

HuLiS a program to recast molecular orbital wave functions into Lewis structures

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Introduction

- Molecular electronic wave function can be hard to read: electrons are delocalized.
- Chemists think with Lewis structures: localize electron pairs on one or two atoms.

Our aim:

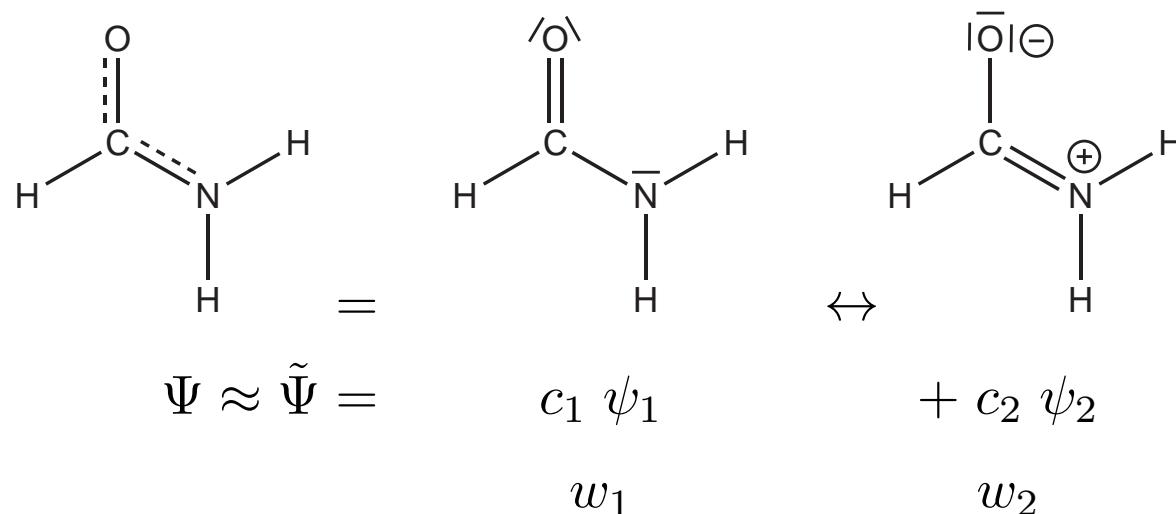
- Simple Web based application to interpret delocalized wave functions: HuLiS^a.
- Rewrite the delocalized wave function on a basis of localized structures.

^a<http://www.hulis.free.fr>

HuLis : Hückel based Java/HTML5 program [1-2]

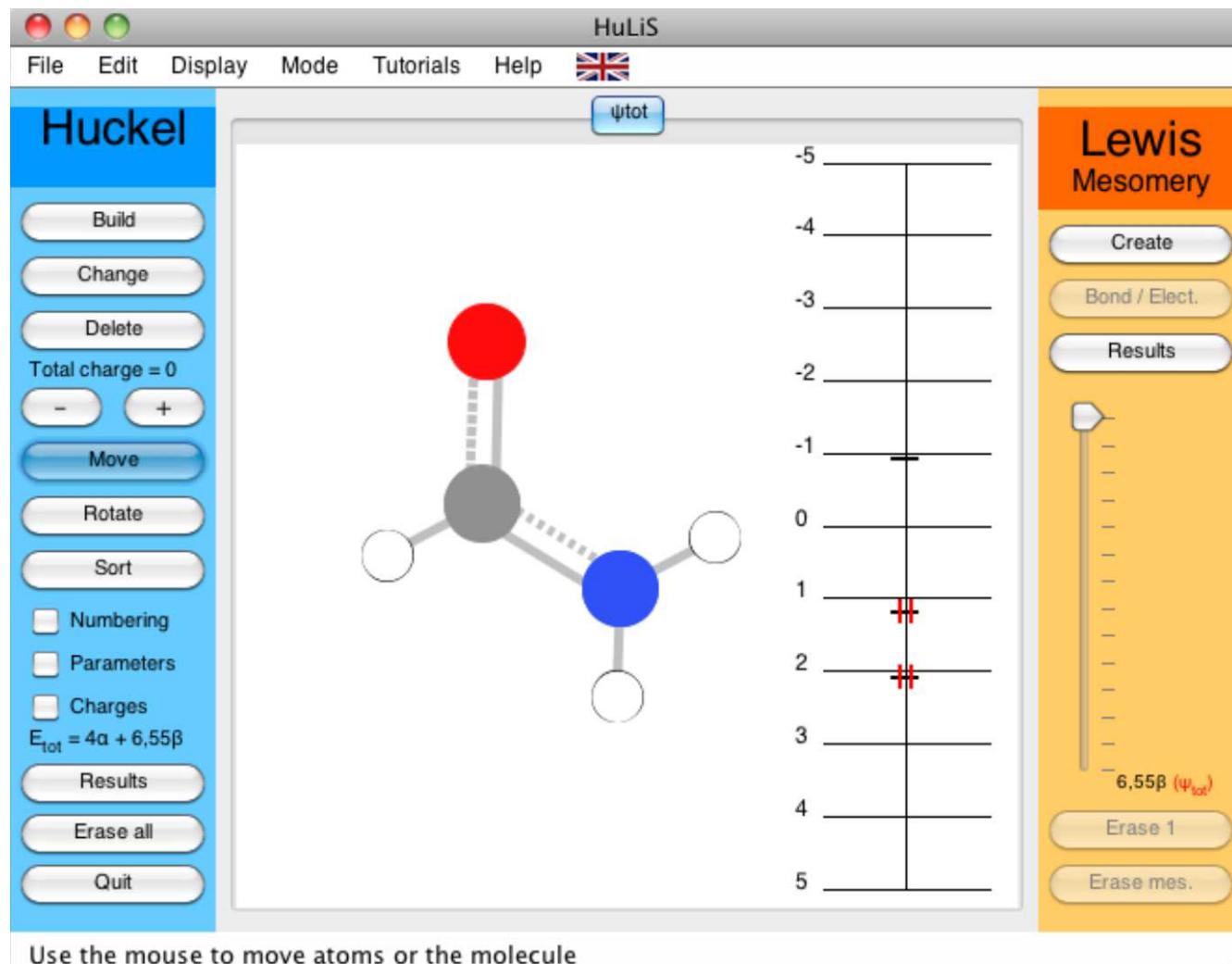
Formamide

Electronic interaction : Hückel (tight binding in the atomic basis)



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

[2] Y. C., D. Hagebaum-Reignier, N. Goudard, S. Humbel, *J. Phys. Chem. A* 2008, **112**, 13256-13262.



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Decomposition of Ψ on N Lewis structures ψ_i

$$|\Psi\rangle \approx |\tilde{\Psi}\rangle = \sum_i^N c_i |\psi_i\rangle$$

Quality of the approximation :

$$\tau = \langle \Psi | \tilde{\Psi} \rangle \begin{cases} \tau \rightarrow 1 \text{ good} \\ \tau \rightarrow 0 \text{ bad} \end{cases}$$

Weight of a Lewis structure (Coulson-Chirgwin [1]) :

$$w_i = c_i \sum_j^N c_j \langle \psi_i | \psi_j \rangle$$

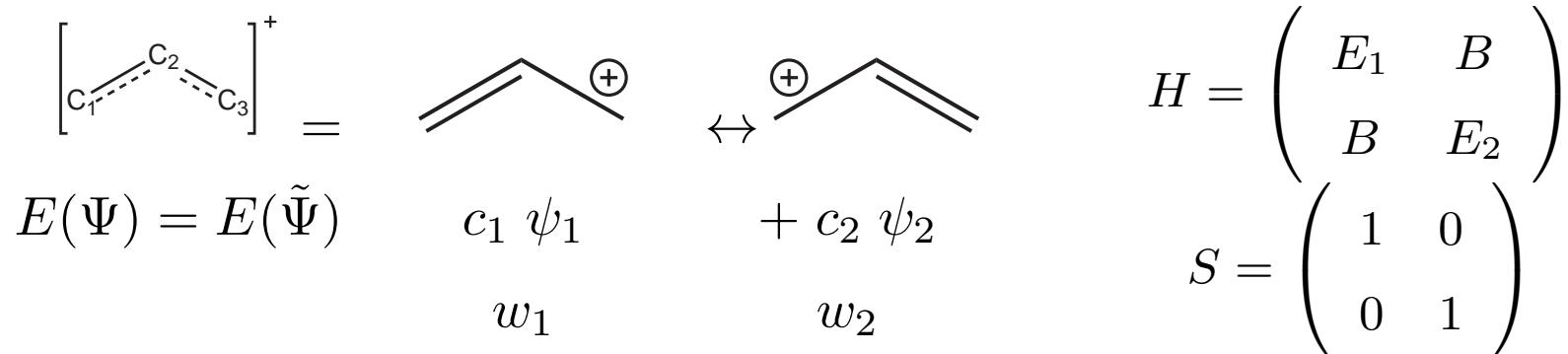
Normalisation of $\tilde{\Psi}$: $\sum_i^N w_i = 1$.

[1] B. H. Chirgwin, C. A. Coulson, *Proc. R. Soc. London A* 1950, **201**, 196-209.

Schemes

1. Energy based scheme
2. Space based scheme

Energy based scheme: HLCI

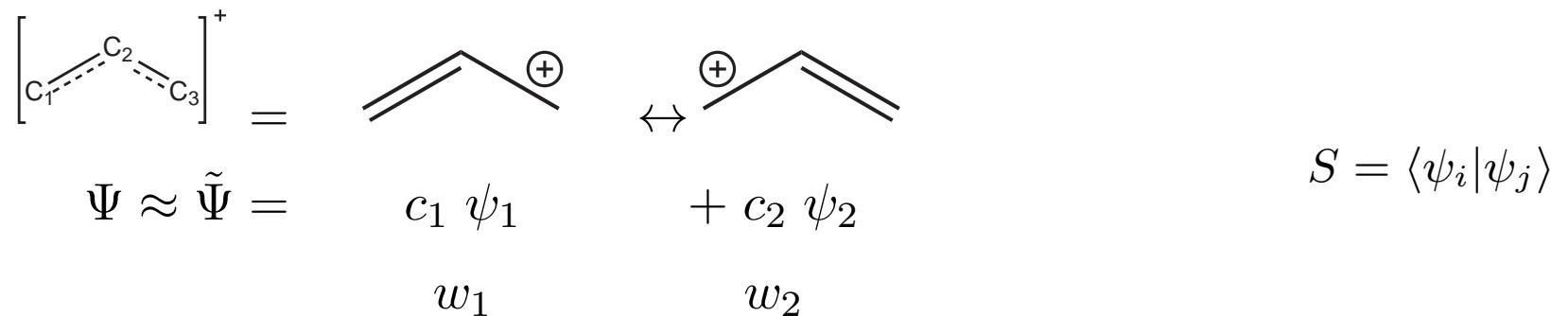


$$\det(H - E) = 0 \implies B = -\sqrt{(E_1 - E_0)(E_2 - E_0)}$$

$$\left. \begin{array}{l} (H - E)C = 0 \\ c_1^2 + c_2^2 = 1 \end{array} \right\} w_i = c_i^2$$

Hückel methodology applied to localized structures.

Overlap based scheme: HLP

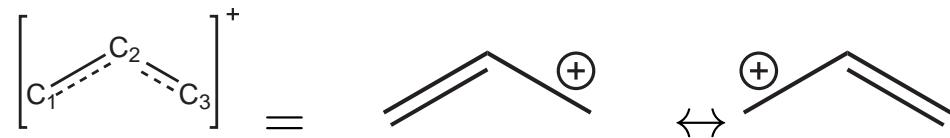


$$\langle \psi_i | \Psi \rangle = S_{\forall}$$

$$\langle \psi_i | \tilde{\Psi} \rangle = \sum_j c_j \langle \psi_i | \psi_j \rangle = CS$$

By resolution of $S_{\forall} = CS$, we obtain C .

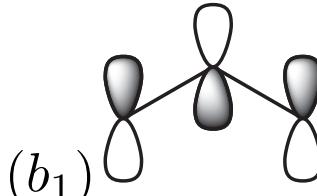
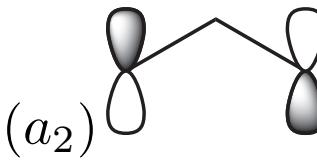
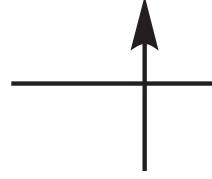
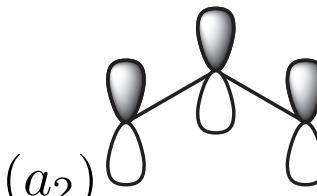
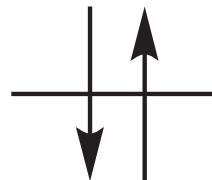
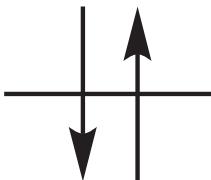
Computation of $\langle \psi_i | \psi_j \rangle$

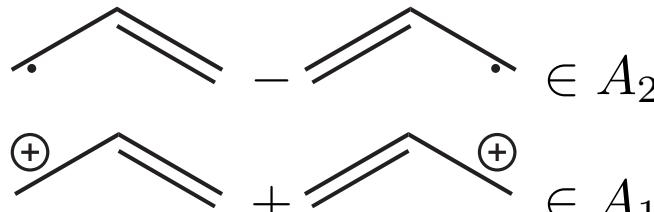


$$\Psi \approx \tilde{\Psi} = \quad c_1 \psi_1 \quad + c_2 \psi_2$$

$$\begin{aligned}
\langle \Psi | \psi_1 \rangle &= \frac{1}{2} \langle |\Phi_1 \bar{\Phi}_1| | | \pi_1 \bar{\pi}_1 | \rangle \\
&= \frac{1}{2} \langle \Phi_1(1) \bar{\Phi}_1(2) - \bar{\Phi}_1(1) \Phi_1(2) | \pi_1(1) \bar{\pi}_1(2) - \bar{\pi}_1(1) \pi_1(2) \rangle \\
&= \langle \Phi_1(1) | \pi_1(1) \rangle \langle \Phi_1(2) | \pi_1(2) \rangle \\
&= \langle \Phi_1(1) | \pi_1(1) \rangle^2 \\
&= \langle \frac{1}{2}(p_1 + \sqrt{2}p_2 + p_3) | \frac{1}{\sqrt{2}}(p_1 + p_2) \rangle^2 = \left(\frac{1}{2} \left(\frac{1}{\sqrt{2}} + 1 \right) \right)^2 \\
&= 0.728...
\end{aligned}$$

Allyl radical & cation

OM	allyl radical	allyl cation
	—	—
		—
		
Symmetry	$\Psi_r \in A_2$	$\Psi_c \in A_1$



$\in A_2$

$\in A_1$

Allyl radical & cation

OM	allyl radical	allyl cation	
(b_1)	—	—	
(a_2)	\uparrow	—	$\cdot\text{---}\text{C}=\text{C}\text{---}\text{C}\text{---}\text{C}\text{---}\in A_2$
(a_2)	$\downarrow\uparrow$	$\downarrow\uparrow$	$\text{C}^+\text{---}\text{C}=\text{C}\text{---}\text{C}\text{---}\in A_1$
Symmetry	$\Psi_r \in A_2$	$\Psi_c \in A_1$	

HLCI $w = 50\%$

HLP $\Psi_r = \frac{1}{\sqrt{2}}(\cdot\text{---}\text{C}=\text{C}\text{---}\text{C}\text{---}\text{C}\text{---} - \text{C}\text{---}\text{C}=\text{C}\text{---}\text{C}\text{---}\text{C}\text{---}\cdot)$

HLP $\Psi_c = \frac{1}{\sqrt{2}}(\text{C}^+\text{---}\text{C}=\text{C}\text{---}\text{C}\text{---}\text{C}\text{---} + \text{C}\text{---}\text{C}=\text{C}\text{---}\text{C}\text{---}\text{C}^+)$

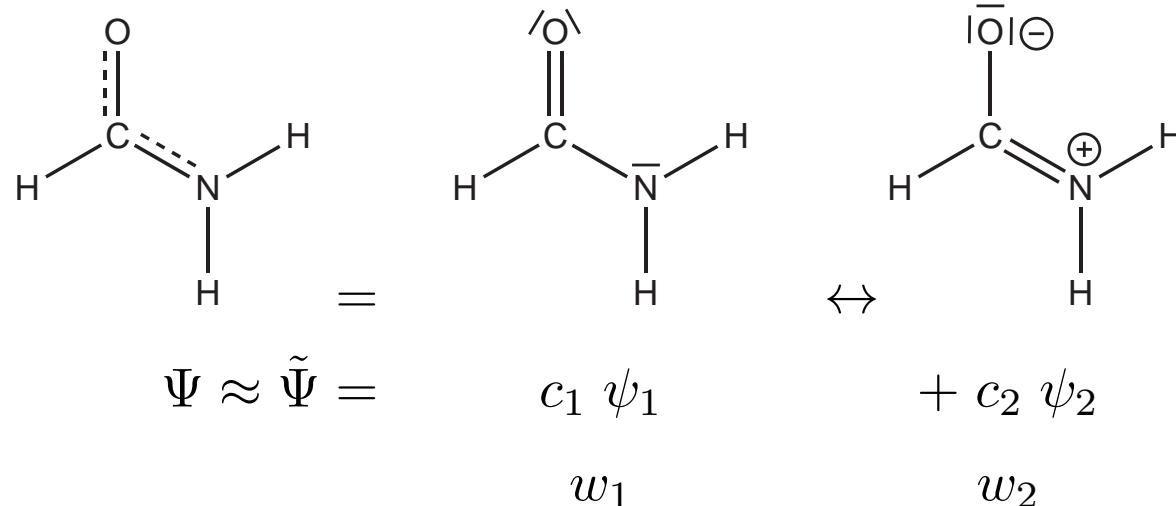
Results

HuLis : Hückel based Java program [1-2]

Electronic interaction : Hückel

Wave function : Slater determinant

Demonstration : formamide



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

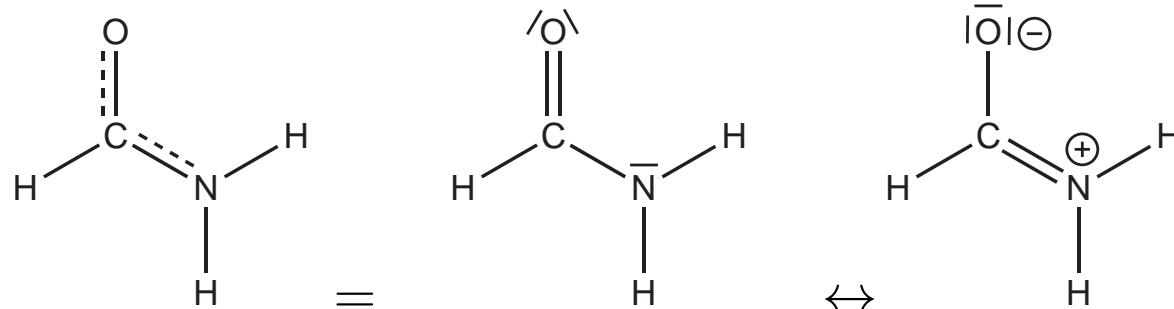
[2] Y. C., D. Hagebaum-Reignier, N. Goudard, S. Humbel, *J. Phys. Chem. A* 2008, **112**, 13256-13262.

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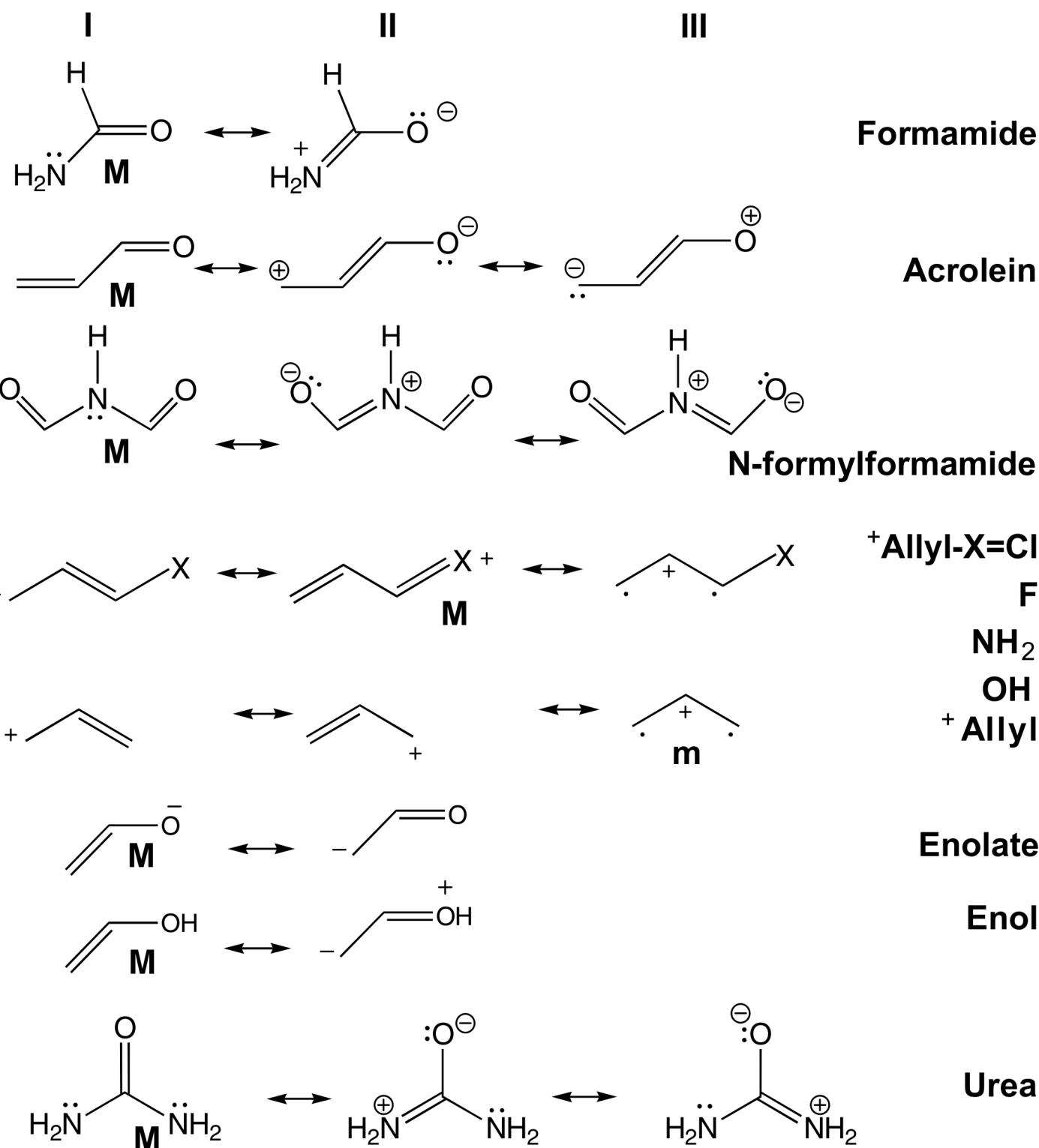
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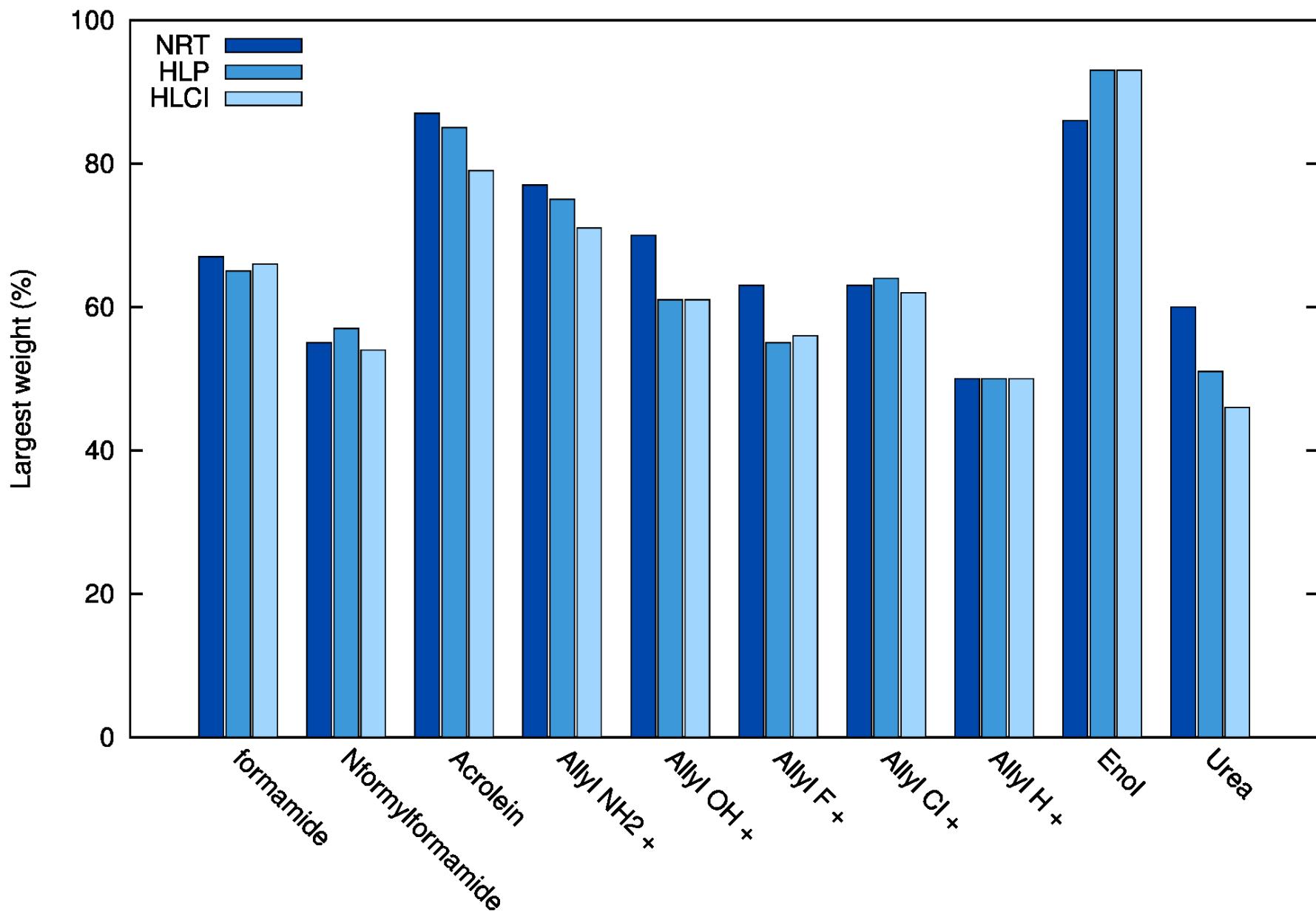


$\Psi \approx \tilde{\Psi} =$	$c_1 \psi_1$	$+ c_2 \psi_2$	τ
HLCI	$w_1 = 66\%$	$w_2 = 34\%$	95%
HLP	$c_1 = 0.81$	$c_2 = 0.58$	90%
	$w_1 = 66\%$	$w_2 = 34\%$	
NRT	$w_1 = 67\%$	$w_2 = 33\%$	

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

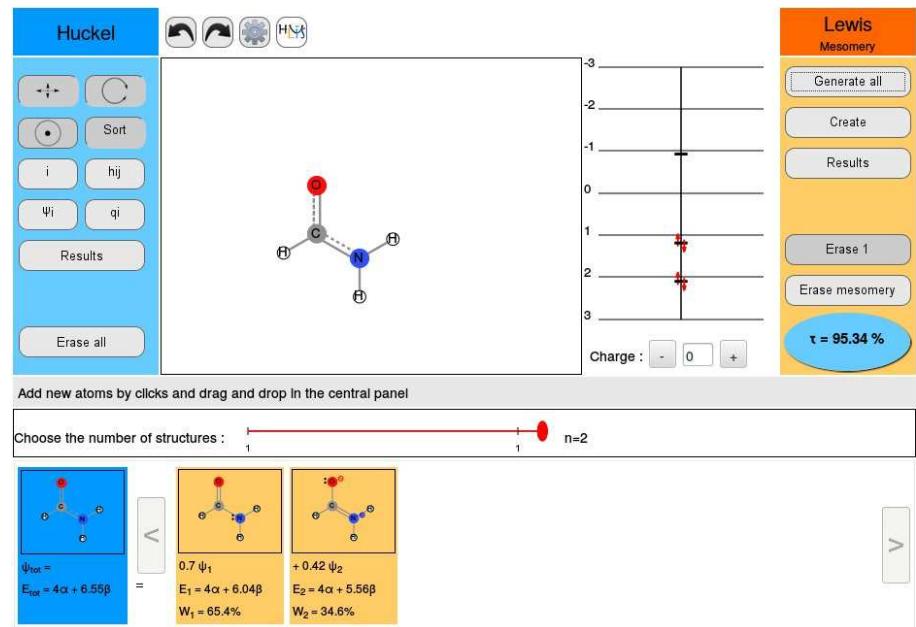
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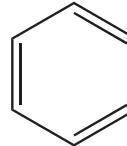
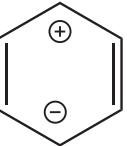
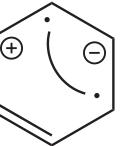
Summary

- Simple to use
- Instantaneous results
- Ideal for teaching
- τ measures the completeness of the structure set
- Hückel framework: planar molecules → generalized[1]



[1] J. Racine, D. Hagebaum-Reignier, Y. C., S. Humbel *J Comput Chem.* 2016 **37** 771-9

HuLis : benzene

					τ
	(2)	(3)	(12)	(24)	
Kekule only	50%	-	-	-	60%
Kekule + Dewar	40%	7%	-	-	65%
K + D + para ionic	29%	7%	4%	-	72%
Best (41 struct.)	22%	6%	3%	1%	95%
Ionic only	-	-	9%	2%	49%