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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 ($S_{IJ} = \langle \Psi_I | \Psi_J \rangle$).

$$\Psi_{\text{Hückel}} = \Psi_{\text{tot}} \\ \Psi_{\text{Lewis}} \\ C_{\{I\}} \\ \Psi_I \Psi_{\{II\}} \\ \omega_{\{I\}} \\ S_{\{IJ\}} = \langle \Psi_I | \Psi_J \rangle$$

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

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

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

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

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.

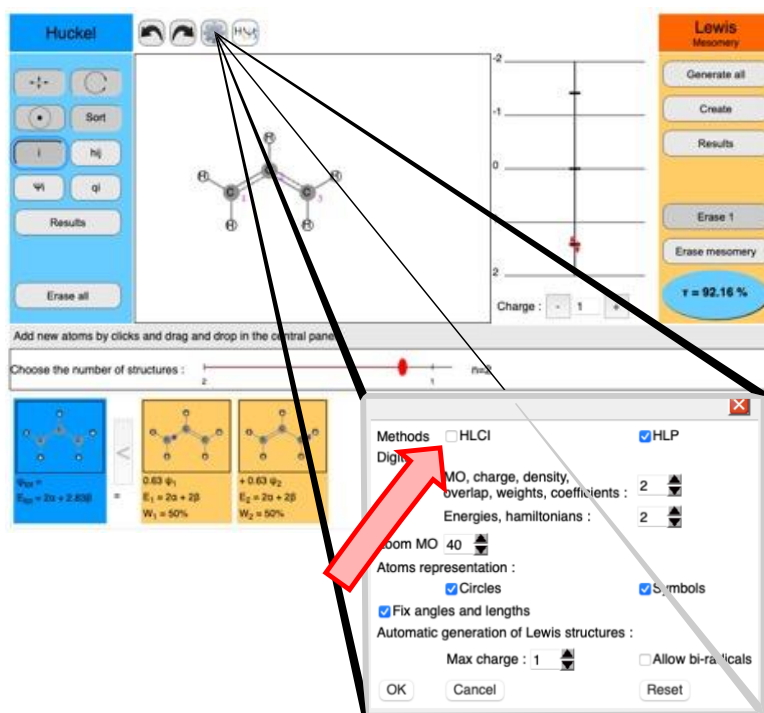
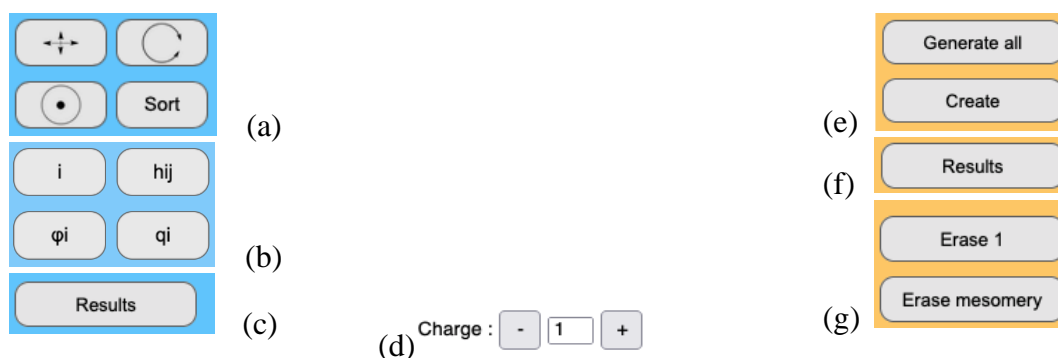


Figure 1: HuLiS GUI, and the preferences panel. By default, the HL-CI check box is unchecked (red arrow) and HLP is checked.

1 2.1. Panels

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

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



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

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

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

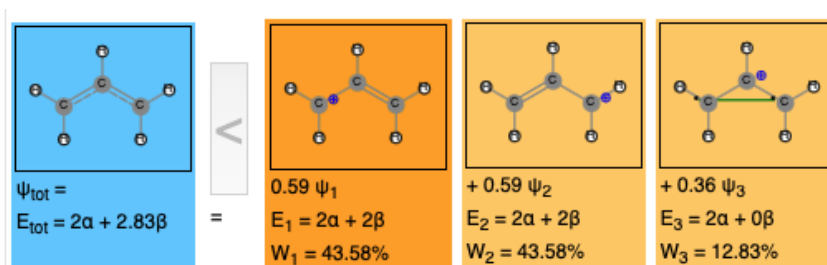
3 2.2. • Results

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

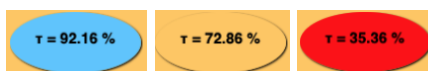
17 Ψ_I
 18 $\omega_{\{I\}}$
 19 C_I

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

24 $\tau = \langle \Psi_{\text{Hückel}} | \Psi_{\text{Lewis}} \rangle$



25
 26 Figure 3: Graphical results for the Lewis expansion.

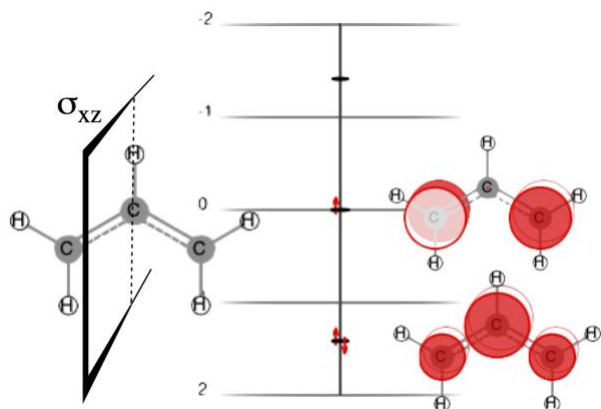


27
 28 Figure 4: Versatile display of the trust factor.

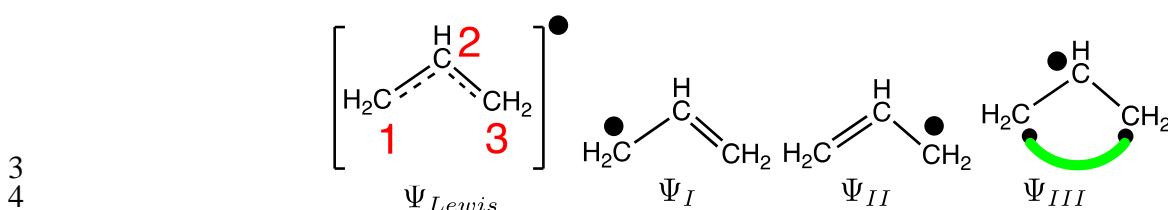
29 More detailed results are displayed in a pop-up window when the button “Results” is pressed.

30 3. • Examples

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



1
2 Figure 5: Main allyl π -orbitals. Example of the allyl radical's electronic configuration.



3
4
5 Scheme 2: Allyl radical's average structure (Ψ_{Lewis}) and the three Lewis structures. For Ψ_{III}
6 the green curve shows the singlet coupling of an electron on atom 1 and another on atom 3.

7 Ψ_{Lewis}
8 Ψ_{III}

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

$$14 \quad \Psi_{HL-P} = (-0.63)\Psi_I + 0.63\Psi_{II} \quad \text{and } \tau=92\% \quad (4)$$

$$15 \quad \Psi_{HL-CI} = 0.71\Psi_I + 0.71\Psi_{II} \quad \text{and } \tau=0\%$$

16
17 $\Psi_{HL-P} = (-0.63)\Psi_I + 0.63\Psi_{II}$ and $\tau=92\%$

18 $\Psi_{HL-CI} = 0.71\Psi_I + 0.71\Psi_{II}$. and $\tau=0\%$

19
20 The allyl radical ground state wave function is anti-symmetric with respect to the (xz) plane
21 because the mono-occupied orbital is anti-symmetric. In other words, the mirror plane operator
22 being $\hat{\sigma}_{xz}$, we can write $\hat{\sigma}_{xz}(\Psi_{Hückel}) = -\Psi_{Hückel}$.

23 $\hat{\sigma}_{xz}$
24 $\hat{\sigma}_{xz}(\Psi_{Hückel}) = -\Psi_{Hückel}$

25
26 As a matter of fact $\hat{\sigma}_{xz}$ interconverts one Lewis structure into the other ($\hat{\sigma}_{xz}(\Psi_I) = \Psi_{II}$ and
27 $\hat{\sigma}_{xz}(\Psi_{II}) = \Psi_I$). The two Lewis structures must then be in an out-of-phase combination to
28 describe the allyl radical wave function. The HL-CI wave function is symmetric, hence does
29 not correspond to the ground state.

30 $\hat{\sigma}_{xz}$
31 $\hat{\sigma}_{xz}(\Psi_I) = \Psi_{II}$
32 $\hat{\sigma}_{xz}(\Psi_{II}) = \Psi_I$

33

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.

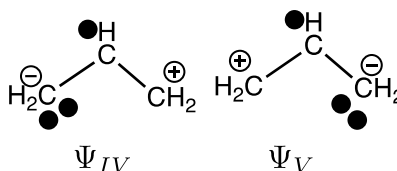
Ψ_{III} $C_{III}=0$ $C_{III}=0.28$

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}

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

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

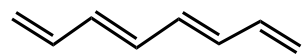


Scheme 3: Allyl radical’s additional structures

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)

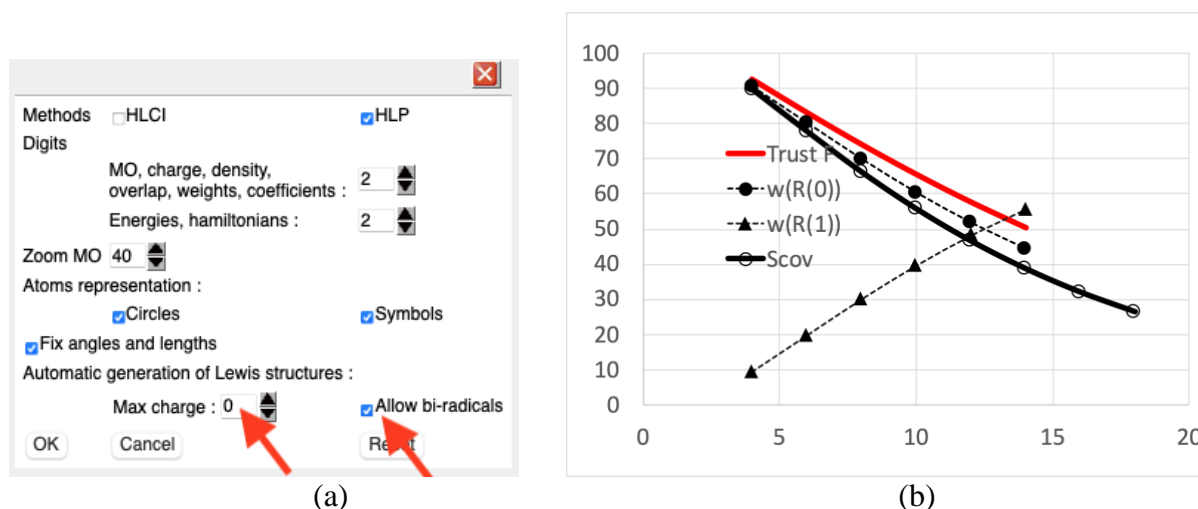
R(1)

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

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



3
 4 (a)
 5 Figure 6 : (a) HuLiS setting for this part : the automatic generation will not allow any charge
 6 separation, but allow one biradical character. (b) Variation of the weights of Lewis contributors
 7 (R(0) and R(1) as a function of the polyene size. Additionally, the trust factor and S_{cov} , the
 8 overlap between the Hückel wave function and that of R(0), the covalent contributor, are
 9 plotted (see text).

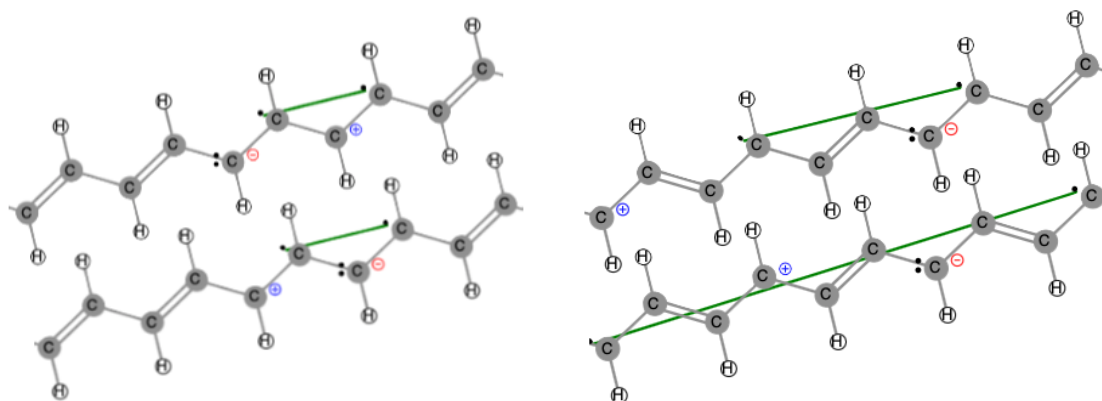
10 The linear polyenes $C_NH_{(N+2)}$ (N even) are then drawn in HuLiS, and for each case we obtain
 11 the useful numbers by the following sequence of two steps.

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

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

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

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



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

9 To conclude on this example one can comment on the curve of S_{cov} (the overlap between the
10 Hückel wave function and the $R(0)$ as a function of the size of the polyene (Black Bold curve,
11 Figure 6). This curve is parallel and close to that of $w(R(0))$. We see the clear decay from about
12 90% (N=4) down to about 25% (N=18). This is very close to the VB results obtained for $C_{18}H_{20}$
13 by Gu et al. This overlap is interesting to use when the trust factor is too small to give credit to
14 the weight of a structure in a calculation. Besides, it is also quick to obtain, as only the covalent
15 structure, $R(0)$, should be drawn, and the S_{cov} overlap does not require many calculations.

16 4. • Conclusion

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

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

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

5 5. • References

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15

16

17 **Optional Elements**

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

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

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

24

25 **RELEVANT WEBSITES:** A list of websites relevant to the chapter

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

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