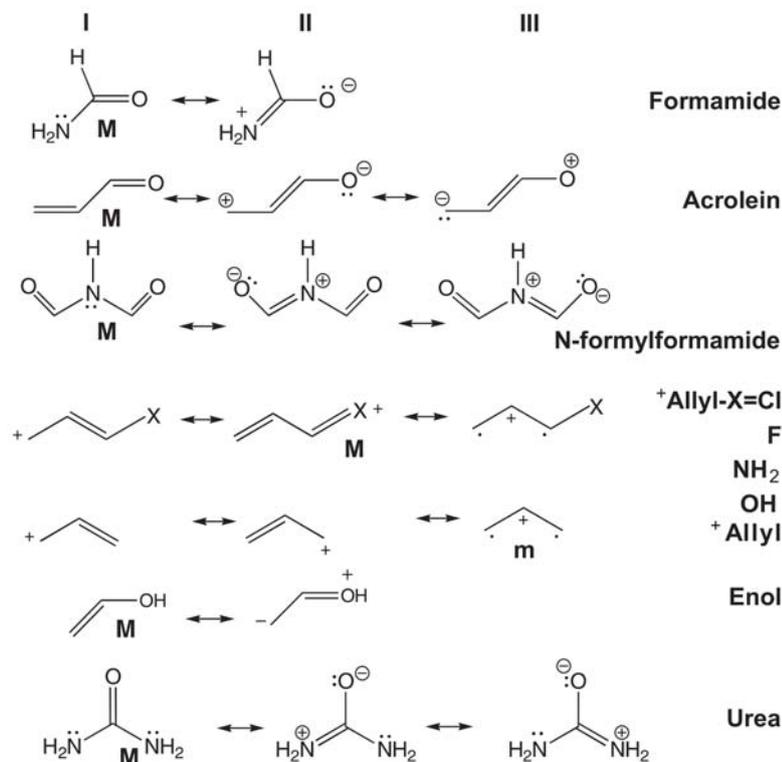
Figure 1. Structures used in the wave function decomposition for benchmark. Weights of structures are presented in Table 1. Reprinted with permission from [12]. Copyright 2008 American Chemical Society.

4. Conclusion

In this contribution, the HuLiS program was briefly presented. This program allows to have a double reading of a π wave function obtained with the Hückel method. The delocalized wave function can be accurately described as a linear combination of few meaningful localized structures. A criterion of the accuracy, τ can be computed and characterizes the set of localized structures used as well as the physical meaning of their linear combination. The two methods implemented show a good agreement with high level quantum chemistry calculation at a fraction of its computational cost.

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Table 1. Weights obtained with HL-P as compared to NRT and HL-CI [8]. Structures used are presented in Figure 1. Reprinted with permission from [12]. Copyright 2008 American Chemical Society.

Molecule	NRT	HL-CI	HL-P	$\tau(\%)$
Formamide	67 / 33	66 / 34	65 / 35	90.9
N-formylformamide	45 / 27.5 / 27.5	46 / 27 / 27	43 / 29 / 29	83.6
Acrolein	87 / 13	79 / 21	85 / 15	85.3
	84 / 11 / 5	78 / 17 / 5	84 / 15 / 1	85.6
$^+$Allyl NH$_2$	23 / 77	29 / 71	25 / 75	84.5
	21 / 75 / 4	24 / 70 / 6	23 / 69 / 8	92.3
$^+$Allyl OH	30 / 70	39 / 61	39 / 61	84.5
	23 / 65 / 12	35 / 58 / 7	34 / 54 / 11	95.1
$^+$Allyl F	37 / 63	44 / 56	45 / 55	84.7
	29 / 56 / 15	40 / 52 / 8	39 / 49 / 12	96.4
$^+$Allyl Cl	37 / 63	38 / 62	36 / 64	84.0
	29 / 58 / 13	33 / 60 / 7	32 / 58 / 11	93.9
$^+$Allyl H	50 / 50	50 / 50	50 / 50	84.9
	39 / 39 / 22	46 / 46 / 8	44 / 44 / 13	97.4
Enol	86 / 14	93 / 7	93 / 7	96.3
Urea	60 / 20 / 20	46 / 27 / 27	51 / 24 / 24	82.6
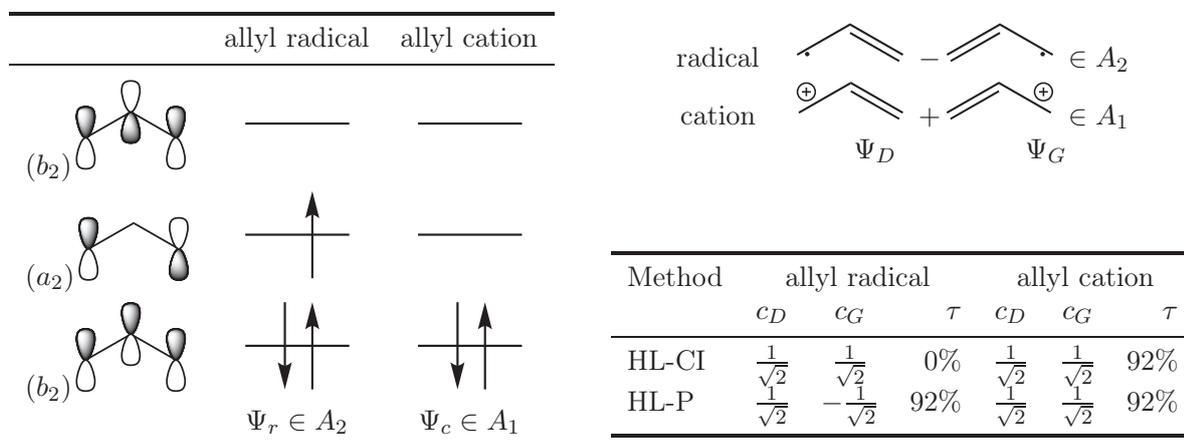
Figure 2. Molecular orbital (left) and Valence Bond (right) visions of the allyl radical and cation wave function. The table shows that the minus sign before c_G obtained by HL-P describes the appropriate physics ($\tau = 92\%$) whereas HL-CI fails to do so (see text) because the A_2 symmetry imposes an out of phase interaction between the localized structures. Such an issue does not occur in the cation as its wave function is of A_1 symmetry.

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