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Tutorial on HuLiS: the two methods implemented in HuLiS (HL-CI and HL-P) and their behavior for a few cases.

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ABSTRACT: The tutorial explains how to use the HuLiS program to compute coefficients and weights of Lewis structures within the Hückel method framework. The interface is described and the two methods available (HL-CI and HL-P) are compared on a few examples.

KEYWORDS: Chemical Bond, Chemistry, Configuration Interaction, Electronic Structure, Hamiltonian, Hückel, Lewis Structures, Molecular Orbital, Overlap Matrix, Resonance Theory, Electronic structure.

KEY POINTS /OBJECTIVES BOX:

- ☒ Fast/Simple concepts for the electronic structure of molecules
- ☒ Local Bonds in the Hückel framework
- ☒ Numerical mesomery
- ☒ Availability

1. Introduction

Conjugated molecules embed a delocalization of the so-called π electrons. This electronic situation is described with a delocalized wave function that is computed here in the framework of the Hückel method. We call the resulting wave function $\Psi_{Hückel} = \Psi_{tot}$. Chemists prefer in general to draw molecules using Lewis structures, that is a σ skeleton and a π system made out of double bonds and lone pairs. Those are doubly occupied orbitals localized either on two neighboring atoms or on a single atom. Radicals and biradicals can also be considered with singly occupied atomic orbitals. When more than a unique Lewis structure is necessary to describe the π system, resonance between at least two Lewis structures is requested, and simple drawings are used for a qualitative description of the electronic structure. With simple rules we expect a specific structure to be the major structure, and others to be of less interest. Such a resonance can however be quantitatively considered, and it is the objective of the HuLiS program. To put quantitative insights into the resonance, we write the wave function of the resonance (Ψ_{Lewis}) as a superposition of the wave functions that describe Lewis structures (Ψ_I, Ψ_{II}, \dots). This is described in equation 1 and the C_I 's are the coefficients of the interaction between the Lewis structures (the Ψ_I 's). These coefficients are related to the weights of the Lewis structures (labeled ω_I) through the Coulson-Chirgwin formula (equation 2), which accounts for the overlap between the wave functions of the Lewis structures ($S_{IJ} = \langle \Psi_I | \Psi_J \rangle$).

$$\begin{aligned} \Psi_{\text{Hückel}} &= \Psi_{tot} \\ \Psi_{Lewis} &= \sum_I C_I \Psi_I \\ \omega_I &= |C_I|^2 \\ S_{IJ} &= \langle \Psi_I | \Psi_J \rangle \end{aligned}$$

$$\Psi_{Lewis} = C_I \Psi_I + C_{II} \Psi_{II} + \dots \quad (1)$$

$$w_I = \sum_J^N C_I C_J S_{IJ} \quad (2)$$

$$C_I \Psi_{Lewis} = C_I \Psi_I + C_{II} \Psi_{II} + \dots$$

$$w_I = \sum_J^N C_I C_J S_{IJ}$$

HuLiS' first goal is the instantaneous computation of these coefficients and weights. As we developed it, we also implemented other tools such as the manual vs. automatic generation of Lewis structures and a trust factor to guide the user to the most relevant structures, and help him/her to have a small number of relevant Lewis structures.

2. The HuLiS program

HuLiS is implemented both as a java applet and a javascript. The java can be downloaded from <http://www.hulis.free.fr>. The javascript version runs from <http://m.hulis.free.fr>. Both do the same computations and have a very similar Graphical User Interface (GUI). The main difference between the two versions is the access to the user's disk: the Java version can read/write files to the user's disk (so the work can be saved for later), while the javascript version cannot. We will take the example of the javascript GUI, as shown in Figure 1. A manual for the java version can be downloaded from the HuLiS website.

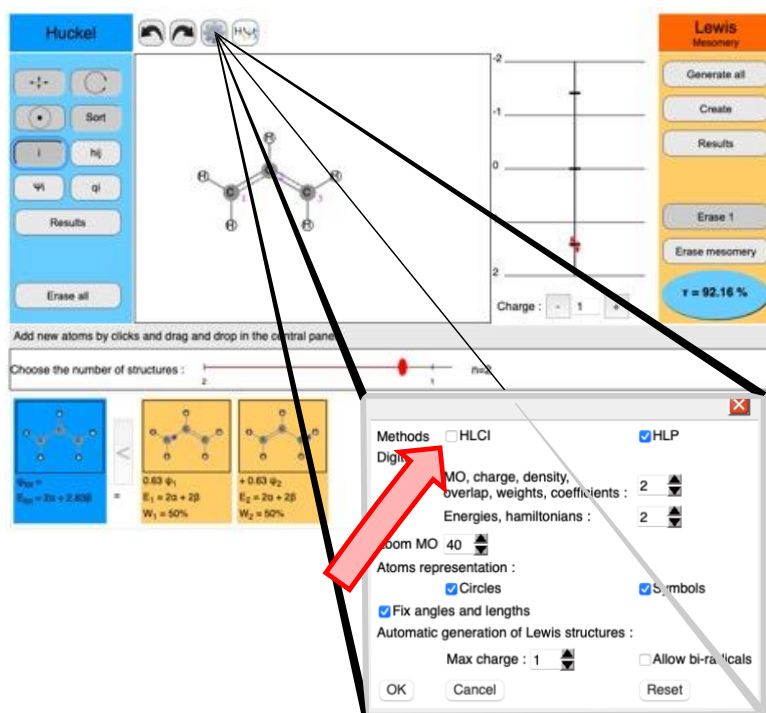


Figure 1: HuLiS GUI, and the preferences panel. By default, the HL-CI check box is unchecked (red arrow) and HLP is checked.

2.1. Panels

The HuLiS interface shows 3 main parts: on the left we have the Hückel tools (in blue) and on the right the Lewis tools (in orange). The middle panel is dedicated to the display of the molecule and orbitals. Above the middle panel are the buttons for **undo/redo**, as well as the setting of the **preferences** and the “**about**” button. With the **preference panel** (Figure 1 insert) one can ask HuLiS to use the HL-CI method (Figure 1, red arrow). The HL-CI method is by default unselected because of its drawbacks. One of the objectives of this tutorial is to illustrate these drawbacks so they can be better understood, and compared to HLP. Hence, before starting the tutorial both the HL-CI and the HLP options should be turned “on” with the two check boxes (red arrow, Figure 1).

Hückel tools: Two sets of four buttons are proposed (Figure 2). The first four are to handle the molecular representation (translate, rotate, center, atoms reordering-sort). They are available until Lewis structures calculations start. To re-access them, the user must click the “Erase mesomery” button of the Lewis tools (orange part). The last four are switches for additional display: atoms numbering, Hückel’s Hamiltonian parameters h_{ii} and h_{ij} , and some results of the Hückel calculation. The button “ ϕ_i ” displays the coefficients of the atomic orbitals in the Molecular Orbital that is selected in the energy diagram (a red circle indicates the selected MO). The button “ q_i ” displays net charges in the π system. The summary of the complete Hückel calculation is given in a pop-up window with the “Results” button. The text of the pop-up can be copied with the contextual menu of the mouse. It shall be noted that the charge of the molecule is modified with +/- buttons which, in the javascript version, are placed below the orbitals display, see Figure 2 (d). The density of dashes used for the drawing of the bonds in the molecule always follows the fractional π -bond order of the Hückel results.

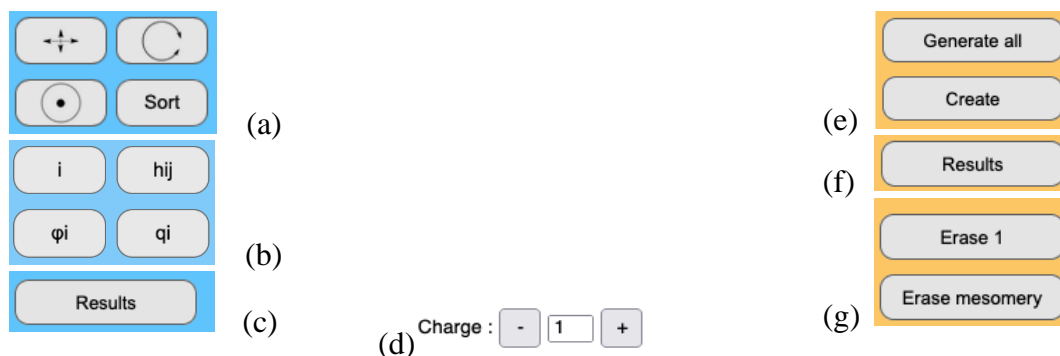


Figure 2: HuLiS tools: (a) Molecule handling, (b) Display tools, (c) Hückel calculation text results, (d) Molecular charge handling, (e,g) Lewis structure handling (create /erase). The “Generate all” button is an automatic structure generator, while the “Create” button requests that the user defines the Lewis structure by hand, (f) Lewis calculation text results

Lewis tools: Lewis structures can be created automatically with the structure generator of the “Generate all” button or manually (“Create”), see Figure 2, (e). The structure generator obeys the constraints settled in the preference panel to allow (or not) charge separation and/or biradicals. When “Create” is pressed a new σ skeleton is displayed without any π electron. Consistently, positive charges are displayed on the atoms and they are recomputed as the user defines bonds and lone pairs. Structures are erased either one by one or all at once (Figure 2, (g)). As for Hückel’s calculations, the complete results for the Lewis calculations are given in a pop-up window with the “Results” button (Figure 2, (f)). The text of the pop-up can be copied

with the contextual menu of the mouse. A slider, situated below the main panel allows to select the active Lewis structures.

2.2. • Results

Hückel results are very common and self-explicit. We will focus on Lewis ones. The main interest of the computations that involve Lewis structures is to answer the question “is this structure important to describe my molecule?”. This is answered by computing the weights of the structures, the ω_I of equation (2): a low weight corresponds to a less important structure, and the larger the weight, the more relevant the structure. As shown in equation 2, weights request the computation of coefficients of the wave function expansion (or Configuration Interaction) shown in equation (1). They are obtained by the calculations described in the HuLiS chapter of this book and described in our corresponding publications.[1,2] These results are displayed under the slider, at the bottom of the window (Figure 3). Hückel is displayed in blue on the left. Lewis structures are displayed in thumbnails, sorted according to their overlap with the Hückel wave function. In each thumbnail, we can see the sketch of the structure, its coefficient in the Lewis expansion (C_I as described in eq. 1), the energy of the structure, and its weight.

Ψ_I
 ω_I
 C_I

In HuLiS we additionally display a trust factor, which is defined as the overlap between the Lewis expansion and the Hückel wave function: $\tau = \langle \Psi_{Hückel} | \Psi_{Lewis} \rangle$. Hückel is considered here as the reference. The color of the ellipsoid indicates if the trust factor is close to 100% (blue) or differs (orange). It becomes red for very small values (Figure 4).

$\tau = \langle \Psi_{Hückel} | \Psi_{Lewis} \rangle$

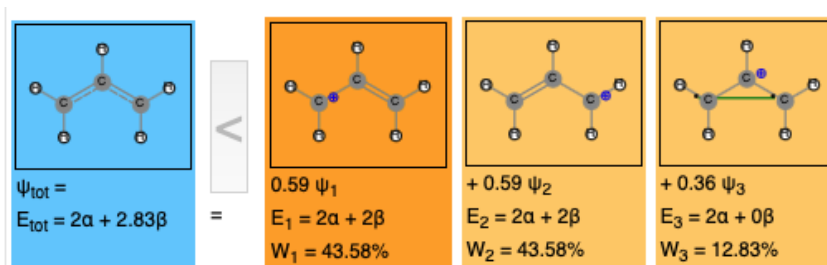


Figure 3: Graphical results for the Lewis expansion.

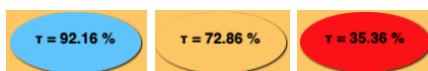


Figure 4: Versatile display of the trust factor.

More detailed results are displayed in a pop-up window when the button “Results” is pressed.

3. • Examples

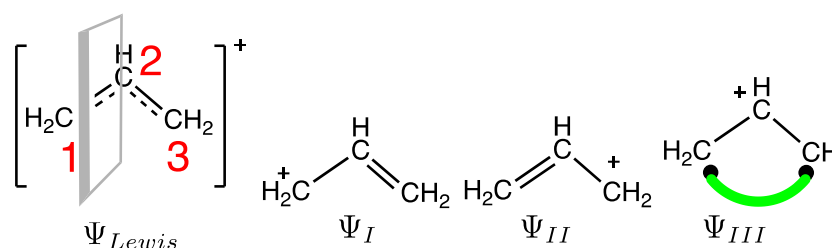
Readers are expected to compute the examples with the online HuLiS. The first two examples are on the allyl cation and radical. The latter has a wave function which is antisymmetric with respect to the (xz) plane (Scheme 1, in gray). This renders the Lewis-resonant wave function particularly interesting, and difficult for the HL-CI method. The last

example concerns the weight of the neutral structures vs biradical's on linear polyenes. This topic comes from a publication by Gu et al.[3]

3.1. Case A // Allyl cation

This molecule in its ground state has a Hückel energy of $2\alpha+2.83\beta$. The corresponding wave function (Ψ_{tot}) is symmetric with respect to the mirror plane that is perpendicular to the plane of the molecule, passing by the central carbon (Scheme 1, sketched in gray). The average structure can be described as a symmetrical resonance between two Lewis structures (Ψ_I , Ψ_{II}), that are mutual mirror images for this symmetry plane. As shown in Scheme 1, a third structure, Ψ_{III} , which is intrinsically symmetric for this plane, can be considered. It was even proved to have a not negligible weight, between 15% and 28% depending on the treatment of σ electrons.[4]

$\Psi_{tot} = \Psi_I + \Psi_{II} + \Psi_{III}$



Scheme 1: Allyl cation's average structure (Ψ_{Lewis}) and the three Lewis structures. For Ψ_{III} the green curve shows the singlet coupling of an electron on atom 1 and another on atom 3.

Ψ_{Lewis}

Ψ_{III}

As it is the case most of the time, HL-CI and HL-P methods give very similar results. At the HL-P level, the third structure weight is $w_{III}=12.8\%$ (Fig. 3), which is not too far from the lowest value found in the literature. HL-CI is a bit too low with about $w_{III}=7.9\%$. For both methods the trust factor is above 98%, which is excellent. This value drops to 92% when structure III is removed from the calculation, using the slider. HuLiS also gives the wave function as an expansion on the Lewis structures (Fig. 3 and eq. 3). The coefficient of Ψ_{III} is as large as 0.36. It cannot be neglected.

Ψ_{III}

$$\Psi_{HL-P} = 0.59\Psi_I + 0.59\Psi_{II} + 0.36\Psi_{III} \quad (3)$$

$\Psi_{HL-P} = 0.59\Psi_I + 0.59\Psi_{II} + 0.36\Psi_{III}$

3.2. Case B // Allyl radical

this molecule has a Hückel energy of $3\alpha+2.83\beta$, and its ground state wave function is antisymmetric with respect to the (xz) plane (Figure 5). The automatic Lewis structure generator gives only the 2 main resonant structures (scheme 2), equiprobable, and the confidence factor for HL-P is 92%. To illustrate the HL-CI drawbacks, remind to turn the HL-CI "on" in the preference panel, so both HL-CI and HLP are activated.

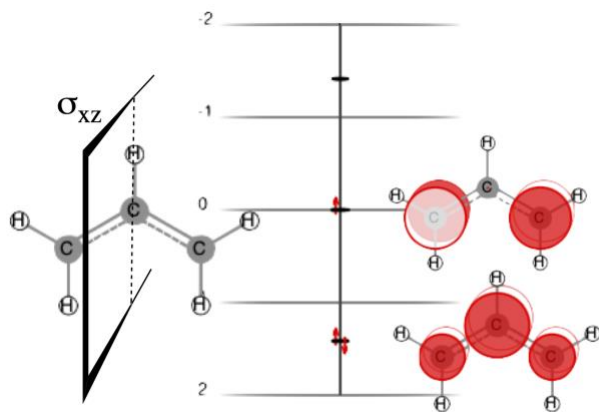
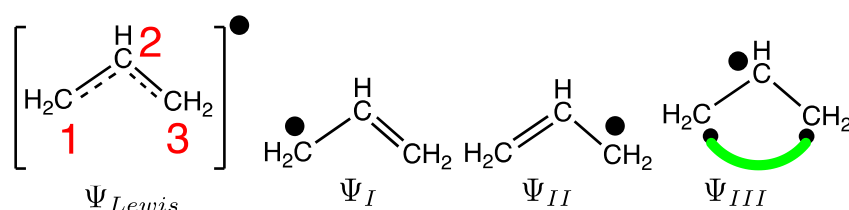


Figure 5: Main allyl π -orbitals. Example of the allyl radical's electronic configuration.



Scheme 2: Allyl radical's average structure (Ψ_{Lewis}) and the three Lewis structures. For Ψ_{III} the green curve shows the singlet coupling of an electron on atom 1 and another on atom 3.

Ψ_{Lewis}

Ψ_{III}

Interestingly, the HL-CI trust factor is 0%, indicating that the Lewis solution is orthogonal to Hückel's. One has to look at the results as text with the "Results" button to obtain this number. We also get the wave functions for these levels and the trust factor values make sense: In HL-P the Lewis structures are combined in an out-of-phase manner, while they are in-phase for HL-CI.

$$\begin{aligned}\Psi_{HL-P} &= (-0.63)\Psi_I + 0.63\Psi_{II} & \text{and } \tau=92\% \\ \Psi_{HL-CI} &= 0.71\Psi_I + 0.71\Psi_{II} & \text{and } \tau=0\%\end{aligned}\quad (4)$$

$\Psi_{HL-P}=(-0.63)\Psi_I+0.63\Psi_{II}$ and $\tau=92\%$

$\Psi_{HL-CI}=0.71\Psi_I+0.71\Psi_{II}$. and $\tau=0\%$

The allyl radical ground state wave function is anti-symmetric with respect to the (xz) plane because the mono-occupied orbital is anti-symmetric. In other words, the mirror plane operator being $\hat{\sigma}_{xz}$, we can write $\hat{\sigma}_{xz}(\Psi_{Hückel}) = -\Psi_{Hückel}$.

$\hat{\sigma}_{xz}$

$\hat{\sigma}_{xz}(\Psi_{Hückel})=-\Psi_{Hückel}$

As a matter of fact $\hat{\sigma}_{xz}$ interconverts one Lewis structure into the other ($\hat{\sigma}_{xz}(\Psi_I) = \Psi_{II}$ and $\hat{\sigma}_{xz}(\Psi_{II}) = \Psi_I$). The two Lewis structures must then be in an out-of-phase combination to describe the allyl radical wave function. The HL-CI wave function is symmetric, hence does not correspond to the ground state.

$\hat{\sigma}_{xz}$

$\hat{\sigma}_{xz}(\Psi_I)=\Psi_{II}$

$\hat{\sigma}_{xz}(\Psi_{II})=\Psi_I$

Moreover, the biradical structure described by Ψ_{III} can be proved to be symmetric, hence it cannot participate to the wave function. This structure can be added manually: click the “Create” button, and single click on each carbon atom will define a radical. Once the three atoms each have a radical dot, the green bond between the appropriate atoms is obtained by drawing a line by drag and drop. When done, we obtain a coefficient $C_{III} = 0$, with the HL-P method, while HL-CI actually does incorporate this third structure to the resonance with a non-zero coefficient ($C_{III} = 0.28$). However, the trust factor for the HL-CI wave function stays at zero, which tells that HL-CI describes a state that is orthogonal to that of Hückel’s ground state.

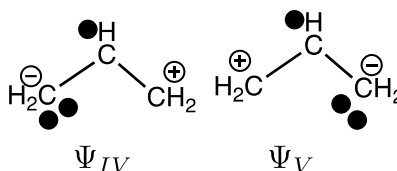
Ψ_{III} $C_{III}=0$ $C_{III}=0.28$

With HuLiS we can add new structures to increase the trust factor up to 98.7%. Those that work best are displayed below (scheme 3, Ψ_{IV} and Ψ_V). They correspond to the ionics of Ψ_{III} , and the wave function shows they are combined in an out of phase manner:

Ψ_{IV} Ψ_{IV} Ψ_{III}

$$\Psi_{HL-P} = (-0.59)\Psi_I + 0.59\Psi_{II} + 0.25\Psi_{IV} - 0.25\Psi_V \quad \text{and } \tau=98.7\% \quad (5)$$

$\Psi_{HL-P}=(-0.59)\Psi_I+0.59\Psi_{II}+0.25\Psi_{IV}-0.25\Psi_V$

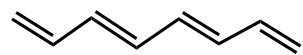


Scheme 3: Allyl radical’s additional structures

Ψ_{IV} Ψ_{IV}

3.3. Case C// Biradical Character in long polyenes

In a recent paper, Gu et al described the increase of biradical character in long linear polyenes.[3] To put it in a nutshell, Lewis structures are sorted with their biradical character: R(0) is for the covalent, with no biradical character, R(1) when one couple of unpaired electrons (one biradical) is in the structure, R(2) for two couples of unpaired electrons (Scheme 4). Valence Bond calculations were done at various levels, and all show that the weight of the covalent drops from about 90% for butadiene (N=4) to about 45% (N=12), and even about 26% for N=18. At the same time the sum of the weights of biradical structures R(1) rises up from about 10% (N=4) to about 55% (N=12). It is even shown that for the largest system, the sum the weights of R(2) structures can be of the same order of magnitude to the weight of R(0) (about 25% each).



R(0)

R(1)

R(2)

Scheme 4: Structure labeling [3], in R(i), i counts the couple of unpaired electrons.

We shall use HuLiS to see how it works for this biradical question. HuLiS can only deal with R(0) and R(1) structures because multiple green bonds, as in R(2) and above, are not

implemented. The first set of calculations are done by setting the preference to allow biradical, but no charge separation (Figure 6 (a)).

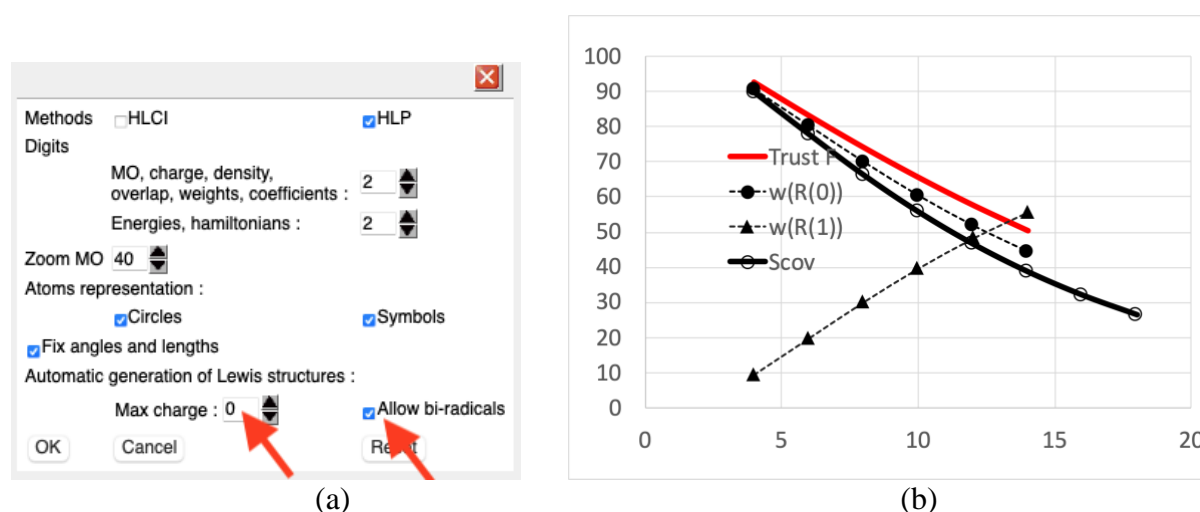


Figure 6 : (a) HuLiS setting for this part : the automatic generation will not allow any charge separation, but allow one biradical character. (b) Variation of the weights of Lewis contributors (R(0) and R(1)) as a function of the polyene size. Additionally, the trust factor and S_{cov} , the overlap between the Hückel wave function and that of R(0), the covalent contributor, are plotted (see text).

The linear polyenes $C_NH_{(N+2)}$ (N even) are then drawn in HuLiS, and for each case we obtain the useful numbers by the following sequence of two steps.

- (a) Create the covalent structure, labeled R(0),
 - pick up in the output S_{cov} which is the overlap between R(0) and the Hückel wave function
- (b) If $N > 14$, skip this second step
 if $N \leq 14$, erase the covalent structure
 - generate all structures and put the slider to the far right
 - pick up the trust factor, and the weight of the covalent : $w_{(R(0))}$.
 note that the weight of the biradicals is just $w_{(R(1))} = 100 - w_{(R(0))}$.

Step (b) is quite slow for N above N=12 and 14. We thus skipped step (b) for N=16 and N=18. In the end of this tutorial we obtain the curves displayed Figure 6(b). It shows the decrease of the weight of covalent contributor and the rising of the biradicals (Figure 6 dashed lines). As in Gu et al. the weight of the covalent is lower than 50% above N=12. HuLiS also computes the trust factor, and its variation shows a decrease from 90% (N=4) to 50% (N=14). That trust factor decrease is an indication that many structures are missing. Of course R(2) structures might be missing, but Gu et al. showed they have a very small weight for $N \leq 10$ (about 6% for N=10).

Ionic structures are implicitly embedded in the covalent structure just because all the symmetric bonds are 50% ionic. However, to adjust the weights of the ionics, they must be explicitly added in HuLiS. To add the zwitterionic contributions we proceed as follows: after erasing all Lewis structures, in the preference panel the user requests a Max charge of 1. Then request the generation of all structures with the appropriate button.

With these new preferences, for $N=8$, for instance the trust factor goes from $\tau=74.1\%$ when only biradicals are generated (7 structures) to $\tau=95.7\%$ (103 structures). For $N=10$, it goes from $\tau=65.4\%$ to $\tau=92.4\%$ (251 structures). HuLiS indicates a number of structures with both the biradical and the ionic characteristics (Figure 7). They weight between 0.8% and 0.02% in the wave function. These results are in line with the conclusion of Gu et al paper that says that the diradical character spreads in many structures.

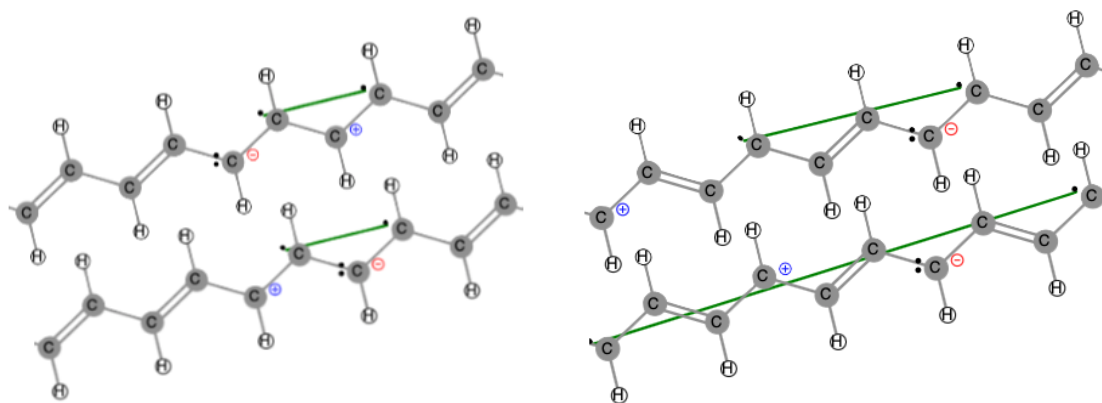


Figure 7 : Examples of structures that have both the covalent and ionic character (in $N=10$).

To conclude on this example one can comment on the curve of S_{cov} (the overlap between the Hückel wave function and the $R(0)$ as a function of the size of the polyene (Black Bold curve, Figure 6). This curve is parallel and close to that of $w(R(0))$. We see the clear decay from about 90% ($N=4$) down to about 25% ($N=18$). This is very close to the VB results obtained for $C_{18}H_{20}$ by Gu et al. This overlap is interesting to use when the trust factor is too small to give credit to the weight of a structure in a calculation. Besides, it is also quick to obtain, as only the covalent structure, $R(0)$, should be drawn, and the S_{cov} overlap does not require many calculations.

4. • Conclusion

The HuLiS program embeds two methods that can be used to numerically describe and explain resonance between Lewis structures with quantum chemistry concepts. Our experience in the field of these schemes, based on the Hückel-derived methods, has shown flaws in HL-CI. We can attribute the fails to the lack of criteria to adjust the off-diagonal terms of the Hamiltonian. By forcing all off-diagonal terms to be equal, and negative, we introduce a bias. There are cases where these assumptions are notoriously false, hence the problems with HL-CI. To avoid wrong results, the trust factor is systematically displayed, and by default HL-CI is disabled in HuLiS.

The common point between the HL-CI and HL-P methods is the writing of a wave function as a combination of electronic configurations (equation 1). As such, a link is created between a very common tool of general chemistry (resonance between Lewis structures) and some tools specific to quantum chemistry (combination of states, configuration interaction, overlap between structures). The notion of confidence, through the trust factor is emphasized in the program. Indeed, a question that a student may ask himself is always "did I take enough structures", "are they representative of the electronic structure I am aiming at?". The trust factor is a strong indication to guide the mind.

One point is never addressed in this use of the trust factor with HuLiS: "does the Hückel method correctly describe this system?" or "Can I use Hückel as a reference in this case?" To the best of our knowledge, the answer is yes for ground states. We devised an ab initio version of HL-P for excited states with strong multi-configurational character.[5]

5. • References

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Optional Elements

GLOSSARY: A dictionary-style definition of any unusual or key terms used in your article
HuLiS: acronym of the **H**ückel-**L**ewis family of method

HL-CI : Hückel-Lewis Configuration Interaction method for calculating resonance using a dressed Hückel Hamiltonian matrix

HL-P : Hückel-Lewis Projected method for calculating resonance using overlaps between the Hückel and the Lewis wave functions

RELEVANT WEBSITES: A list of websites relevant to the chapter

Main HuLiS web site : <http://www.hulis.free.fr>

HuLiS mobile web site : <http://m.hulis.free.fr>