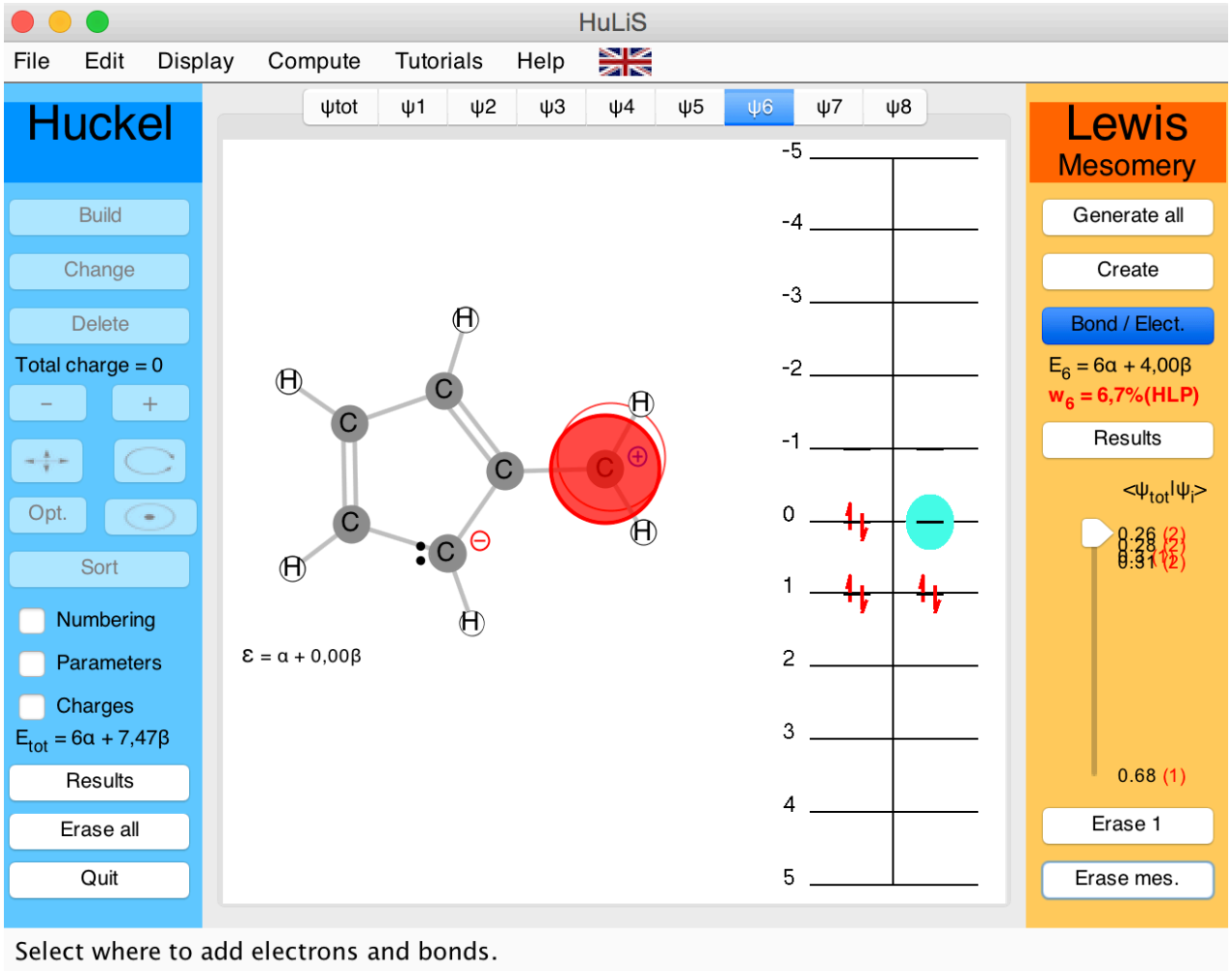
Valence Bond-like wave functions with huckel

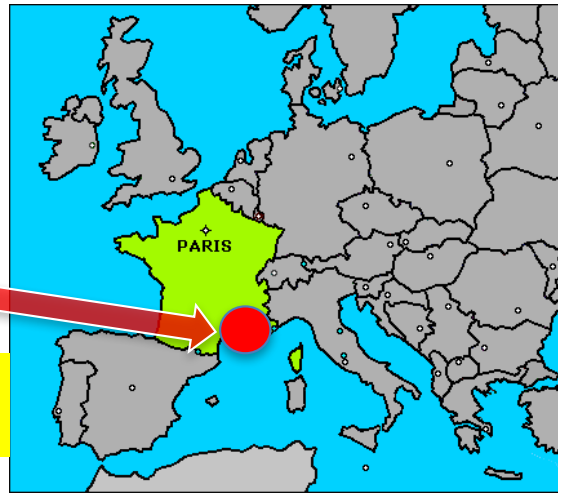
(ground state)



[For mobile http://m.hulis.free.fr](http://m.hulis.free.fr)

Point

Stéphane Humbel @ Aix-**Marseille** Univ.

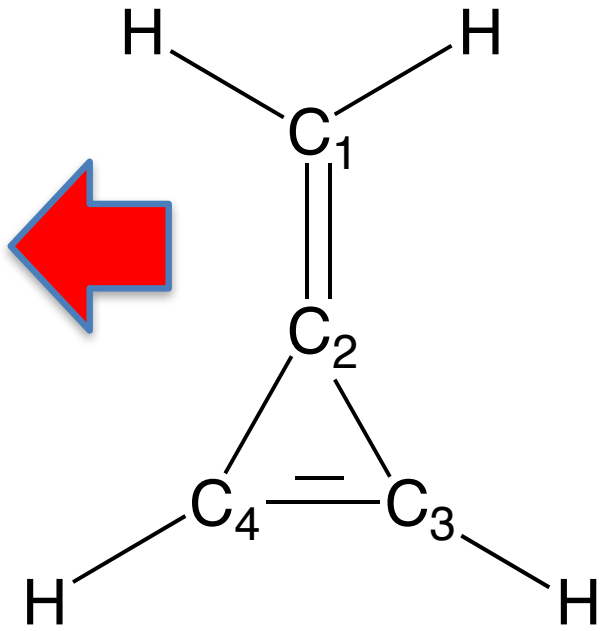


Valence Bond & Excited states; interpretations

- G. Brillouin optim. for Breathing Orb. VB*

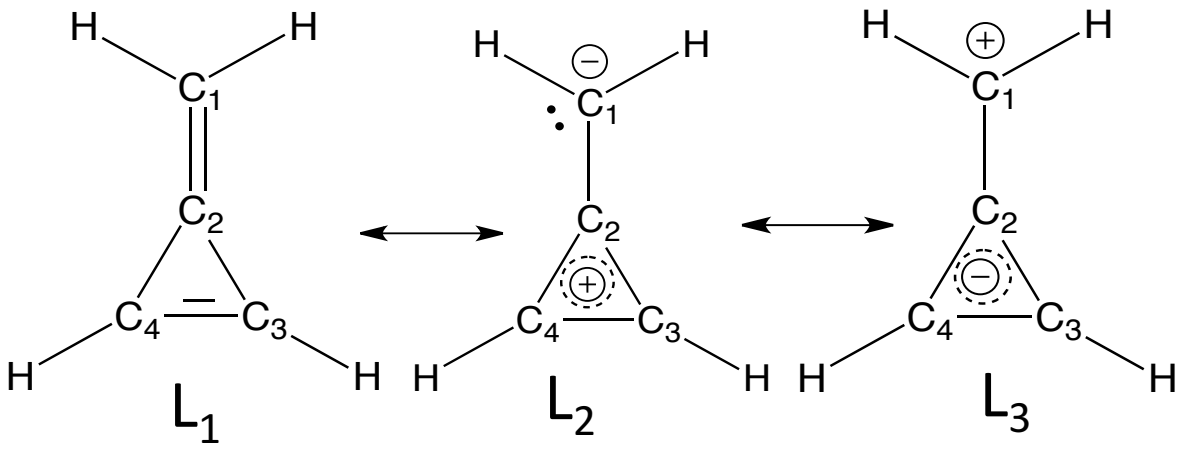
  for the n^{th} state, Super-CI including n-1 states

- Overlap <VB*|MO-CI*>
- MCP dipole inversion case
  - $1\ ^1A_1$
  - $1\ ^1B_2$

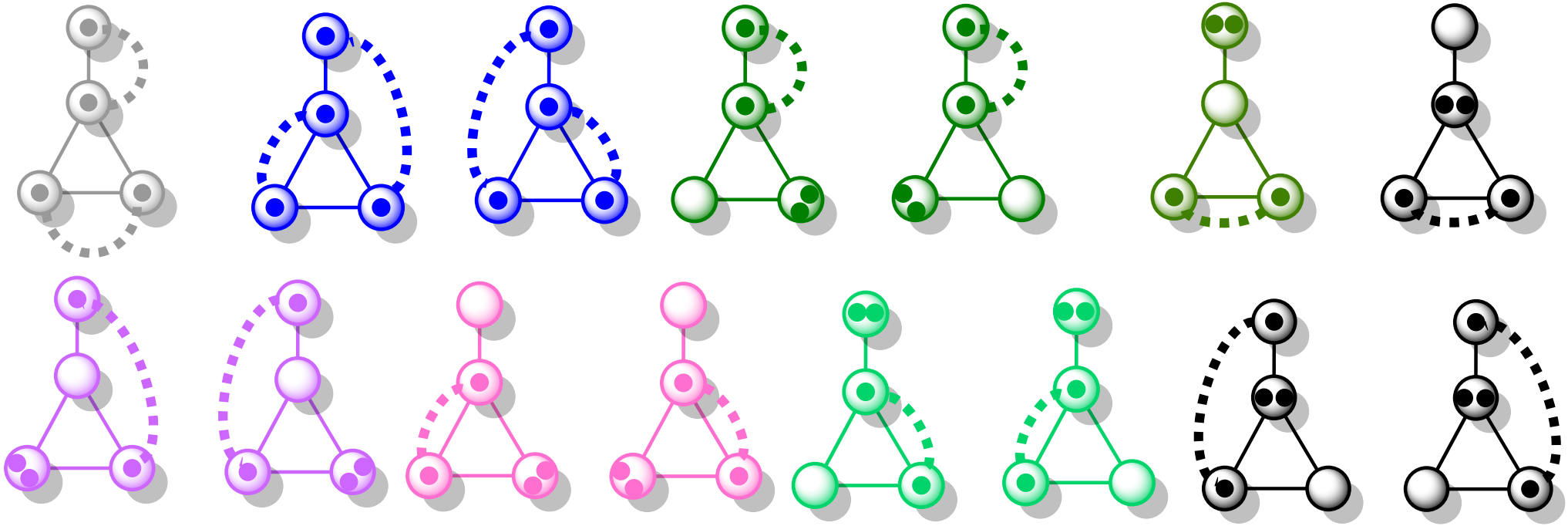


20 VB structures

6-311+G(d)	VE (eV)	DMz	
		$1\ ^1A_1$	$1\ ^1B_2$
RASSCF	4.79	-1.90	+1.80
CASSCF	4.54	-1.78	+1.93

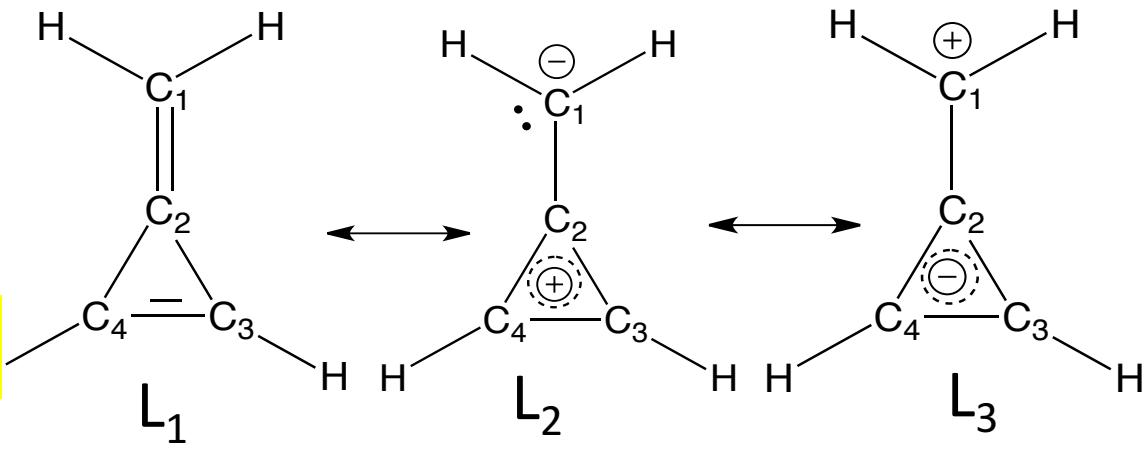


20 VB structures

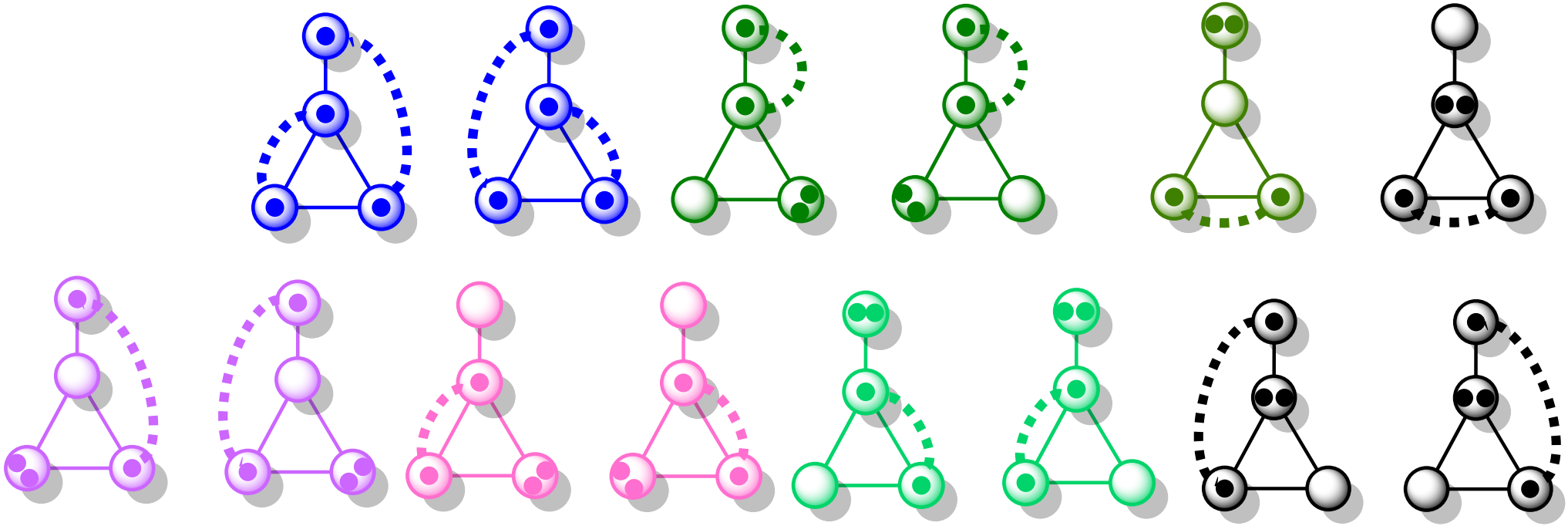


+ 6 di ionics

6-311+G(d)	VE (eV)	DMz	
		$1\,^1A_1$	$1\,^1B_2$
RASSCF	4.79	-1.90	+1.80
CASSCF	4.54	-1.78	+1.93
BOVB(π)	**5.22**	**-1.81**	**+2.04**

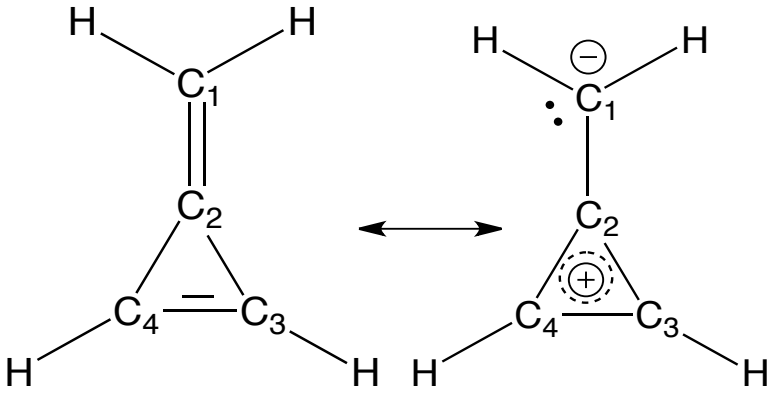


20 VB structures

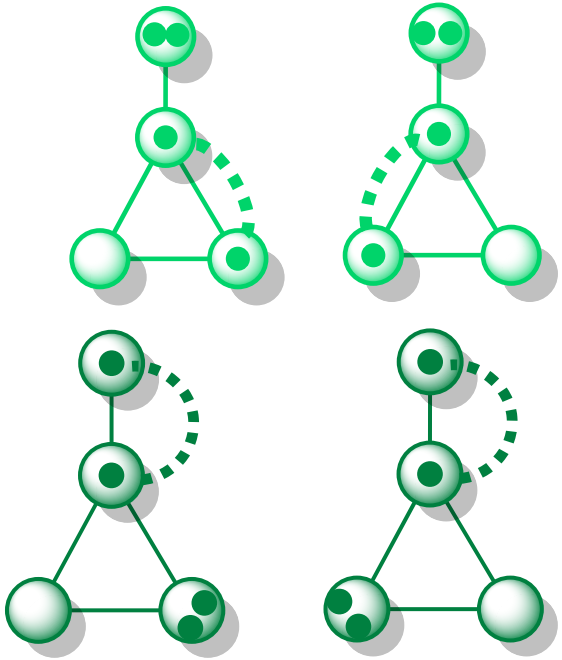


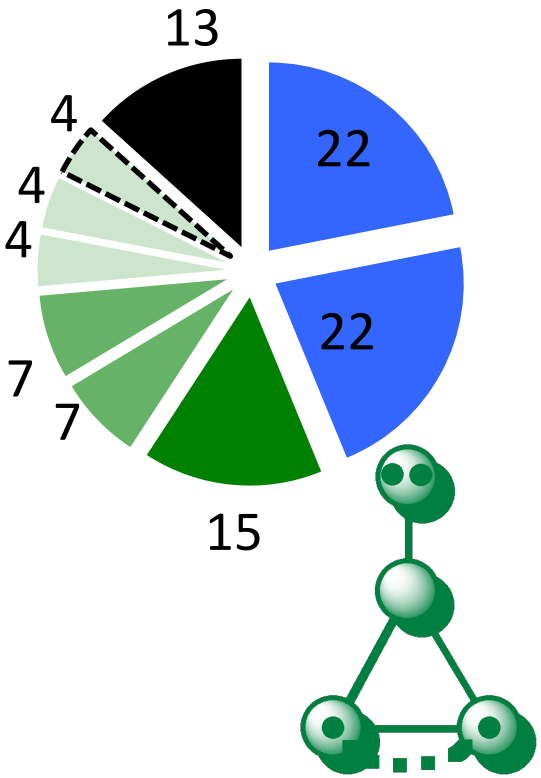
+ 6 di ionics

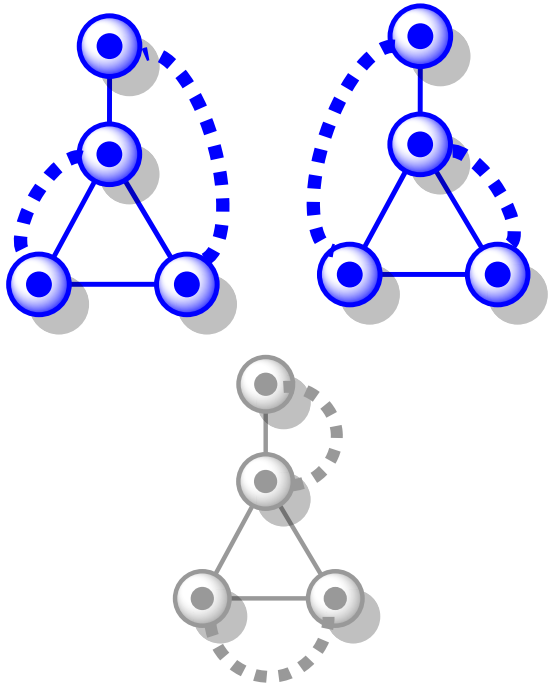
6-311+G(d)	VE (eV)	DMz $1\,^1A_1$	DMz $1\,^1B_2$
RASSCF	4.79	-1.90	+1.80
CASSCF	4.54	-1.78	+1.93
BOVB(π)	5.22	-1.81	+2.04
<CAS|VB>		**0.98**	



Ground state $^1A_1$ $\Psi^{VB}(^1A_1)$=**0.44 (c_2+c_3)** – 0.22 i_{11} – 0.13 (i_1+i_2) + . . .







Point

Stéphane Humbel @ Aix-**Marseille** Univ.

Ground States drawings (& VB, Lewis) are OK

Excited States …

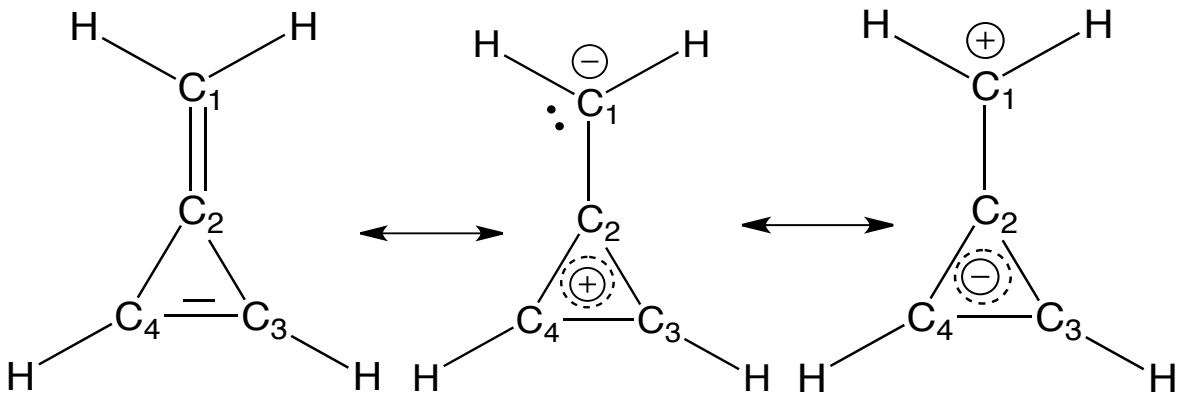
C_{2n} H_{2n+2} Valence states ..

recoupling of spin

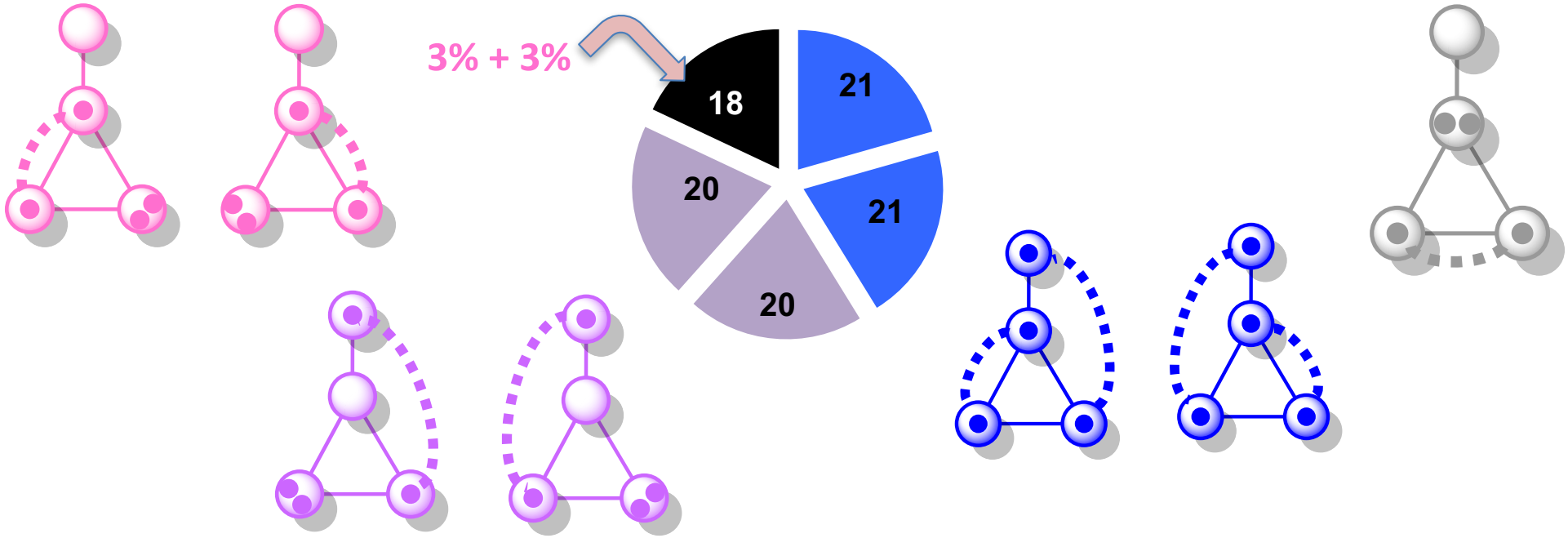
MCP cases

DMz

	VE (eV)	$1\,^1A_1$	$1\,^1B_2$
RASSCF	4.79	-1.90	+1.80
CASSCF	4.54	-1.78	+1.93
BOVB(π)	5.22	-1.81	+2.04
<CAS|VB>		**0.98**	**0.97**



Excit. state $\Psi^{VB}(^1B_2)$=**0.32 (n_2–n_3)** + **0.30 (i_4–i_6)** + **0.16 (i_1–i_2)** + . . .



Point

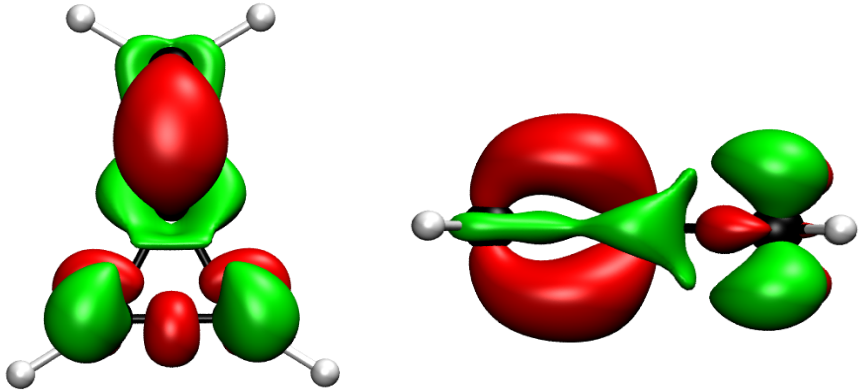
Stéphane Humbel @ Aix-**Marseille** Univ.

Ground States drawings (& VB, Lewis) are OK

Excited States drawings need some new insights

Isosurfaces of density difference upon excitation

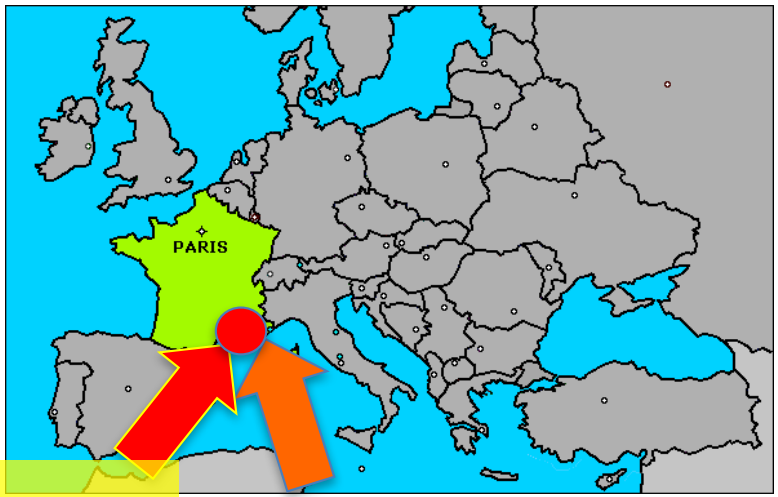
BOVB(π) (same as CASSCF)



Shows the CT from the π bond to the cycle

As a Satellite to ICQC 2018

ValBO-2018: "Understanding Chemistry and Biochemistry with Conceptual Models"



ICQC @ Menton

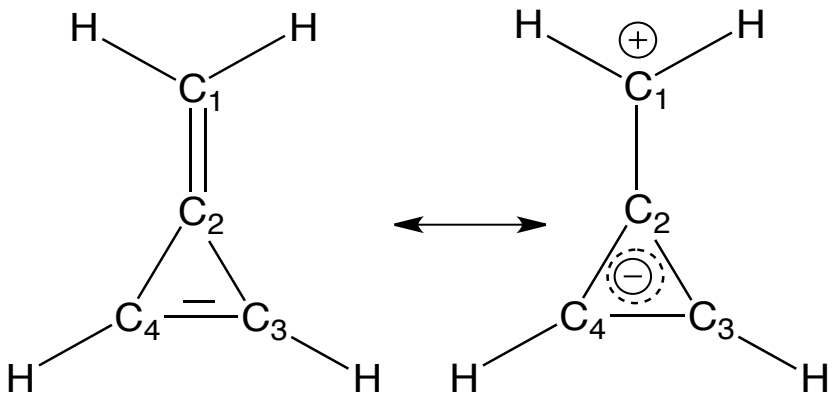
ValBO @Marseille

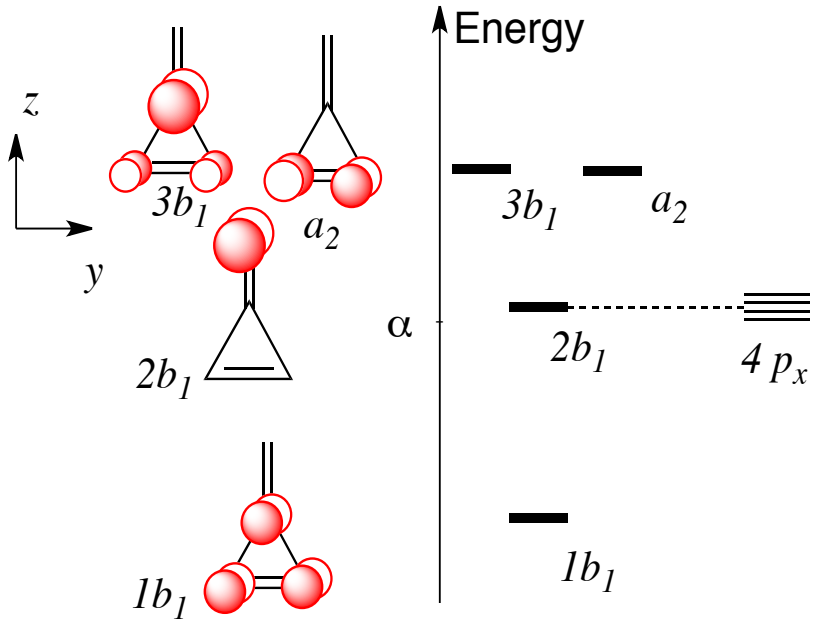
Point

Stéphane Humbel @ Aix-**Marseille** Univ.

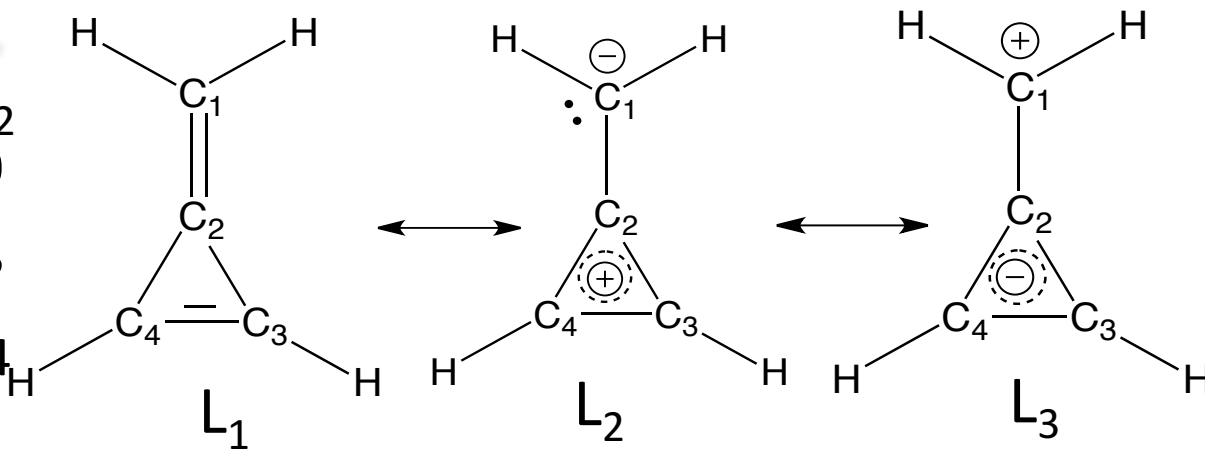
Ground States drawings (& VB, Lewis) are OK

Excited States drawings need some new insights





6-311+G(d)	VE (eV)	DMz 1 $^1A_1$	DMz 1 $^1B_2$
RASSCF	4.79	-1.90	+1.80
CASSCF	4.54	-1.78	+1.93
BOVB(π)	5.22	-1.81	+2.04

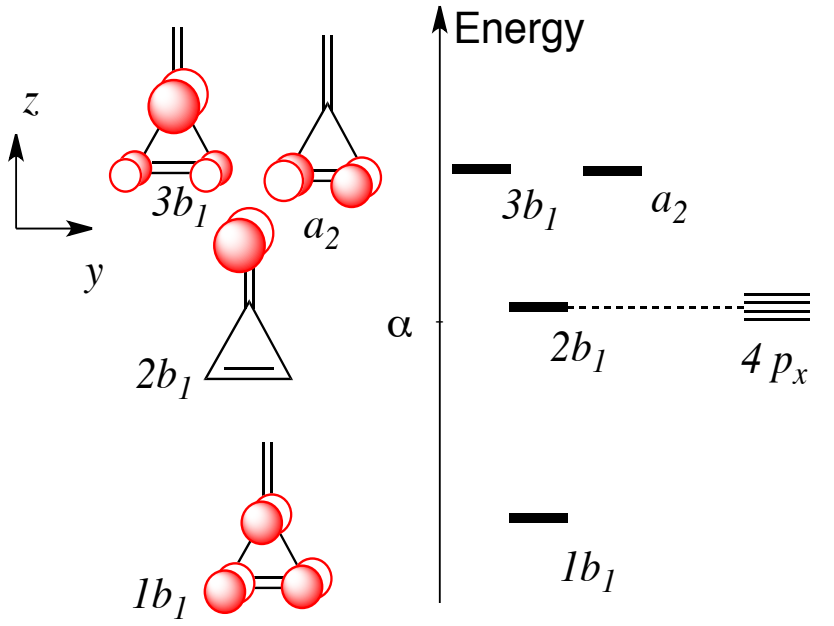


$(1b_1)^2\ (2b_1)^2$

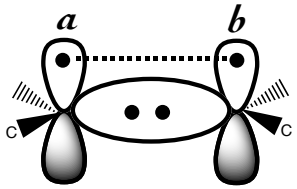
$(1b_1)^2\ (3b_1)^2$
$(1b_1)^2\ (a_2)^2$
$(1b_1)^2\ (a_2)^1(3b_1)^1$

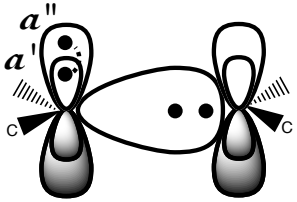
Lewis structures with optimized orbitals can't be used for ground state nor for the excited state

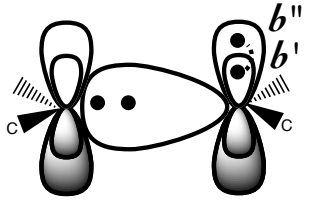
- Bond Distorded Orbitals … DISTORDED
- ..

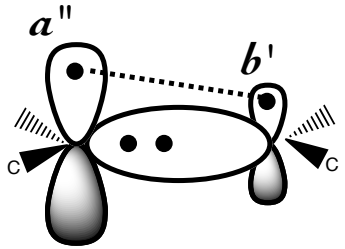


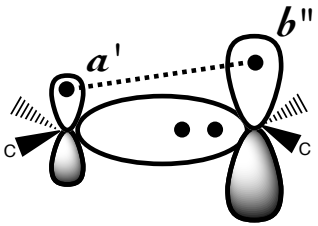
Ethylene : V state wave function











$^1A_{1g}$	C_i	0.76	0.19	0.19	-	-		
	w_i	74	13	13	-	-		
$^1B_{1u}$	C_i	-	0.98	-0.98	0.92	-0.92		
	w_i	-	50	50	-0	-0		