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Comprehensive Computational Chemistry

CHAPTER TITLE: Local Description with Lewis Structures at the Hückel Level

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ABSTRACT: The chapter describes two approaches that aim at a semi-empirical description of Lewis structures and their interaction, within the Hückel method framework. They have been embedded in the HuLiS program, which is freely available since 2008. Two methods are described and discussed here. They are based either on a dressed Configuration Interaction (CI) hamiltonian matrix, called Hückel-Lewis-CI (HL-CI), or on an overlap-based approach, called the Hückel-Lewis-Projection method (HL-P).

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

KEY POINTS /OBJECTIVES BOX:

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

1 INTRODUCTION

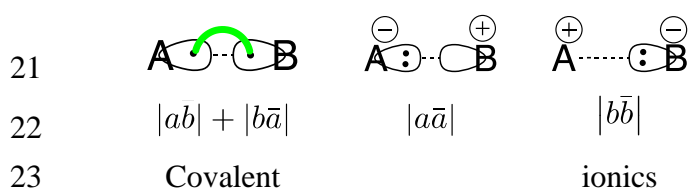
Electronic structures in chemistry can be described either with delocalized or localized orbitals, in the framework of wave-function theory

Delocalized orbitals have gained large popularity with the advent of the Hückel method, Molecular Orbital interaction diagrams, and a nowadays variety of fast quantum chemistry programs and methods. The localized vision is somehow restricted to simplified drawings. Computed localized electronic structures are still rare, and reputedly more complicated to handle. The HuLiS program aims at reconciling simplicity and localized electrons. It targets at computing the key components of the resonance between resonant structures in (flat) conjugated organic systems. Namely, it provides at the Hückel level coefficients and weights of resonant (Lewis) structures.

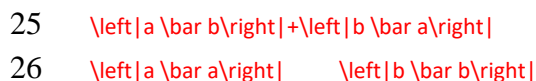
Delocalized Molecular Orbitals: In chemists' toolbox there is a large space for the Molecular Orbital approaches, with two complementary approaches. On the one hand, we use the qualitative MO diagrams with drawings and analyses that can provide an elegant understanding

1 of chemistry on the back of an envelope, and on the other hand, we perform computations, with
 2 Density Functional Theory (DFT), or Hartree-Fock (HF) / post-Hartree-Fock methods, which
 3 provide quantitative results. Both the qualitative and the quantitative approaches provide to a
 4 deep understanding of chemistry. The Hückel method lies in between these two. It provides
 5 easy-to-understand and easy-to-obtain concepts or numbers from the Molecular Orbital theory.
 6 Charges on atoms, HOMO-LUMO gap, etc, can be computed in the Hückel framework. It is in
 7 principle taught to all chemists at universities, and it strongly contributes to introduce in our
 8 minds how concepts and numerical values from the delocalized Molecular Orbitals are useful
 9 both to the understanding of chemistry as well as to gain useful insights into quantum chemistry
 10 basics.¹

11 **Localized Descriptions:** Chemists however consider a molecule as a construction made of
 12 bonds between atoms, and this localized viewpoint is deeply rooted in our minds. As it is
 13 discussed along this VB section (see for instance the introductory chapter of this VB section),
 14 the Valence Bond (VB) approach describes a bond as a resonance between covalent and ionic
 15 configurations (Scheme 1). The equivalent to the MO diagrams can be found in the Valence
 16 Bond Configuration Mixing Diagrams (see for instance the chapter on Valence Bond diagrams
 17 in this VB section). With a very small amount of numerical knowledge (a few ionisation or
 18 electron affinity energies), one connects VB configurations from reactants to products in
 19 Valence Bond State Correlation Diagrams, and clear insights about bond breaking / bond
 20 forming and transition states are obtained.²⁻⁴



24 *Scheme 1: Valence Bond components of a bond $A\text{---}B$, 2 active electrons.*



27 Ab initio VB wave functions can also be computed with efficient programs.⁵⁻⁷ However, their
 28 use for large systems is still uncommon. Indeed, in the VB framework, a pair of active electrons
 29 gives rise to three structures: a covalent and two ionics (Scheme 1), and the number of
 30 structures increases rapidly with the size of the system.⁸⁻¹⁰ The six π -electrons of benzene for
 31 instance require 175 VB structures.¹¹ Apart from the computational cost, this increase in the
 32 number of structures makes the VB method lose its main asset: its simplicity and readability.
 33 Other approaches in the family of computational VB methods, such as the Spin Coupled VB,

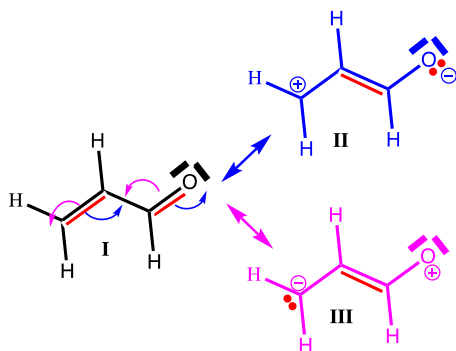
1 which uses Overlap Enhanced Orbitals (OEO)¹² help reduce the number of structures.
2 However, the most natural way of considering a molecule for a chemist is certainly to follow
3 the Lewis intuition that leads to structures involving pairs of bonding electrons, lone pairs, and
4 radicals, which are all localized concepts, and reduce the number of structures compared to the
5 VB wave functions.

6 **1.1 Lewis Qualitative Methodology**

7 Many, if not most, chemists think in terms of local bonds and lone pairs. We see molecules
8 (conjugated molecules, for example) as sets of alternating single and double bonds, with (or
9 without) lone pairs. When this picture does not "work", π -electron mobility is evoked, namely
10 resonance. In resonance, a delocalized π -system is described as a superposition of localized
11 resonant Lewis structures. The ratio of the superposition is given (qualitatively) with the labels
12 "major" or "minor" for the contributors, with the idea that a "major" structure weights more
13 (has a larger weight) than a "minor". The weight of a structure is usually *qualitatively*
14 estimated, and it is larger if:

- 15 -a- the structure fulfils the octet rule.
- 16 -b- the structure avoids charge separations.
- 17 -c- the charge separation (if any) in the structure follows the electronegativity of the atoms.¹

18 The qualitative weights estimation is best illustrated using the typical example of the resonance
19 in acrolein (Scheme 2). Structure **I** fulfils rules **a**, **b** and **c**, and **II** fails on rules **a** and **b**, while
20 **III** fails on rules **a**, **b** and **c** (because O is more electronegative than C, O should get negatively
21 charged rather than positively). Hence the qualitative weights: **I** is the major contributor, **II** is
22 minor, and **III** can be neglected.



23
24

Scheme 2: Some resonance contributors for the acrolein.

¹ The average electronic structure obtained from the resonance between these contributors can also lead to partial charges (q+/q-).

1 When describing the electronic structure of a molecule with the qualitative resonance of Lewis
2 structures, two questions arise: (i) are my structures wisely chosen, and (ii) have I enough of
3 them? Most of the time, the three aforementioned rules help to wisely chose the Lewis
4 structures and the electronic structure of a molecule can be outlined with a very small number
5 of structures. However, a simple quantitative tool is welcome. It shall define numerical
6 descriptors of the relevance of a Lewis structure for a molecule. It is one of the objectives of
7 the HuLiS family of methods to provide these numerical descriptors that enhance the
8 qualitative label major/minor contributor. Another objective is to introduce the quantum
9 chemistry concept and vocabulary of configuration interaction into organic chemistry, where
10 the mixture between Lewis structures is well-established. Last, it introduces VB concepts about
11 overlapping electronic structures into the archetype of the Molecular Orbital method: the
12 Hückel framework where even atomic orbitals are orthogonal !

13 1.2 Lewis Quantitative

14 From the perspective of the theoretical chemist, the superposition of resonance structures is
15 understood as a configuration interaction. An example is given in equation 1 for a Lewis wave
16 function (Ψ_{Lewis}).

17 Ψ_{Lewis}

18

$$19 \Psi_{Lewis} = C_I \Psi_I + C_{II} \Psi_{II} + \dots \quad (1)$$

20 $\Psi_{Lewis} = C_I \Psi_I + C_{II} \Psi_{II} + \dots$

21 Each resonance structure corresponds to an electronic configuration, built on π bonds and lone
22 pairs. Modern approaches to quantum chemistry, although often based on a delocalized wave
23 function, successfully integrate tools allowing to extract from the wave function (or from its
24 density) those terms related to localized (Lewis) structures.¹³⁻¹⁸ Lewis' intuition of electron-
25 pair bond between only two atoms often served as a guideline to devise orbitals and wave
26 functions.¹⁹ Bond Distorted Orbitals (BDO),²⁰ Lewis VB,²¹ or the VB BOND (for Bond
27 Orbitals Naturally Delocalized, VBB),^{22,23} are examples of approaches that use two-center
28 bonding orbitals to describe bonds, and atomic orbitals for radical centers and lone pairs. They
29 allow to follow Lewis' intuition in quantum chemistry computations. It is also on the footsteps
30 of other approaches like Goddard's GVB methods.^{24,25}

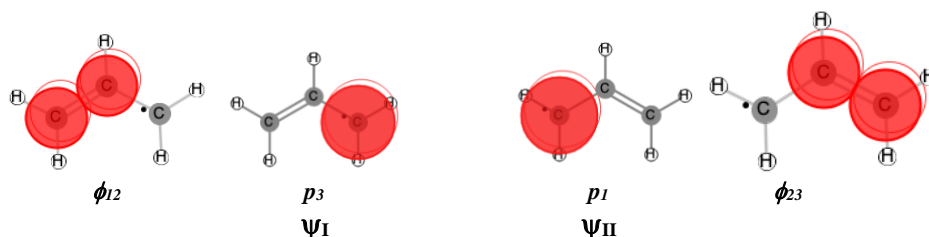


Figure 1: Resonance between two Lewis structures for the allyl radical. The orbitals are drawn in red. They are either bond distorted orbitals (BDO) $\{\phi_{12}, \phi_{23}\}$ or atomic centered orbitals $\{p_1, p_3\}$. In principle, structures do not share the same orbital set.

Explicit "Lewis-like" approaches must use different orbitals for different configurations: the double bond of a Lewis structure (as Ψ_I in Figure 1 left) is described with a BDO (ϕ_{12}) that cannot be reused in the other structure because the resonance has modified the localization of the electron pairs (Figure 1).

2 HuLiS basics

The "HuLiS" (for **H**ückel-**L**ewis) family of methods is grounded on the Hückel Hamiltonian. As a consequence, it can be applied to molecules that are "Hückel compatible": flat and conjugated. It targets at describing the electronic structure of the delocalized π system as a combination, a resonance, of user-defined localized structures (Lewis structures).² In the HuLiS methods we use Lewis structures: a bond corresponds to two electrons in a single BDO, while in VB a bond is a mixture of the covalent and ionic components of purely atomic orbitals (Figure 1 vs Scheme 1). The advantage of BDO's is that it reduces the number of structures, and it preserves the Lewis intuition. Hence, HuLiS uses three types of π -electron pairs:

- The π bond pairs, drawn as standard double bonds. They contain both ionic and covalent components (50% each for symmetrical atom pair).

- The π lone pairs, drawn as two dots on a single atom.

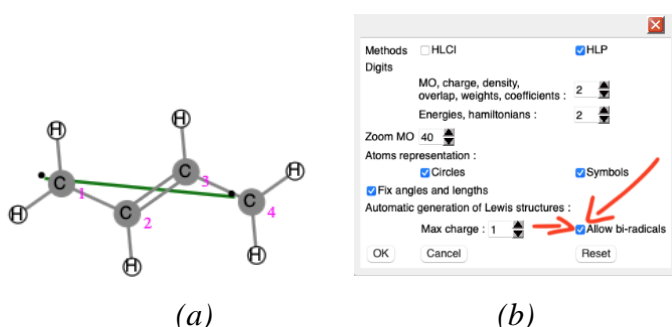
- The π covalent pair, drawn as a green bond. It corresponds to the covalent component of the VB formalism shown in Scheme 1. Only one covalent pair can be defined for a structure. When such a covalent pair is defined between atoms A and B, only the covalent component of this bond is considered ($|a\bar{b}| + |b\bar{a}|$) and no ionics. Such two electrons, coupled as singlet, describe an open shell singlet bi-radicals component. An example for butadiene is shown in Figure 2. By default, the structure generator does not search for these bi-radical covalent pairs.

² HuLiS embeds a structure generator, so Lewis structures can be automatically generated. However, the user can bypass the generator and/or manually add/remove specific Lewis structures.

1 They are in principle manually specified. However, an option in the preference panel can be
 2 set to ask their automatic search (Figure 2b).

$$3 \quad |\left| a \right\rangle \langle b| + \left| b \right\rangle \langle a|$$

4 Radicals (doublet states) can also be considered for odd electron systems. HuLiS methods aim
 5 at describing the superposition of structures in the Lewis framework (mesomery). In the
 6 following we shall review the two methods embedded in HuLiS. In a last part we briefly show
 7 how the overlap is computed and apply the schemes to some exemplary cases. We particularly
 8 focus our attention on the trust factor that can be defined in the context of numerical
 9 evaluations.



12 *Figure 2 : Covalent (bi-radical) component. (a) The biradical coupling for atoms 1 and 4 in butadiene is highlighted by a*
 13 *green “bond”, (b) preference panel for the automatic search (red arrows).*

14 2.1 Configuration Interaction with a dressed Hamiltonian: HuLiS – CI

15 HL-CI is the first method we implemented.^{26,27} The basic idea is to build the Hamiltonian matrix
 16 of the interaction between Lewis structures on the basis of the Lewis structures. To do so, we
 17 define the following approximations and constraints:

- 18 - The diagonal terms are the energies of each Lewis structure (labelled E_I, E_{II}, \dots). They are
- 19 computed at the Hückel level with modified Hamiltonian matrices (see Appendices A and B)
- 20 - The off-diagonal terms (labelled B) are all negative, and all equal.
- 21 - The first eigenvalue of the Hamiltonian between Lewis structures is equal to the energy of
- 22 the molecule at the Hückel level (eq. (2), $E_{Hückel} = \Lambda$).

$$23 \quad E_{\{I\}} \quad E_{\{II\}} \\ 24 \quad \$E_{\{\textit{H}^{ückel}\}} = \Lambda\$$$

25
 26 The value of the off-diagonal terms B , is obtained with these constraints. The expression is
 27 straightforward in a 2x2 case, as shown in eq. (2). We obtain B as the negative root of a
 28 polynomial expression of degree 2 ($P_2(B) = 0$).

$$29 \quad P_2(B)=0$$

$$1 \quad \begin{pmatrix} \Psi_I & \Psi_{II} \\ E_I & B \\ B & E_{II} \end{pmatrix} \Rightarrow \begin{vmatrix} \Psi_I & \Psi_{II} \\ E_I - \Lambda & B \\ B & E_{II} - \Lambda \end{vmatrix} = 0 \Rightarrow B^2 = (E_I - \Lambda) \times (E_{II} - \Lambda) \quad (2)$$

2 $B^2 = \left(E_I - \Lambda \right) \times \left(E_{II} - \Lambda \right)$
3 $\left(E_I - \Lambda \right) \times \left(E_{II} - \Lambda \right)$
4 $\left(E_I - \Lambda \right) \times \left(E_{II} - \Lambda \right)$

5 For larger (n,n) CI matrices, this requires some care, but we proved that we can find an
6 appropriate B as a root of the polynomial expression of degree n ($P_n(B) = 0$).²⁶ We proved

7 that one and only one root is negative, hence our HL-CI procedure has always a solution for B .

8 With this dressed Hamiltonian, the coefficients of the Lewis wave function (equation 1) can be
9 found. In the implementation of HL-CI, we initially worked with the approximation of non-

10 overlapping Lewis structures ($\tilde{\Psi}_{Lewis} = \tilde{C}_I \Psi_I + \tilde{C}_{II} \Psi_{II} + \dots$); we label here with a tilde

11 these non-overlapping coefficients (\tilde{C}_I). In this context, the non-overlapping weights are

$$12 \quad \tilde{w}_I = (\tilde{C}_I)^2; \text{ and } \sum_I \tilde{w}_I = 1.$$

13 $\tilde{w}_I = (\tilde{C}_I)^2$
14 $\tilde{\Psi}_{Lewis} = \tilde{C}_I \Psi_I + \tilde{C}_{II} \Psi_{II} + \dots$
15 \tilde{C}_I
16 $\tilde{w}_I = (\tilde{C}_I)^2$
17 $\sum_I \tilde{w}_I = 1$

18 Quite curiously, despite the numerous approximations, and particularly despite the one that
19 postulates that all the off-diagonal terms are equal, the HL-CI method performs well. It gives

20 usually good results, at least comparable to those of the very popular Natural Bond Orbital
21 (NBO) method (actually Natural Resonance Theory - NRT). For the 5-structure resonance of

22 pyrrole for instance (Table 1), the HL-CI calculation gives an off-diagonal term of $B = 0.57\beta$
23 , and a weight of $\tilde{w}_I = 38\%$ for the major structure while NRT gives a value between 42 and

24 47%, depending on the level of calculation (B3LYP vs HF). Hence, the discrepancies within
25 NRT (5%), have the magnitude of the difference between the HL-CI and the NRT(DFT) results

26 (+4%).

27 $B = 0.57 \beta$
28 $\tilde{w}_I = 38\%$

29

30

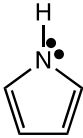
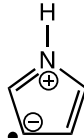
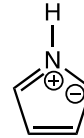
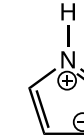

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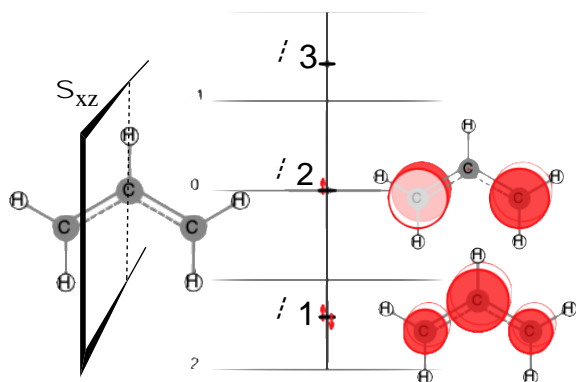
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1 *Table 1: HuLiS and NRT weights (in %) obtained for the pyrrole. The trust factor τ is defined in the following section*

						
2						
3						
4	ψ_I	ψ_{II}	ψ_{III}	ψ_{IV}	ψ_V	
5	NRT(DFT) ^(a)	42	10.5	18.5	10.5	18.5
6	NRT(HF) ^(a)	47	9.5	17.5	9.5	17.5
7	HL-CI ^(a)	38	15.5	15.5	15.5	15.5
8	HL-P ^(b)	50	12	13	12	13

9 (a) from ²⁶ (b) this work .

10 Finally, the weights for the minor structures, at 15.5%, are in the correct range, well situated
 11 between the NRT values of 10.5% and 18.5%. This is not bad, particularly considering all the
 12 approximations at work. The HL-P method (vide infra) gives results with a similar pattern.



13 *Figure 3: With respect to the σ_{xz} plane, the allyl cation has an antisymmetric ground state, due to the mono-occupied π_2 orbital.*

15 There are however notable failures of the HL-CI approach, and the most remarkable are due to
 16 in-phase combinations of the Lewis structures, which is requested by the constraint to have a
 17 negative off-diagonal term. This leads only to symmetric wave functions. When antisymmetric
 18 wave functions are the target, HL-CI can only give a wrong result. The allyl radical (Figure 3)
 19 is an emblematic example of an antisymmetric ground state. ^{23,28-30} We use it as an example for
 20 a tutorial in this VB section. It is of course a superb opportunity to develop a tool to detect, and
 21 finally correct these well identified failures, which is the objective of the next part.

22 2.2 Overlaps and trust factor

23 A very simple and efficient way to detect significant failures of Lewis (or VB) wave functions
 24 with respect to Hückel's is to compute the overlap between the two wave functions, which we
 25 called the trust factor τ , equation 3.

$$26 \tau = \langle \Psi_{Lewis} | \Psi_{Hückel} \rangle \quad (3)$$

$$27 \tau = \langle \Psi_{Lewis} | \Psi_{Hückel} \rangle$$

1 The use of such an overlap has been seldomly reported in the framework of VB computations,
 2 but it proved to be efficient.^{18,31} The wave functions involved in τ are built on Slater
 3 determinants, and the computation of this overlap requests the computation of overlaps
 4 between determinants in the Hückel framework.

5 2.2.1 Overlaps in the Hückel framework, application to Hückel-Lewis

6 In the Hückel framework all the atomic orbitals overlaps are neglected, but MOs of the Hückel
 7 wave function actually overlap with the BDOs, with lone pairs, and more generally with
 8 orbitals of the Lewis structures. Such an overlap between orbitals of two different calculations
 9 lead to an overlap between the corresponding determinants.

10 For the overlap between two determinants, one can just follow the “Guide”.⁹ On the left hand
 11 side we use the diagonal product of the determinant, and on the right hand side we use selected
 12 transpositions (permutations, noted P) of the diagonal product of the other determinant, as
 13 shown in equation 4 for determinants built on the basis of atomic orbitals a , b and c , d .⁹ The
 14 parity of the transposition is noted t , and it is used to change the sign of the corresponding
 15 transposed product. The selected permutations of the right-hand side product are shown in red
 16 in equation 5. They are pairwise transpositions between spin orbitals of the same spin, and $t=0$
 17 for the non-permuted product. The one electron overlap integral between spin orbitals a and b
 18 is noted $s_{ab} = \langle a|b \rangle$.

19 $s_{\{ab\}} = \langle \text{left} \langle a \mid b \mid \text{right} \rangle$

20

21
$$\langle |a\bar{a}b\bar{b}\rangle | |c\bar{c}d\bar{d}\rangle \rangle = \left\langle a\bar{a}b\bar{b} \left| \sum_P (-1)^t P_t(c\bar{c}d\bar{d}) \right. \right\rangle \quad (4)$$

22
$$\begin{aligned} \langle |a\bar{a}b\bar{b}\rangle | |c\bar{c}d\bar{d}\rangle \rangle &= \langle a\bar{a}b\bar{b} | c\bar{c}d\bar{d} \rangle - \langle a\bar{a}b\bar{b} | d\bar{c}c\bar{d} \rangle - \langle a\bar{a}b\bar{b} | c\bar{d}d\bar{c} \rangle + \langle a\bar{a}b\bar{b} | d\bar{d}c\bar{c} \rangle \\ &= s_{ac}^2 s_{bd}^2 - s_{ad} s_{ac} s_{bc} s_{bd} - s_{ac} s_{ad} s_{bd} s_{bc} + s_{ad}^2 s_{bc}^2 \end{aligned} \quad (5)$$

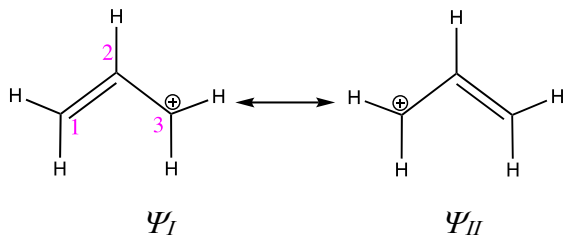
23 $\langle \text{left} \langle \text{left} | a\overline{a}b\overline{b} \mid \text{right} \mid \text{middle} | \text{left} | \{\color{black}c\}\overline{\{\color{black}c\}}\{\color{black}d\}\overline{\{\color{black}d\}} \mid \text{right} \rangle$
 24 $\text{right} \mid \text{right} \rangle = \langle \text{left} \langle a\overline{a}b\overline{b} \mid \text{middle} | \sum_P \text{left} (-1)^t$
 25 $P_t(\{\color{black}c\}\overline{\{\color{black}c\}}\{\color{black}d\}\overline{\{\color{black}d\}}) \mid \text{right} \rangle$

26

27 $\begin{array}{c} \backslash \text{begin}\{\text{array}\}\{\text{cccccc}\} \\ \backslash \text{begin}\{\text{aligned}\} \\ \text{left} \langle \text{left} | a\overline{a}b\overline{b} \mid \text{right} \mid \text{middle} | \text{left} | \{\color{red}c\}\overline{\{\color{red}c\}}\{\color{red}d\}\overline{\{\color{red}d\}} \\ \text{right} \mid \text{right} \rangle \\ \&= \& \langle \text{left} \langle a\overline{a}b\overline{b} \mid \text{middle} | \{\color{red}c\}\overline{\{\color{red}c\}}\{\color{red}d\}\overline{\{\color{red}d\}} \mid \text{right} \rangle \\ \&- \& \langle \text{left} \langle a\overline{a}b\overline{b} \mid \text{middle} | \{\color{red}d\}\overline{\{\color{red}d\}}\{\color{red}c\}\overline{\{\color{red}c\}} \mid \text{right} \rangle \\ \&- \& \langle \text{left} \langle a\overline{a}b\overline{b} \mid \text{middle} | c\{\color{red}\}\overline{\{\color{red}\}} d\{\color{red}\}\overline{\{\color{red}\}} \mid \text{right} \rangle \\ \&+ \& \langle \text{left} \langle a\overline{a}b\overline{b} \mid \text{middle} | d\{\color{red}\}\overline{\{\color{red}\}} c\{\color{red}\}\overline{\{\color{red}\}} \mid \text{right} \rangle \\ \&= \& s_{\{a\color{red}c\}}^2 s_{\{b\color{red}d\}}^2 \\ \&- \& s_{\{a\color{red}d\}} s_{\{a\color{red}c\}} s_{\{bc\}} s_{\{bd\}} \\ \&- \& s_{\{ac\}} s_{\{a\color{red}d\}} s_{\{bd\}} s_{\{b\color{red}c\}} \\ \&+ \& s_{\{a\color{red}d\}}^2 s_{\{b\color{red}c\}}^2 \end{array}$

1 `\end{aligned}`
 2 `\end{array}`
 3 Using the simple example of the resonance in the allyl cation (Figure 4), we can show on a
 4 very simple two-electron case, how the overlap is computed in HuLiS. Let us consider the
 5 overlap between the Hückel wave function ($\Psi_{Hückel}$) with that of the Lewis structure (Ψ_I)
 6 (equation 6). At the Hückel level, the first MO of the allyl cation (labeled π_1 in Figure 3) is the
 7 only bioccupied orbital, hence $\Psi_{Hückel} = |\pi_1 \bar{\pi}_1|$. The wave function of the first Lewis structure
 8 corresponds to the doubly occupied BDO between atoms 1 and 2. It is actually the same as the
 9 one of the allyl radical, labelled ϕ_{12} in Figure 1, hence $\Psi_I = |\phi_{12} \bar{\phi}_{12}|$, and $\phi_{12} = \frac{1}{\sqrt{2}} (p_1 + p_2)$
 10 . The developments in equation 6 are straightforward.

```
11  $\Psi_{Hückel}$ 
12  $\Psi_I$ 
13  $\pi_1$ 
14  $\Psi_{Hückel} = \left| \pi_1 \bar{\pi}_1 \right|$ 
15  $\phi_{12}$ 
16  $\Psi_I = \left| \phi_{12} \bar{\phi}_{12} \right|$ 
17  $\phi_{12} = \frac{1}{\sqrt{2}} (p_1 + p_2)$ 
```



18
19
20 *Figure 4: Two-structure resonance for the allyl cation.*

$$\begin{aligned}
 \langle \pi_1 \bar{\pi}_1 | | \phi_{12} \bar{\phi}_{12} \rangle &= \left\langle \pi_1 \bar{\pi}_1 \left| \frac{1}{\sqrt{2}} (p_1 + p_2) \frac{1}{\sqrt{2}} \overline{(p_1 + p_2)} \right. \right\rangle \\
 &= \frac{1}{2} \langle \pi_1 \bar{\pi}_1 | p_1 \bar{p}_1 + p_2 \bar{p}_2 + p_1 \bar{p}_2 + p_2 \bar{p}_1 \rangle \\
 &= \frac{1}{2} \{ s_{\pi_1 p_1}^2 + s_{\pi_1 p_2}^2 + s_{\pi_1 p_1} s_{\pi_1 p_2} \times 2 \}
 \end{aligned}
 \tag{6}$$

```
22  $\begin{array}{c}
23 \left\langle \left\langle \pi_1 \bar{\pi}_1 \right| \middle| \left| \phi_{12} \bar{\phi}_{12} \right| \right\rangle = \left\langle \pi_1 \bar{\pi}_1 \overline{\pi_1} \right. \\
24 \middle| \frac{1}{\sqrt{2}} (p_1 + p_2) \frac{1}{\sqrt{2}} \overline{(p_1 + p_2)} \middle| \\
25 \left. \frac{1}{2} \left\langle \pi_1 \bar{\pi}_1 \middle| p_1 \bar{p}_1 + p_2 \bar{p}_2 + p_1 \bar{p}_2 + p_2 \bar{p}_1 \right\rangle \right. \\
26 \left. \frac{1}{2} \left\{ s_{\pi_1 p_1}^2 + s_{\pi_1 p_2}^2 + s_{\pi_1 p_1} s_{\pi_1 p_2} \times 2 \right\} \right. \\
27 \left. \end{array} \right\rangle$ 
28  $\end{array}$ 
```

29 The orbitals are then expressed on the orthonormal basis set of the atomic orbitals $\{p_i\}$, as
 30 approximated in the Hückel framework. With $\pi_1 = \frac{1}{2}p_1 + \frac{1}{\sqrt{2}}p_2 + \frac{1}{2}p_3$, we get for instance
 31 $s_{\pi_1 p_1} = \frac{1}{2} \langle p_1 | p_1 \rangle = \frac{1}{2}$, $s_{\pi_1 p_2} = \frac{1}{\sqrt{2}}$. Finally, we obtain the overlap of the Hückel wave
 32 function with a Lewis structure: $\langle \pi_1 \bar{\pi}_1 | | \phi_{12} \bar{\phi}_{12} \rangle = 0.73$

```
33  $p_i$ 
34  $\pi_1 = \frac{1}{2}p_1 + \frac{1}{\sqrt{2}}p_2 + \frac{1}{2}p_3$ 
35  $s_{\pi_1 p_1} = \frac{1}{2} \langle p_1 | p_1 \rangle = \frac{1}{2}$ 
36  $s_{\pi_1 p_2} = \frac{1}{\sqrt{2}}$ 
37  $\begin{array}{c}
38 \left\langle \left\langle \pi_1 \bar{\pi}_1 \right| \middle| \left| \phi_{12} \bar{\phi}_{12} \right| \right\rangle$ 
```

1 =0.73\end{array} \$

2 Using the same technique, many useful overlaps can be computed, such as the overlap between
3 the two Lewis structures $\langle |\phi_{12}\bar{\phi}_{12}| | |\phi_{23}\bar{\phi}_{23}| \rangle = \frac{1}{4}$.

4 \$ \begin{array}{c} \text{cclccccccc} \end{array} \$

5 \left\langle \left| \phi_{12} \overline{\phi}_{12} \right| \middle| \left| \phi_{23} \overline{\phi}_{23} \right| \right\rangle

6 = \frac{1}{4} \end{array} \$

7 The Hückel-Lewis overlaps were compared to *ab initio* values based on “transferable
8 orbitals”.³² The transferable orbitals can be those of a single π atom (for instance a planar $\text{CH}_3\bullet$),
9 computed at the HF/6-31+G level, that is without d orbitals to avoid polarization effects. The
10 overlaps obtained with the HuLiS approach show a pattern similar to those *ab initio* values.⁵

11 The computation of the overlaps lead to substantial updates in HuLiS.

12 2.2.2 Coefficients and normalization of the wave functions

13 In the initial HL-CI implementation, the wave function was normalized in the approximation
14 of non-overlapping Lewis structures. With the computation of the overlap, we get the
15 opportunity to make a *fair normalization*. Hence, the coefficients of the Lewis structures (C_I
16 in Equation 1, $C_I \neq \tilde{C}_I$) were updated. However, for the sake of consistency with the previous
17 version, the “non-overlapping” coefficients (\tilde{C}_I) are still displayed when HL-CI is requested.
18 The coefficients in the overlapping framework are displayed only for the HL-P method (vide
19 infra).

20 \$ C_I \$

21 \$ C_I \neq \widetilde{C}_I \$

22 \$ \widetilde{C}_I \$

23 2.2.3 Coulson-Chirgwin weights

24 As it was the case with the coefficients, in the initial implementation of HL-CI, with non-
25 overlapping Lewis structures, the Lewis structure weights were only approximated (\tilde{w}_I). With
26 the overlaps at hand, we had the opportunity to use the Coulson-Chirgwin weights (equation
27 7), just as any VB program. Again, for the sake consistency with the previous version, for HL-
28 CI only the “non-overlapping” weights \tilde{w}_I are displayed. The Coulson-Chirgwin weights are
29 displayed only for the HL-P method (vide infra).

30 \$ \widetilde{w}_I \$

$$w_I = \sum_J (C_I C_J S_{IJ})$$

31 (7)

32 \$\$ w_I = \sum_J \{ C_I C_J S_{IJ} \} \$\$

33 2.2.4 Evaluation of a trust factor

34 With the *fair normalization* of the Lewis wave function and all the overlaps between Lewis
35 structures and the Hückel wave function, we computed the trust factor (equation 3). It proved
36 to be a useful indicator of the completeness of the Lewis structure basis set, and also of possible

1 failures. The example of the allyl cation is studied in the tutorial. It shows very clearly that the
 2 HL-CI wave function is not suitable, simply because its overlap with the Hückel wave function
 3 is too low (actually $\tau = 0\%$ which is understandable when symmetry is considered). Another
 4 case will be shown in the last part of the present chapter.

5 With the words “trust factor” we made Hückel our reference wave function, assuming that it is
 6 correct for a quick description of the ground state of a molecule. It might appear that in some
 7 cases such a reference is not appropriate, but for most conjugated cases, the Hückel resolution
 8 gives a reasonable description of the electronic structure of the molecule. Somehow on the
 9 footpath of Cooper et al,³¹ we also used a similar trust factor for the localized description of
 10 excited states, using MCSCF reference wave function.^{18,33}

11 **2.3 HL-P approach**

12 Having the overlaps at hand, we significantly improve HuLiS results with the Hückel-Lewis
 13 Projected method (HL-P).³² The principle is to project the Hückel wave function onto a set of
 14 Lewis structures and obtain the coefficient of the Lewis expansion. The improvement was so
 15 effective that it relegates the HL-CI approach to the early stages of HuLiS program settings.
 16 Hence, we buried HL-CI in the depths of a preferences menu, so that no one could use it unless
 17 they specifically requested it. HL-P was introduced in details as a “weights watcher” for Lewis
 18 structures, and this is the occasion of a slightly different description, consistent with the present
 19 chapter.

20 Let us consider that the Lewis wave function is a combination of (overlapping) Lewis
 21 structures, for instance $\Psi_{Lewis} = C_I\Psi_I + C_{II}\Psi_{II}$, and let us call $C_\epsilon\Psi_\epsilon$ the difference between
 22 Hückel and Lewis wave functions. Somehow, considering that Hückel is the reference, one can
 23 consider that Ψ_ϵ is the normalized missing part of the Lewis wave function (equation 8).

$$24 \Psi_{Lewis} = C_I\Psi_I + C_{II}\Psi_{II} \quad ;$$

$$25 C_\epsilon\Psi_\epsilon$$

$$26 \Psi_{Hückel} = \Psi_{Lewis} + C_\epsilon\Psi_\epsilon \quad (8)$$

$$27 \Psi_{\text{Hückel}} = \Psi_{Lewis} + C_\epsilon\Psi_\epsilon$$

28

29 Moreover, we make the assumption that Ψ_ϵ is orthogonal to each of the Lewis structures. This
 30 assumption is naively justified by the idea that the missing part of a sum of contributors cannot
 31 be a part of the contributors. Even if it is not exact in the context of non-orthogonal CI, it
 32 provides a clear understanding of the strategy at work. Besides, C_ϵ is normally small, and in
 33 the developments, we will neglect the corresponding contributions: $C_\epsilon \langle \Psi_I | \Psi_\epsilon \rangle \approx 0$ for all
 34 Lewis structures. In the end, we calculate the trust factor, which is actually a safeguard.

1 We can project equation (8) on each Lewis structure to obtain a system of equations (equations
 2 9 and 10) that give the coefficients (C_J) of the Lewis wave function.

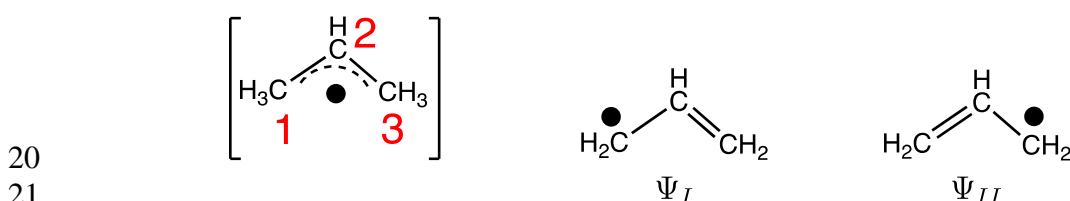
$$3 \left\{ \begin{array}{l} \langle \Psi_I | \Psi_{Hückel} \rangle = \langle \Psi_I | C_I \Psi_I + C_{II} \Psi_{II} + \dots + C_\epsilon \Psi_\epsilon \rangle \\ \langle \Psi_{II} | \Psi_{Hückel} \rangle = \quad \quad \quad \cdot \\ \quad \quad \quad \cdot \\ \quad \quad \quad \cdot \end{array} \right. \quad (9)$$

$$4 \left\{ \begin{array}{l} \langle \Psi_I | \Psi_{Hückel} \rangle = \sum_J C_J \langle \Psi_I | \Psi_J \rangle + \underbrace{C_\epsilon \langle \Psi_I | \Psi_\epsilon \rangle}_{\approx 0} \\ \langle \Psi_{II} | \Psi_{Hückel} \rangle = \quad \quad \quad \cdot \\ \quad \quad \quad \cdot \\ \quad \quad \quad \cdot \end{array} \right. \quad (10)$$

5 We can label (\mathbf{S}_{HuLiS}) the (vertical) vector that describes the overlap of each Lewis structure
 6 with the Hückel wave function, and (\mathbf{C}) the (vertical) vector of the coefficients of the Lewis
 7 wave function on the Lewis structure basis set. Last, (\mathbf{S}) is the overlap matrix between Lewis
 8 structures. The normalized vector of the Lewis wave function (\mathbf{C}) is obtained by the resolution
 9 of equation 11, and the weights (w_I) are obtained with the Coulson-Chirgwin formula (7).

$$10 \quad \mathbf{S}_{HuLiS} = \mathbf{S}(\mathbf{C}) \quad (11)$$

11 The results of HL-P are similar to those of HL-CI when HL-CI is correct. For pyrrole for
 12 instance (Table 1) the two HuLiS methods provide Lewis wave functions with a good trust
 13 factor ($\tau > 85\%$), the weights are similar, and in the range of the NRT values. This is the case
 14 in all the non-pathological cases we studied.^{32,34} The real improvement of HL-P over HL-CI
 15 comes for cases where HL-CI cannot give the Lewis wave function, because of the assumption
 16 of a negative off diagonal term. This is the case notably for the allyl radical which has an
 17 antisymmetric ground state due to the mono occupation of its highest occupied orbital (Figure
 18 3). The Lewis wave function must then be an out-of-phase combination of Ψ_I and Ψ_{II} :
 19 $\Psi_{Lewis} = N(\Psi_I - \Psi_{II})$.



22 Scheme 3: Allyl radical Lewis structures

23 When HL-CI is used, HuLiS gives the in-phase combination $\Psi_{Lewis} = N(\Psi_I + \Psi_{II})$ with a
 24 trust factor of $\tau = 0\%$, indicating that the results are not representative of the state found by
 25 the Hückel method. *A contrario*, the HL-P method gives the appropriate wave function
 26 $\Psi_{HL-P} = N(\Psi_I - \Psi_{II})$ with a correct trust factor (92%).

3 Conjugated radicals in HuLiS.

We shall present here two cases that show the out-of-phase combination of Lewis structures.

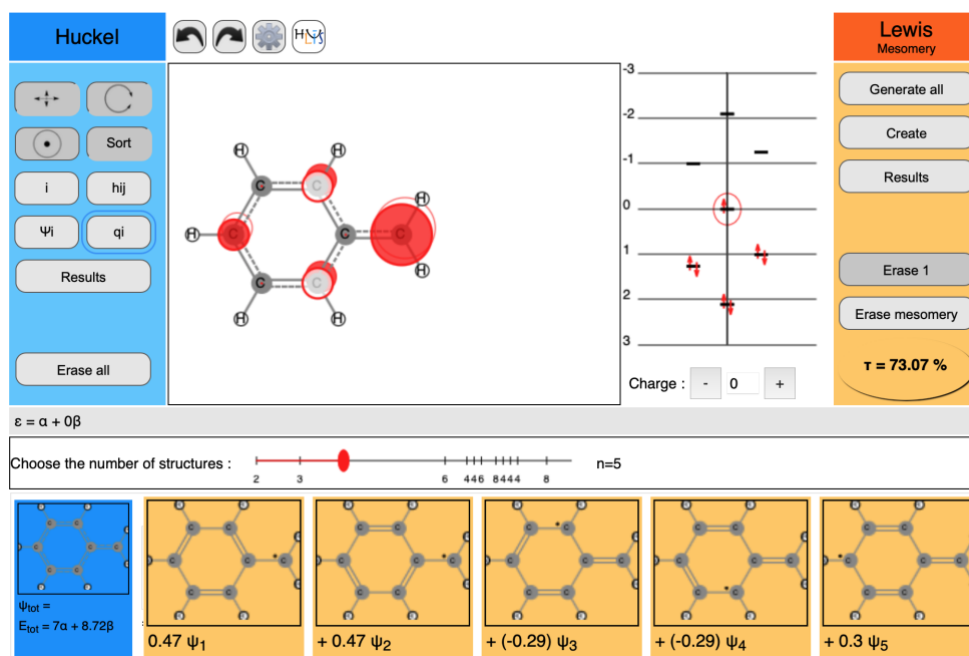
3.1 The benzyl radical – a symmetric case with out of phase Lewis components

For the benzyl radical, our automatic generation of the Lewis structures finds 53 structures, and the trust factor is 88% for HL-P against only 15% for HL-CI. Reducing the number of structures from 53 to 5, a similar pattern is obtained: the trust factor for HL-P (73%) is still much larger than that of HL-CI (27%). The screenshot in Figure 5 shows the results that are obtained for 5 structures.

The reason for the difference comes from the in-phase/out-of-phase combination of the structures (equations 12 and 13). HL-CI only finds an in-phase combination (eq. 12), while the coefficients in the HL-P expansion are alternatively positive and negative (eq. 13). The pattern of the HL-P coefficients actually follows the one of the coefficients of the Semi Occupied Molecular Orbital (SOMO) displayed in the middle of Figure 5. Whenever the coefficient is positive (red) at a position, the structures that embed the radical at that position have positive coefficients, and a negative value for a negative orbital coefficient.^{29,35,36}

$$\Psi_{HL-CI} = 0.45(\Psi_I + \Psi_{II} + \Psi_{III} + \Psi_{IV} + \Psi_V) \quad (12)$$

$$\Psi_{HL-P} = 0.47(\Psi_I + \Psi_{II}) - 0.29(\Psi_{III} + \Psi_{IV}) + 0.30\Psi_V \quad (13)$$

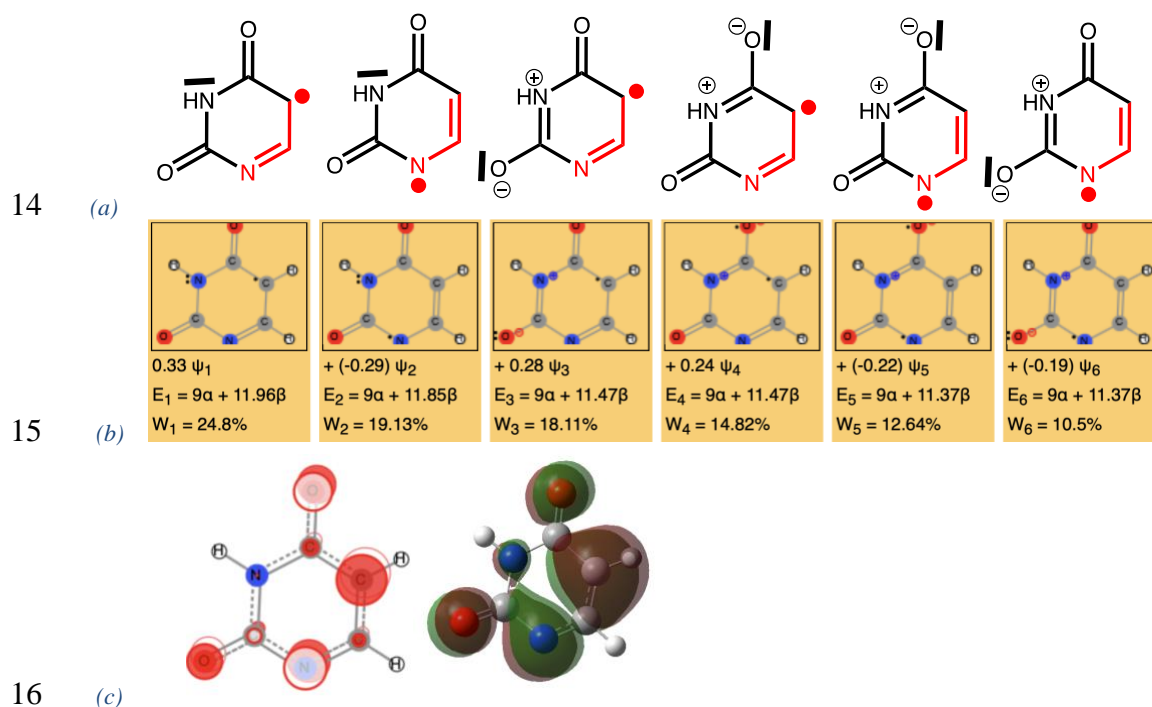


18
19 *Figure 5: Screen copy of the HuLiS computation of the benzyl radical in HuLiS (mobile version).*

20 3.2 Uracil dehydrogenated radical - out of phase Lewis components

21 This π -radical is delocalized on mainly two atoms, the dehydrogenated nitrogen, $N\bullet$ and its
22 conjugated carbon $C\bullet$. This radical intermediate is believed to play a role in prebiotic

1 interconversions of DNA bases.^{37,38} In the path that connects uracil to thymine, an important
 2 intermediate is the radical species stabilized by the delocalization shown in Figure 6. It is
 3 noteworthy that the delocalization is said to mainly concern the dehydrogenated nitrogen and
 4 the conjugated carbon (i.e. the part highlighted in red in Figure 6). HuLiS calculation shows
 5 indeed the tendency to develop the radical on the two atoms C• and N• proposed by the authors.
 6 Furthermore, it shows that the rest of the cycle does not really participate to the radical
 7 delocalization. Finally, HuLiS shows a slightly larger participation of the C• compared to N•:
 8 in structures Ψ_1 , Ψ_3 and Ψ_4 the radical is on the carbon (C•), and the sp₃ nitrogen lone pair is
 9 delocalized toward the two carbonyls. Those three have positive coefficients (C₁=+0.33,
 10 C₃=+0.28, C₄=+0.24). The structures with a radical character on the sp₂ nitrogen N• have a bit
 11 smaller (and negative) coefficients (C₂=-0.29, C₅=-0.22, C₆=-0.19). Weights follow the
 12 tendency of the SOMO's coefficients. In the next step of this specific reaction, the radical C•
 13 reacts with formaldehyde, and, *in fine*, builds the methyl group of the thymine.³⁷



17 *Figure 6: Main π -radical delocalization in the dehydrogenated uracil: (a) drawings (b) HuLiS results (only the 6 first*
 18 *structures were used (c) SOMO orbital at the Hückel level (left) and B3LYP/6-31G(d) (right).*

19 4 CONCLUSION/SUMMARY/OUTLOOK:

20 Very much like the MO theory, the resonance theory (VB – like) uses complementary tools.
 21 They range from the simplest quick drawings obtained via Lewis structures and mesomery
 22 (back of the envelop strategy), up to high-level Valence Bond numerical computations with
 23 efficient and available programs. However, to obtain numerical values requires to use programs
 24 that require some skills. Even though online tools that use useful graphical interfaces are

1 emerging, there is still room for tools that give numerical insight into resonance theory without
2 getting familiar in computational chemistry tools. We like to see the Hückel-Lewis approach,
3 implemented in the HuLiS tools suite, as an “in-between” tool that provides easy-to-
4 understand, but also numerically appropriate results about the electronic structure of molecules
5 in the resonance framework. It provides coefficients and weights of the Lewis structures with
6 a reasonable accuracy. As far as we tested it by comparing to the NBO-NRT, or actual VB
7 results,^{32,39} the HL-P strategy gives accurate numbers for the resonance between Lewis
8 structures. The HL-CI method fails in some well identified cases, but it opens an interesting
9 bridge between the world of Lewis resonance, which is widely used by chemists, and the more
10 confidential world of multiconfigurational calculations (MCSCF). So many chemists, and
11 particularly organic chemists, like Monsieur Jourdain speaking prose all his life without
12 knowing it, are experts in non-orthogonal MCSCF concepts without knowing it, just through
13 the resonance between Lewis structures.

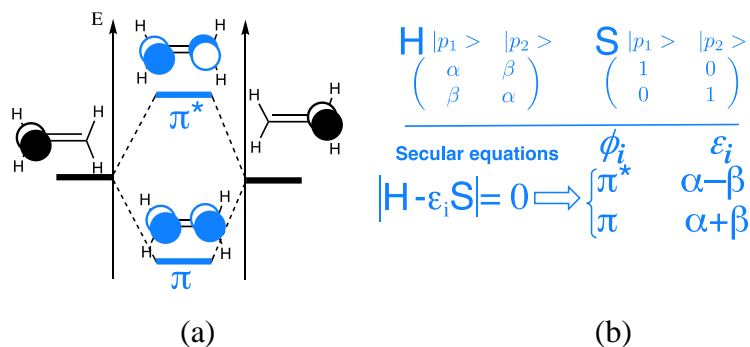
14 Finally, the HuLiS tools suite introduces in a systematic way the use of the trust factor which
15 is the overlap between the Lewis wave function and the delocalized Hückel wave function.
16 This correspondence is of course interesting as a safeguard when looking for a reasonable
17 number of Lewis structures: the trust factor $\tau = \langle \Psi_{Lewis} | \Psi_{Hückel} \rangle$ is a simple indicator of the
18 quality of the Lewis wave function. Provided that the reference (Hückel) is reliable, it might
19 also indicate the limits of the localized descriptions. This confidence rate can be useful in *ab*
20 *initio* Valence Bond wave function studies. In the context of a study of the excited "V" state of
21 ethylene, we have used it for the construction and interpretation of Breathing Orbital VB
22 (BOVB) wave functions, with reference to Multi Reference Configuration Interaction (MRCI)
23 wave functions ($\tau = \langle \Psi_{BOVB}^* | \Psi_{MRCI}^* \rangle$).¹⁸

24 As an evolution of our HuLiS tool, we are currently implementing the possibility of
25 delocalization into blocks, in the spirit of the Block Localized Wave function (BLW) method.⁴⁰
26 A block is the delocalization of N electrons on M centers (or atoms) and is noted (Ne,Mc).
27 Blocks shall extend the concepts of lone pairs and bonds. Lone pairs are blocks of two electrons
28 on one center (2e,1c) and bonds are blocks of two electrons on two centers (2e,2c). Blocks
29 allow to consider for instance benzene as a block of six electrons on six centers (6e,6c) and
30 cyclopentadienyl anion as a block of six electrons on five centers (6e,5c). This new
31 implementation will significantly open the playground of HuLiS to complementary studies of
32 aromaticity in fused rings.

33

1 **Appendice A: Hückel method in a nutshell**

2 The electronic delocalization between two atoms is defined within the simple qualitative
 3 approach of the Molecular Orbitals by Linear Combination of Atomic Orbitals (MO-LCAO).
 4 Two laterally overlapping atomic orbitals interact and generate π bonding / π^* anti-bonding
 5 orbitals (Figure A- 1(a)). Those can be occupied with an appropriate number of electrons, and
 6 in addition to bond order, other charge delocalization quantities can be qualitatively discussed,
 7 particularly for unsymmetrical systems where the MOs are distorted.



8
 9
 10 *Figure A- 1: π orbitals in ethylene. (a) qualitative orbital interaction diagram to obtain π and π^* orbitals. (b) Hückel method:*
 11 *α and β are negative energetic quantities.*

12 Complementary to this qualitative approach, the well-known simple Hückel quantum empirical
 13 method can be considered to get some numerical insights about the π systems. A Hamiltonian
 14 matrix is built on the basis of the atomic orbitals (here $\{p_1, p_2\}$, Figure A- 1(b)). The diagonal
 15 terms of the Hamiltonian matrix (α) correspond to the energy of the isolated AOs (those are
 16 carbon AOs for instance). As such, α is a negative quantity. Similarly, the off-diagonal terms
 17 (β) represent the interaction between the AOs, and is also a negative quantity. The electro-
 18 negativity of an atom can be taken into account by adding a parametrized amount of β to the
 19 corresponding diagonal term. For instance, the sp_2 Oxygen atom that is encountered in ketones
 20 is more electronegative than a carbon sp_2 , and we can use for its diagonal term $\alpha_O = \alpha + 0.97\beta$,
 21 so $\alpha_O < \alpha$. Similarly, the off-diagonal terms are also parameterized. The parameters in HuLiS
 22 come from Van-Catledge's contribution.⁴¹

23 In the Hückel method only neighboring atoms have a non-zero off-diagonal term. Setting β to
 24 zero for non-neighboring atoms usually does not isolate one AOs from the rest of the molecule
 25 because conjugation goes through neighbors of neighbors. Simple Hückel theory lays on an
 26 initial definition of the σ electron (skeleton), although those electrons are not explicitly
 27 considered. The scheme works well for π systems which seem to be parameterized quite easily.
 28 Moreover, the physical/mathematical techniques used are simple and can be used for any
 29 interacting system.

1 Simple Hückel theory uses the identity matrix for the overlap. The interactions between centers
 2 rest entirely on the off-diagonal terms of the Hamiltonian matrix. Yet the Simple Hückel
 3 scheme gives much information for reactivity, as well as quite a few structural interesting data
 4 such as bond indices, partial atomic charges, etc, all those data result from the electronic
 5 delocalization that occurs throughout the molecule. In HuLiS we particularly make use of the
 6 total energy, which is the sum of the energies of all the π electrons (equation A-1). We also
 7 define the Hückel wave function, and define it as the Slater determinant constructed on the
 8 occupied spin orbitals (equation A-1).

$$E_{Hückel} = \sum_i^{\pi \text{ electrons}} \epsilon_i \quad (\text{A-1})$$

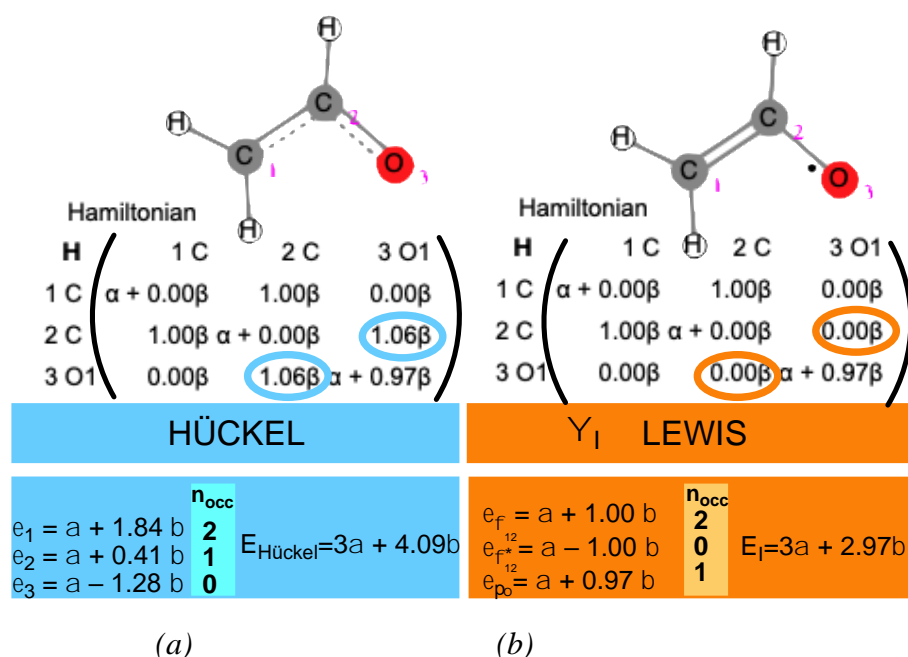
$$\Psi_{Hückel} = |\pi_1 \bar{\pi}_1 \pi_2 \dots| \quad (\text{A-2})$$

11 $E_{\text{Hückel}} = \sum_i^{\pi \text{ electrons}} \epsilon_i$
 12 $\Psi_{\text{Hückel}} = \left| \pi_1 \bar{\pi}_1 \pi_2 \dots \right|$

1 Appendix B: Lewis structures in Hückel

2 Each Lewis structure is grounded on a delocalized π system that is partly localized. Such a
 3 localization is obtained by a modified Hamiltonian matrix called here the Lewis Hamiltonian
 4 Matrix (LHM) of a defined Lewis structure. This LHM is a copy of the Hückel Hamiltonian
 5 matrix with modifications that account for the localization requested by the Lewis structure.
 6 The off-diagonal terms of the LHM obey the Lewis structure drawing as follows: terms that
 7 correspond to single bonds are set to zero, the others are taken from the Hückel Hamiltonian
 8 matrix. An example is given bellow (Figure B-1).

9 The diagonalization of the LHM gives block-localized orbitals that have to be filled with the
 10 appropriate number of electrons to fully correspond to the Lewis structure. In the example
 11 bellow (Figure B-1), we obtain three localized orbitals (not shown): one Bond Distorted
 12 Orbital between atoms 1 and 2 (ϕ_{12}), plus its antibonding orbital (ϕ_{12}^*), and p_O (the oxygen
 13 atomic orbital). To describe the requested Lewis structure, the configuration must be $(\phi_{12})^2$ (
 14 p_O)¹. We obtain from such a calculation both the energy of the Lewis structure and its wave
 15 function written as a single Slater determinant.³ Here $E_I = 3\alpha + 2.97\beta$ and $\Psi_I = |\phi_{12}\bar{\phi}_{12}p_O|$
 16 .



17

18

19 *Figure B-1: Modification of the Hückel Hamiltonian matrix (a) \rightarrow to (b) to describe a Lewis structure. Eigenvalues of the*
 20 *Hamiltonian matrices, occupation number of the orbitals for the corresponding cases and energies of the electronic*
 21 *configurations.*

22

23

³ Biradical singlets require two determinants, like $|a\bar{b}| + |b\bar{a}|$.

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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>