Hückel-Lewis Projection Method: A "Weights Watcher" for Mesomeric Structures[†]

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A new approach to extract the coefficients and weights of Lewis structures from the Hückel wave function is designed: Hückel-Lewis projection (HL-P). The weights are obtained by projection on overlapping Lewis structures. This straightforward alternative to ab initio approaches is detailed and used on typical cases, including acrolein, allyl radical, pyrrole-like systems, and imidazolylidene. A trust parameter is defined and shown as a guide to retrieve the most important Lewis structures. The emblematic examples of butadiene and benzene are chosen to illustrate the use of this parameter.

1. Introduction

The chemical bond somehow takes its root in Lewis legacy, which has been discussed in a recent issue of the *Journal of Computational Chemistry*.[1] This localized vision of the electronic structure is however too restricted, and electronic delocalization has been essential for a better understanding of chemistry and material science in general. Electronic delocalization and the related concept of aromaticity are commonly used to better understand the stabilization of conjugated (or aromatic) molecules, and various criteria based on geometric, energetic, magnetic, and electronic properties have been proposed to characterize these not directly measurable quantities.[2–4] Delocalized ab initio techniques are now routinely used to compute molecular properties. Despite (or thanks to) its simplicity, the Hückel approach is still an important qualitative tool to learn and discuss these chemical concepts on a sound basis.

Chemists also routinely handle electronic delocalization through mesomery, which can be viewed as a "superposition" of several Lewis structures (also called "contributors").[5,6] A large part of the thinking in chemistry comes from simple drawings that are Lewis structures in resonance. This mesomery is a necessary rationalization when the electronic structure of a molecule cannot be accounted for by a single Lewis structure. The delocalized system obtained by this resonance between Lewis structures is called a "resonant hybrid".

This concept of mesomery probably takes part of its root in early one- and three-electron bond studies[7] but is much used in organic chemistry in general to draw molecules. The stability of a π system is related to the quality and the quantity of its Lewis contributors. Despite its simplicity, the Lewis representation also has the advantage to give some insight in the covalent/ionic nature of the resonating structures, through the formal charges. In certain cases, it also has the virtue to predict the planar geometry of molecules. The simple case of the two resonant contributors of formamide[8] suffices to explain for example the local planarity of the amide group in peptide sequences.

There are however no simple method to address the contribution of a Lewis structure to the resonant hybrid. To do so, one usually relies on qualitative rules, based on chemical "intuition":

1. the octet rule, the most important one: the more it is fulfilled, the more the Lewis structure contributes.
2. the charge separation rule: the less formal charges, the more the Lewis structure contributes, unless rule (1) is not fulfilled.
3. the electronegativity rule: if there are formal charges, the best Lewis contributor places the negative (positive) charges on the most (less) electronegative atom, unless rule (1) is not fulfilled.
4. the adjacent charge rule:[6] if there are charges of same sign within the Lewis contributor, the farthest the charges, the better.

Such simple rules have even recently been used to automatically generate the most stable Lewis structure and assign the correct bond order of small molecules from the protein data bank.[9]

Because they are so important to communicate between chemists, Lewis structures together with mesomery and resonance in general, have attracted much consideration from quantum chemists. We shall divide the efforts made in this field into two families: (i) the Configuration Interaction methods (CI), and (ii) the Projection methods.

(i) The first family encompasses both those built with orthogonalized orbitals (MO-CI related methods)[10–12] and those built on nonorthogonal orbitals (valence bond (VB) such as VB-CI, and VB-SCF related).[13–16] They proceed a priori: the delocalization is obtained by the resonance between localized structures that are predefined. These localized structures can be either true VB structures, where each bond is separated into its covalent and ionic components, or "true" Lewis structures, where a bond embeds at once covalent and ionic structures.[17,18,19]

(ii) The second family concerns a posteriori methods and aims at projecting a predefined delocalized state onto localized structures. They can proceed by projecting the delocalized wave function, or its corresponding one-electron density, onto those of localized structures.[20–24] Topological analysis of the wave function also gives an interesting reading of the delocalized state as a combination of localized states.[25–32] Either VB or Lewis structures are used to obtain the weights.

All these methods have their advantages and drawbacks. VB approaches permit a clear definition of mesomery as a config-

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uration interaction but are computationally expensive. This is particularly true when the CI space must be enlarged by additional structures and/or when each configuration have its specific set of orbitals, as in the breathing orbital valence bond (BOVB) approach.[14,15] Besides, there are no numerical criteria to decide when to stop the CI expansion.

Projection methods somehow correct both problems. They are computationally more efficient and could contain a built-in target that can give an indication on how good the expansion is. However, they proceed a posteriori and cannot attain such a precise envision of the electronic delocalization, as VB methods can, for instance through the BOVB approach. Projection methods, as they are commonly used in the natural resonance theory (NRT) approach,[26–28] do not provide the coefficient of the simulated CI but directly give the weights of Lewis structures. This precludes any discussion on the sign of the coefficients of the CI, which can be negative or positive.[33] Recent work on the projection of the wave function, rather than the one-electron density, opens the possibility to easily access to this sign.[24]

However, all these approaches require some technique to handle geometrical optimizations and a specific strategy to localize the orbitals on bonds and lone pairs, such as the natural bond orbitals (NBO).[29] There is a large gap between the simple chemical drawings and the ab initio approaches required to address the question of mesomery quantum mechanically. We recently developed a straightforward alternative, which fills this gap. Based on the Hückel methodology, the Hückel-Lewis Configuration Interaction (HL-CI)[34,35] recasts the concept of Lewis structures into the Hückel formalism. It is free of any geometrical optimization, and the orbitals localization can be considered as built-in. It aims at giving to mesomery the simplicity and readability that the Hückel method gives to delocalized molecular orbitals. However, the HL-CI approach suffers from defaults that are presented and corrected in this article.

In the next section, we shall analyze important defaults of HL-CI. We then turn to present the new HL-P approach and use it on typical cases of mesomery that are allyl radical, butadiene, and benzene. In section 3 we compare HL-P to the ab initio NRT approach.

2. Methods

The HL-CI method belongs to the CI family: it relies on the determination of the interaction term between two any Lewis structures wave functions. The expansion coefficients of each Lewis structure in the Hückel wave function (hence the weights) are obtained on an energetic criteria. The HL-P method on the other hand belongs to the projection family: the weights are obtained from the determination of overlap between Lewis structures and the Hückel wave function as well as the overlap between two any Lewis structures.

To describe each Lewis structure *i*, we define a wave function ϕ_i with the following requirements:

- ϕ_i is written as a Slater determinant of local spin-orbitals (see for instance[25]);
- the local spin-orbitals are obtained in the Hückel framework. Localization is done by canceling resonance terms in the Hückel Hamiltonian: $\beta_{ab} = 0$ if atoms *a* and *b* are linked by a single bond in the considered Lewis structure.[34,35]
- Spin-orbitals are topologically populated according to the Lewis structure sketch.[36]

Finally, the wave function of the resonant hybrid, noted, $\tilde{\psi}$ is written as a linear combination of Lewis structures.

$$\left|\tilde{\psi}\right\rangle = \sum_{j=1}^{N_{\mathrm{struct}}} c_j|\phi_j\rangle \tag{1}$$

In order to compare to the NRT approach, we use the Coulson-Chirgwin weights[37]

$$w_i = c_i \sum_{j=1}^{N_{\mathrm{struct}}} c_j S_{ij} \tag{2}$$

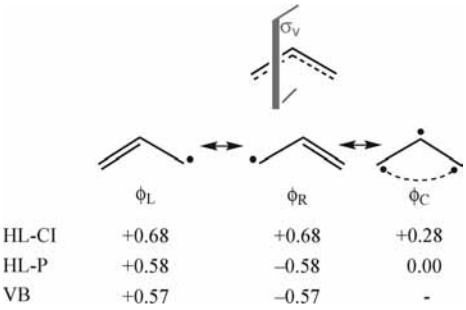
In what follows, we will make use of the Hückel wave function, noted $\Psi_\forall$ and written as a Slater determinant of standard Hückel molecular orbitals. In the following methods the molecular wave function of the delocalized ground state $\Psi_\forall$ is considered to approximately equalize that of the resonant hybrid $\tilde{\Psi}$:

$$\left|\psi_\forall\right\rangle \simeq \left|\tilde{\psi}\right\rangle \tag{3}$$

2.1. HL-CI Method. In the HL-CI approach, the overlap between Lewis structures is neglected, that is, the overlap matrix between the Lewis structures wave functions ϕ_i is set to the identity matrix. The overlap between structures is implicitly taken into account through the off-diagonal terms of the Hamiltonian. In this respect, there is an evident parallel between the interacting Lewis structures in the HL-CI method and the interacting p neighbor orbitals in the Hückel method. In the latter, this interaction is the so-called "resonance" parameter β and corresponds to an off-diagonal term in the Hückel Hamiltonian. Whereas it is straightforward to define a vicinity between atomic orbitals, it is not possible-at least in a topological sense-to define such a vicinity between Lewis structures. Thus, to account for the interaction between Lewis structures, we introduced a parameter, named *B*, by analogy with the Hückel parameter β. In the HL-CI approach, we set all extra-diagonal terms to the same (negative) *B* value. This is equivalent to say that each structure interacts with all others in the same manner. This is obviously a crude approximation. Requiring $\Psi_\forall$ to be the function associated to the lowest energy $E_\forall$ leads to the determination of the unknown *B* term. It is important to point out here that the criterion for finding the optimal value of *B* is energetic: this *B* value corresponds to a solution $\tilde{\Psi}$, which has the same energy as the Hückel solution $\Psi_\forall$ (eq 3).

We obtain Lewis structures' weights for a set of about 20 molecules. Despite the crude approximations involved in this approach, these weights are in very good agreement with respect to more sophisticated ab initio calculations performed in the NRT framework. However, we highlighted "pathological" cases, where the method failed to give reasonable results. The caveats are identified in the next paragraphs.

First of all, $\tilde{\Psi}$ is not required to have the same space symmetry as $\Psi_\forall$ in the HL-CI formalism. The allyl radical is a perfect illustration of this weakness. It has been emphasized elsewhere[10,38] that among the three structures ϕ_L, ϕ_R,and ϕ_C which describe the allyl radical, ϕ_C can not contribute to the wave function (see VB coefficients in Figure 1). Symmetry evidences very nicely the matter. With respect to the σ_v symmetry plane perpendicular to the molecule (see Figure 1), ϕ_C is symmetric, while $\Psi_\forall$ is antisymmetric with respect to the same symmetry plane (see Figure 2). The antisymmetric combination of ϕ_L and ϕ_R is the only possibility to describe the ground state $\Psi_\forall$.[10] Because it does not account for any symmetry, HL-CI gives a symmetric wave function with a coefficient of 0.28 for ϕ_C and 0.68 for ϕ_L and ϕ_R (Figure 1). The new method described in the next section, contains symmetry as it relies on the overlap of each Lewis structure



	ϕ_L	ϕ_R	ϕ_C
HL-CI	+0.68	+0.68	+0.28
HL-P	+0.58	–0.58	0.00
VB	+0.57	–0.57	-

Figure 1. Coefficients in the CI expansion of the threes Lewis structures which describe the allyl radical ground state. VB results are taken from ref 38.

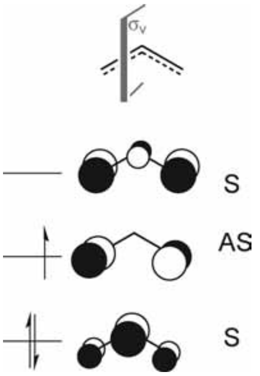


Figure 2. Molecular orbital diagram of π orbitals of the allyl radical. S and AS denote that the orbital is symmetric or antisymmetric with respect to the plane perpendicular to the molecule. Due to the occupation by one electron only of the HOMO which is antisymmetric with respect to the σ_v plane of the molecule, the total wave function must be antisymmetric.

and the Hückel wave function. Thus, coefficients obtained with this method reproduces nicely the VB results (Figure 1). Second, some examples like imidazolylidene and CCl_2 showed problems we attributed to the redundancy between Lewis structures. This redundancy originates from a strong overlap between them, which is not explicitly taken into account in the method. This leads to an overestimation of the minor structure compared to NRT results for which the minor structure has a weight of zero. This will be further discussed in section 3.

Finally, the Hückel method was sometimes found to be poorly parametrized. We encountered the case for only a very few specific anionic species, but one cannot elude this drawback, inherent to any parametrized approach such as Hückel. In such cases, HL-CI and the other method presented here (HL-P) could give poor results as compared to NRT. Since a reparametrization is not the aim of this work, this issue will always occur for such situations.

2.2. Hückel-Lewis Projection (HL-P). In this section, we present an alternative approach to the HL-CI method. It exclusively relies on the calculation of overlaps between Lewis structures $\langle\phi_i|\phi_j\rangle$ on one hand and between the Hückel resonant hybrid (delocalized solution) and Lewis structures $\langle\phi_i|\Psi_\forall\rangle$ on the other hand. Projecting each Lewis structure wave function ϕ_i onto $\Psi_\forall$, we obtain from eqs 1 and 3

$$\langle\phi_i|\Psi_\forall\rangle \simeq \sum_{j=1}^{N_{\rm struct}} c_j\langle\phi_i|\phi_j\rangle = \sum_{j=1}^{N_{\rm struct}} c_jS_{ij} \tag{4}$$

If we do so for the whole set of Lewis structures considered, we obtain the following system of linear equations:

$$(\mathbf{S})(\mathbf{C}) = (\mathbf{S}_{\rm tot}) \tag{5}$$

where $\mathbf{S}$ is the overlap matrix and $\mathbf{S}_{\rm tot}$ is the vector of $S_{i\Psi_\forall} = \langle\phi_i|\Psi_\forall\rangle$ elements. $\mathbf{C}$ is the vector of the unknown c_i coefficients obtained by solving this system of linear equations.[39–41] The weights of the structures can then be computed using the Coulson-Chirgwin formula (eq 2). Unlike HL-CI and density based approaches, HL-P gives directly the signed coefficient of the development $\tilde{\Psi}$ rather than the weights (see Figure 1). The sign can indicate the in-phase or out-of-phase interaction. Weights are then obtained from equation 2.

The set of Lewis structures which is chosen to best represent the delocalized solution is a priori not complete. A measure of its completeness can be obtained by summing up the weights of all structures

$$\tau = \left\langle\Psi_\forall\middle|\tilde{\Psi}\right\rangle = \sum_i c_j\sum_j c_jS_{ij} = \sum_i w_i \tag{6}$$

This τ parameter plays the role of a “trust” parameter: it gives a measure of how good the set of Lewis structures is to describe the resonant structure. If the space spanned by $\Psi_\forall$ is completely spanned by the set of Lewis structures, τ should be equal to unity, that is 100%. Thus, τ is a good indicator of whether Lewis structures were chosen wisely in quality and in number.

2.2.1. Computation of the Overlap. The overlap is computed as a standard overlap between Slater determinants expressed in a nonorthogonal basis set.[42] The overlap between adjacent p-orbitals is neglected, as it is the case in the standard Hückel method. Integration is performed over space and spin. In order to assess the validity of these Hückel-derived overlaps, we compare them with those obtained with a standard Gaussian basis set and appropriate local and transferable orbitals (see Appendix A for details). The overlaps between the Lewis structures of formamide, acrolein, and butadiene, computed with the Xiamen program,[43] are reported in Table 1 together with the overlap matrices obtained with the HL-P approach.[44]

Inspection of this table shows that the HL-P overlaps are qualitatively correct in sign and magnitudes, although they are lower than their Gaussian-based counterparts. It is likely to be due to the Hückel approximation considering a zero overlap between neighbor atomic orbitals.[45]

2.2.2. Overlap Completeness Examples. We considered two systems as test examples that illustrate both the normalized weights and the Lewis basis completeness. In Tables 2 and 3, Lewis structures are sorted by chemical relevance from left (most relevant) to right (less relevant).

The first example is the butadiene with a maximum of four structures. As shown in Table 2, the first Lewis structure overlaps by 80.5% with the delocalized Hückel wave function $\Psi_\forall$. Increasing the number of well chosen structures gives an increasingly better fit, up to 90% with only four structures. Case 4 shows how important it is to choose carefully the Lewis structures to span the delocalized wave function $\Psi_\forall$: when omitting the first structure, τ drops down to 27.4%. It illustrates nicely the octet rule. Second, case 4 shows the effect of normalizing the weights: the biradical structure weights 50% in case 4 and only 9% in case 3, which uses the most complete Lewis structure set. Normalizing the weights without checking the value of τ can lead to misleading solutions.

A second illustration is given in Table 3 with benzene. It has been shown that most of the 175 VB structures contribute to the total resonance and that the simple Kekule resonance is clearly not sufficient to describe the benzene π delocalization.[46,47] In case 1, the two Kekule structures were used to represent the resonant structure. As expected from the literature,[47] we find a

TABLE 1: Comparison of the Overlap Matrices Obtained with VB Methodology and by Calculations As Described in Section 2.2[a]

	Valence Bond (transferable orbitals)	HL-P
Formamid	$\left(\begin{array}{ccc} & I & II \\ I & 1.00 & 0.67 \\ II & & 1.00 \end{array}\right)$	$\left(\begin{array}{ccc} & I & II \\ I & 1.00 & 0.57 \\ II & & 1.00 \end{array}\right)$
Acrolein	$\left(\begin{array}{cccc} & I & II & III \\ I & 1.00 & 0.34 & 0.19 \\ II & & 1.00 & 0.00 \\ III & & & 1.00 \end{array}\right)$	$\left(\begin{array}{cccc} & I & II & III \\ I & 1.00 & 0.17 & 0.07 \\ II & & 1.00 & 0.00 \\ III & & & 1.00 \end{array}\right)$
Butadiene	$\left(\begin{array}{ccccc} & I & IV & III & II \\ I & 1.00 & -0.41 & 0.29 & 0.29 \\ IV & & 1.00 & -0.10 & -0.10 \\ III & & & 1.00 & 0.00 \\ II & & & & 1.00 \end{array}\right)$	$\left(\begin{array}{ccccc} & I & IV & III & II \\ I & 1.00 & -0.18 & 0.13 & 0.13 \\ IV & & 1.00 & 0.00 & 0.00 \\ III & & & 1.00 & 0.00 \\ II & & & & 1.00 \end{array}\right)$

[a] Structures used are presented in Figure 3.

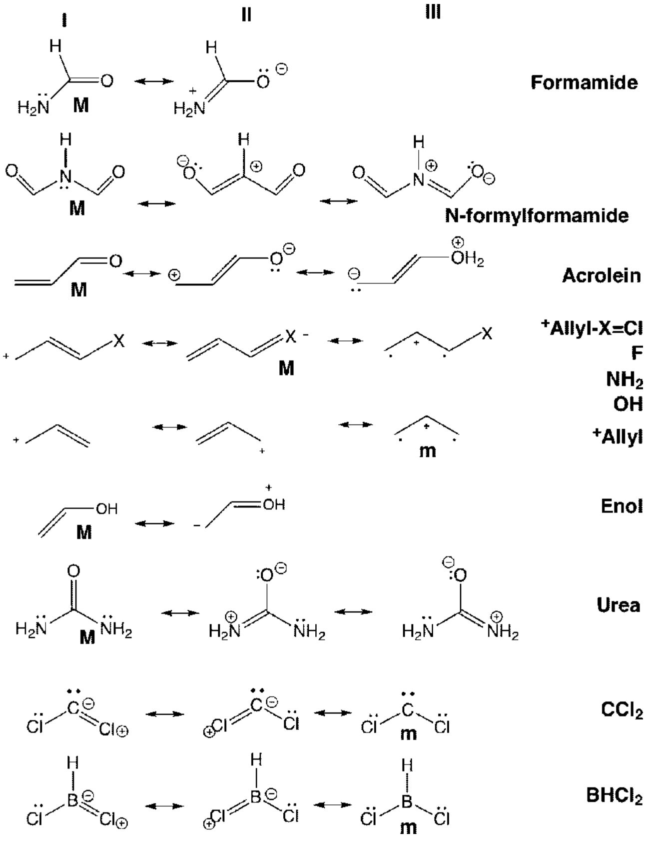
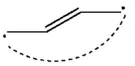
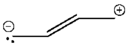


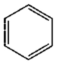
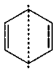
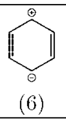
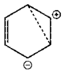
Figure 3. Structures used in the wave function decomposition for benchmark. Weights of structures are presented in Table 4.

TABLE 2: Normalized Weights and τ Trust Parameter Obtained with HL-P for the Butadiene Molecule with Different Sets of Structures[a]

	I  (1)	II  (1)	III,IV  (2)	τ
Case 1	100%			80.5%
Case 2	91%	9%		85.1%
Case 3	81%	9%	5%	90.0%
Case 4	- %	50%	25%	27.4%

[a] The number of equivalent structures are indicated in brackets.

TABLE 3: "Trust Parameter" (See Section 2.2) and Weights Obtained with the Method of Different Lewis Contributors Used to Describe Resonance in Benzene in Three Different Cases[a]

	 (2)	 (3)	 (6)	 (24)	τ
Case 1	50%	-	-	-	60%
Case 2	40%	7%	-%	-	65%
Case 3	28%	7%	4%	-	72%
Case 4	22%	5%	3%	1%	94%

[a] The number of equivalent structures are indicated in brackets.

low value of τ (60%). Following Norbeck et al,[47] we added the three Dewar structures and their six ionic contributors. τ increased by 12% with each structure contributing for 7% (Dewar) or 4% (ionic) to the delocalized wave function. About 28% of the space is still not spanned even with the nine-structure set. Finally, in case 4, the space spanned by a 35-structure set, which corresponds to 94% of the space, indicates a correct fit of the "aromatic delocalization" as described by $\Psi_{\forall}$. The 35 Lewis structures correspond to 145 among the 175 VB structures.

3. Results and Discussion

In this section, we compare both methods HL-CI and HL-P with respect to NRT, which is our reference. NRT weights are computed in the framework of natural bond orbitals methodology (NBO)[29] using a B3LYP/6-31+G(d) wave function and optimized geometry.

3.1. Two and Three Structures Cases. We discuss here the results obtained for a set of molecules (see Figure 3) for which 2 or 3 structures are included in the expansion of $\tilde{\Psi}$.[48] For the sake of comparison, we used the same set of molecules as in ref 34.

The corresponding data are collected in Table 4. We can highlight from this table the following trends:

- Like HL-CI and NRT, the HL-P method gives weights which are consistent with the qualitative rules stated in the Introduction.
- The completeness of each two- or three-structures set, given by the τ value, is greater than 80% and increases with the number of Lewis structures given in the expansion. This indicates that our sets of Lewis structures are appropriate and adding a new structure improves the description of the systems.

TABLE 4: Weights Obtained with HL-P as Compared to NRT and HL-CI

Molecule	NRT	HL-CI	HL-P	τ (%)
formamide	67/33	66/34	65/35	90.9
N-formylformamide	45/27.5/27.5	46/27/27	43/29/29	83.6
acrolein	87/13	79/21	85/15	85.3
	84/11/5	78/17/5	84/15/1	85.6
$^{+}$allyl NH_2	23/77	29/71	25/75	84.5
	21/75/4	24/70/6	23/69/8	92.3
$^{+}$allyl OH	30/70	39/61	39/61	84.5
	23/65/12	35/58/7	34/54/11	95.1
$^{+}$allyl F	37/63	44/56	45/55	84.7
	29/56/15	40/52/8	39/49/12	96.4
$^{+}$allyl Cl	37/63	38/62	36/64	84.0
	29/58/13	33/60/7	32/58/11	93.9
$^{+}$allyl H	50/50	50/50	50/50	84.9
	39/39/22	46/46/8	44/44/13	97.4
enol	86/14	93/7	93/7	96.3
urea	60/20/20	46/27/27	51/24/24	82.6
CCl_2	50/50	50/50	50/50	93.1
	51/49/0	43/43/14	77/77/-55	98.4
$BHCl_2$	50/50	50/50	50/50	96.8
	51/49/0	42.5/42.5/15	90/90/-80	99.7

[a] Structures used are presented in Figure 3.

TABLE 5: Weights Obtained with HL-P as Compared to NRT and HL-CI for Cases with more than Three Structures[a]

molecule	NRT	HL-CI	HL-P	τ (%)
furan	52.5/7/16.5/7/16.5	54/11.5/11.5/11.5/11.5	74/5/8/5/8	75.3
pyrrole	42/10.5/18.5/10.5/18.5	38/15.5/15.5/15.5/15.5	50/12/13/12/13	69.7
thiophene	49/8.5/17/8.5/17	44/14/14/14/14	56/10/12/10/12	71.4
uracil	23/25/24/15/13	25/19/19/19/19	20/24/16/19/21	55.4

[a] Structures used are presented in Figure 4.

- The HL-P method performs in average as good as HL-CI when compared to NRT. For two-structure cases, the weights of both approaches compare within 2%, except for the acrolein and allylamine cation, for which HL-P significantly improves the HL-CI results compared to NRT. For three-structure cases, HL-P tends to lower the weight of the major structure and enhance the weight of the minor structure, when compared to HL-CI. Finally, when compared to NRT, the weight of the minor structure is generally better than its HL-CI counterpart.
- For ill-defined systems (see the last two entries in Table 4), HL-P gives clearly unphysical results. This will be discussed hereafter.

In what follows, we go through and comment each example of Table 4.

Formamide and N-Formylformamide. The three methods agree within 2%. For formamide, two structures span 90.9% of the total space.

Acrolein. HL-CI and HL-P give very similar results with respect to NRT. In the 2-structure calculation, HL-P is slightly better than HL-CI, it differs only by 2% from NRT. In the 3-structure case, the value of τ increases only by 0.2%: no extra information is brought by the exotic third structure. As a consequence, computed weights for this additional structure are negligible.

X-Substituted-Allyl Cations. Two-structure calculations provide very close results. The HL-P performs better than HL-CI on most cases, provided the addition of a third radical structure. Such a structure is important for the description of the system, as the 10% increase of τ indicates.

Enol. Both HL-CI and HL-P overestimate by 7% the weight of the major structure.

Urea. HL-P slightly improves over HL-CI but HL-P is still 9% away from NRT. This is likely due to the small value of τ, which indicates that structures are missing to describe properly the delocalized system.

CCl_2 and $BHCl_2$. They exhibit the same behavior. In the 2-structure calculation, 50/50 weights are obtained by all methods. However, HL-P gives negative weights in the 3-structure case. This indicates a redundancy in the basis of localized structures. The diagonalization of the overlap matrix between Lewis structures reveals a value close to zero, which is characteristic of a linear dependency in the basis. This prompts us to discard the third structure, which, in addition, does not follow the octet rule.

3.2. More than Three Structures Cases. In Table 5, we present results for cases that need more than three structures to reproduce properly the Hückel solution: furan, pyrrole, thiophene, and uracil.

For these systems we use 5 structures in our expansion (see Table 5). Nevertheless, values of τ are low, between 55.4% and 75.3%, whereas in the previous cases they are always larger than 80%. In light of what we learned from the benzene example, a correct mesomeric description for these systems would require many more structures. However, in order to compare to published HL-CI results, we decided to keep this small Lewis basis set expansion. The conclusion for these data is that, as compared to NRT, HL-CI provides slightly better weights for the major structures than HL-P does; however, the main achievement is that HL-P is able to differentiate the weights of minor structures.

In Table 6 we report results for imidazolylidene. For this example, we use different sets of up to 8 structures (Figure 5). This leads to values of τ, between 60.2% and 76.0%. In a previous work, we underlined that HL-CI provides poor results, since the weight of structure I is nonzero.[35] We argued that a set of the five first structures of Figure 5 should be enough to describe the system. They are reported in the first two rows of Table 6. For this structure, HL-P shows a negative weight: there is a redundancy in the set and structure I should be discarded. Without structure I, NRT and HL-CI are in good agreement, whereas HL-P underestimates the weights of minor structures.

In the present work we were able to extend this 5-structure set to the more complete 8-structure set. Our discussion here aims at determining what set best represents the system.

TABLE 6: Weights Obtained with HL-P as Compared to NRT and HL-CI for Imidazolylidene[a]

NRT	HL-CI	HL-P	τ (%)
0/40/40/10/10/−/−/−	16/33.5/33.5/8.5/8.5/−/−/−	-54/72/72/5/5/−/−/−	68.5
−/40/40/10/10/−/−/−	−/39/39/11/11/−/−/−	−/48/48/2/2/−/−/−	60.2
0/29.5/29.5/0/0/11/15/15	11/25/25/6/6/9/9/9	-36/55/55/-3/-3/5/14/14	76.0
−/29.5/29.5/0/0/11/15/15	−/28/28/6/6/11/11/11	−/36/36/-8/-8/6/20/20	72.0
−/29.5/29.5/−/−/11/15/15	−/31/31/−/−/13/13/13	−/35/35/−/−/6/11/11	69.4

[a] Structures used are presented in Figure 5.

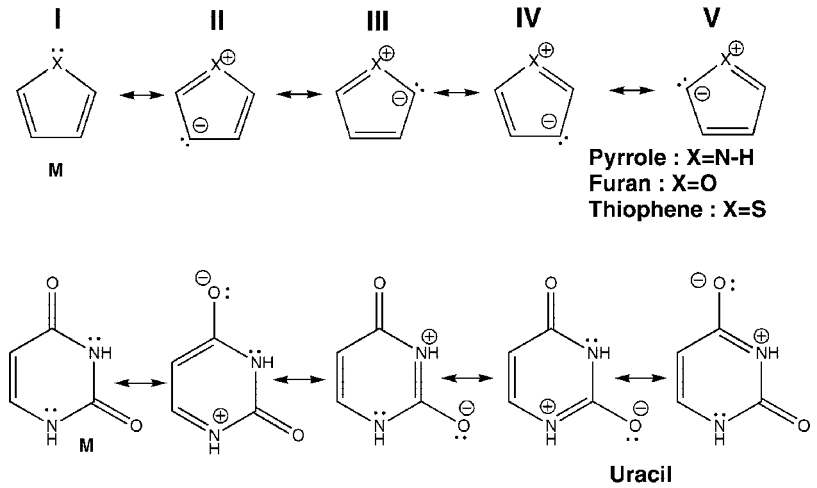


Figure 4. Structures used in the wave function decomposition which weights are presented in Table 5.

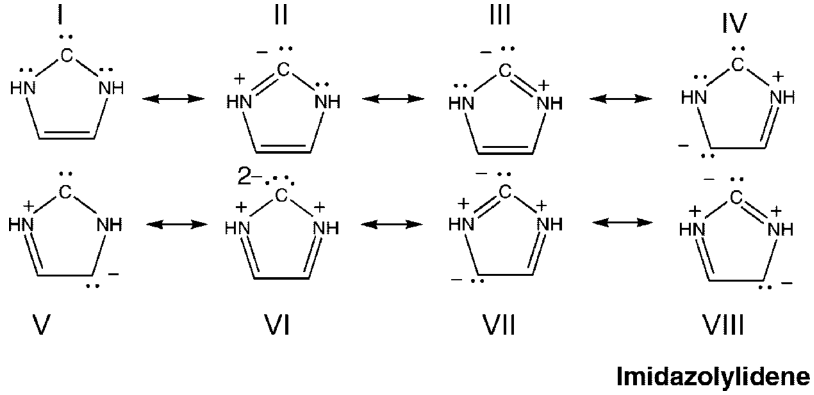


Figure 5. Structures used in the wave function decomposition of imidazolylidene which weights are presented in Table 6.

HL-P gives a large negative weight for structure I (third row of Table 6). This implies a redundancy between localized structures. In addition, structure I does not respect the octet rule as discussed for CCl_2 and $BHCl_2$. After removal of structure I, only IV and V have negative weights (fourth row). These two structures must be discarded for redundancy reasons as well. The last row shows the final results with the 5-structure set obtained after removing structures I, IV and V. The τ value is quite low (69.4%) but this 5-structure set is better than the one we chose in our previous work. It is interesting to note that, in this last case, HL-CI and HL-P agree within a few percent. As a conclusion for this part, we can say that HL-P overestimates the weights of the two major structures, as observed in the previous examples. This overestimation is partly due to the low values of τ, employed for the normalization. Furthermore, HL-P is a better tool than HL-CI as it helps determining a non redundant set of structures.

4. Conclusion

In this paper, we compare three methods (NRT, HL-CI, and HL-P) that consider mesomery as an interaction between Lewis structures.

NRT, based on the NBO formalism, is taken as the reference along our work because it is the method of choice for an accurate evaluation of the weights when VB related approaches are computationally too heavy. While it is convenient and accurate, NRT does not provide the coefficients of the interaction but rather the weights.

HL-CI is a method we developed in a previous work and is based on a simulated CI. It can provide coefficients as well as the weights of this simulated CI. It is based on an effective interaction Hamiltonian between Lewis structures which energies are obtained by Hückel calculations. Despite undeniable successes, this initial approach suffers from defaults related to the fact the CI is simulated on the basis of only energetic considerations. Symmetry considerations on the allyl radical exemplified some important defaults of this approach. HL-CI provides positive coefficients for the CI, whereas they should be of opposite signs, as published in VB studies. In this case, NRT cannot be used for comparison as it only gives access to the weights.

The HL-P method corrects this caveat of HL-CI. It is based on a totally different approach where the overlap between Lewis structures and that between each Lewis structure and the Hückel solution is used to get the coefficients of the CI expansion. Weights are then obtained through the Coulson-Chirgwin formula. Together with this development, we named τ a “trust parameter” that ranges between zero and one, the larger the better the quality of the set of Lewis contributors used is. Such a parameter can be defined only in projection methods because the simulated CI has to be compared to a reference state. Except for some specific and well-identified cases, a good general agreement is found between the three methods. Unlike HL-CI, HL-P provides a clear signal to identify strong redundancies in the set of Lewis structures.

Appendix A

HL-P uses orbitals that are local and transferable from one system to another. They can be local on one atom (for lone pairs or radicals) or between two atoms (for π bonds). In order to compare the Hückel-derived overlaps between Lewis structures to the Gaussian based overlaps, we looked for optimized orbitals that most likely share the same qualities. We used small C_s symmetric systems with only one (respectively two) π center(s). These systems were optimized using the program Gaussian 03[49] at the B3LYP/6-31+G(d) level. The orbitals themselves were obtained from a simple HF/6-31+G single-point calculation, where the unpolarized basis set ensures the transferability of the orbitals. The fragment systems we used and the corresponding orbitals obtained are displayed in Table 7. These orbitals were then used to build Lewis structures of a few systems (cf. Table 1).

TABLE 7: HF 6-31+G Optimized Orbitals and Fragments

		gaussians (or contraction)					
		atom 1			atom 2		
atom type	system used	p3	p1	p+	p3	p1	p+
C(•)	CH_3•(D_{3h})	0.585	0.494	0.096			
C(-)	CH_3(-) (D_{3h})	0.442	0.399	0.428			
N:	NH_3 (D_{3h})	0.587	0.493	0.117			
O(-)	HO(-) ($C_{\infty h}$)	0.602	0.429	0.200			
C=C	$H_2C{=}CH_2$ (C_{2v})	0.377	0.281	0.047	0.377	0.281	0.047
C=N	$H_2C{=}NH_2^+$ (C_{2v})	0.274	0.069	−0.008	0.438	0.272	0.018
C=O	$H_2C{=}O$ (C_{2v})	0.343	0.198	0.025	0.491	0.346	0.013

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