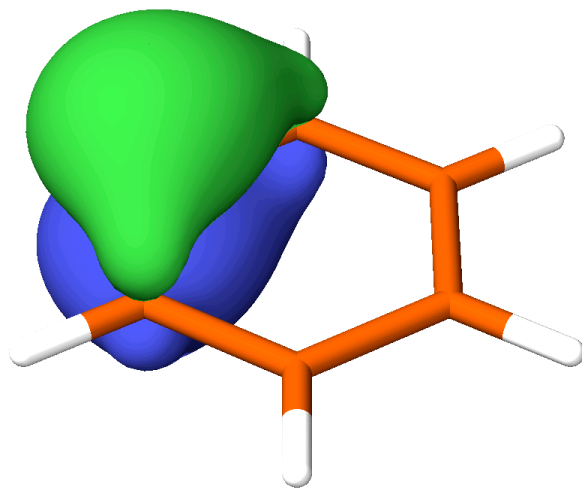
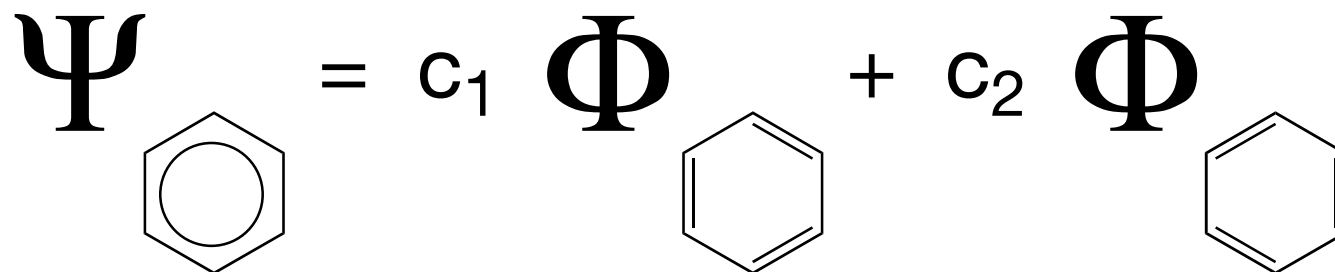


Valence bond theory and the (delocalised) chemical bond



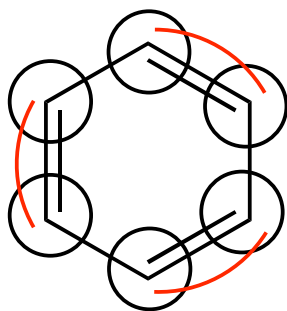
*Remco W. A. Havenith
Theoretical Chemistry Group
Utrecht University
The Netherlands*

Delocalised (π -)systems

- Multiple structures mandatory
 - Orbitals may delocalise or be kept strictly atomic
- Resonance energy according to Pauling
 - Energy difference between total energy and the energy of the most stable structure
 - Measure for *aromaticity*
 - *What is a proper description for the hypothetical, non-aromatic reference compound?*

Valence bond description of benzene

- Multi-determinant wavefunction for 1,3,5-cyclohexatriene

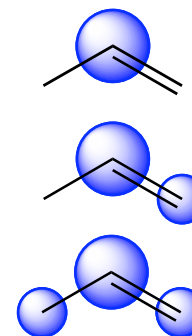


p-orbitals:

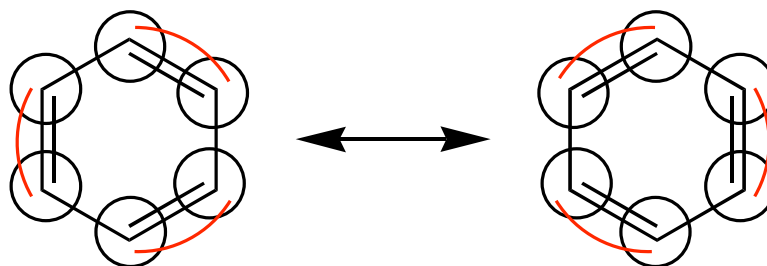
Strictly Atomic (VB-Atomic)

Partial Delocal (VB-Partial)

Delocal (VB-Delocal)

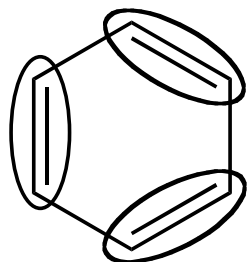


Compare with two resonating 1,3,5-cyclohexatrienes:



Block-Localised-Wavefunctions[†]

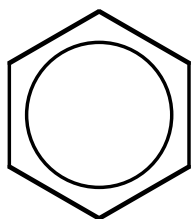
- BLW can be built using orbital restrictions, as in the strictly atomic or partial delocal VB
- Hartree-Fock like (one-determinant) description of localised reference molecule



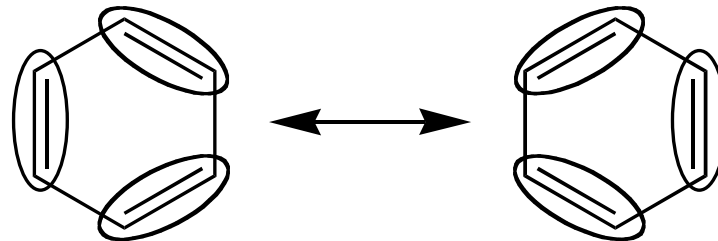
Localised, ethene-like bonds due to restrictions of orbitals

Note that the orbitals can be orthogonalised!

Compare to HF benzene or two resonating BLW's:



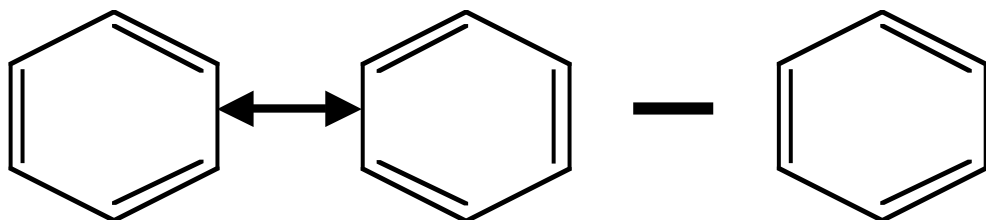
or



[†]see Y. Mo, P. v. R. Schleyer, *Chem. Eur. J.* **2006**, *12*, 2009-2020.

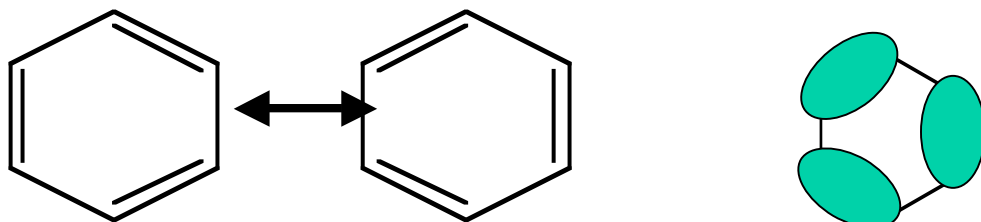
Resonance Energies (Kcal/mol)

Same orbitals - Pauling resonance energy



25	(local),
19.8	(delocal)
44.1	(breathing)
29.5	(breathing D_{3h})

Different orbitals - “Shaik” resonance energy,
using bond-distorted orbitals (Wu,Mo,Zhang(1993))



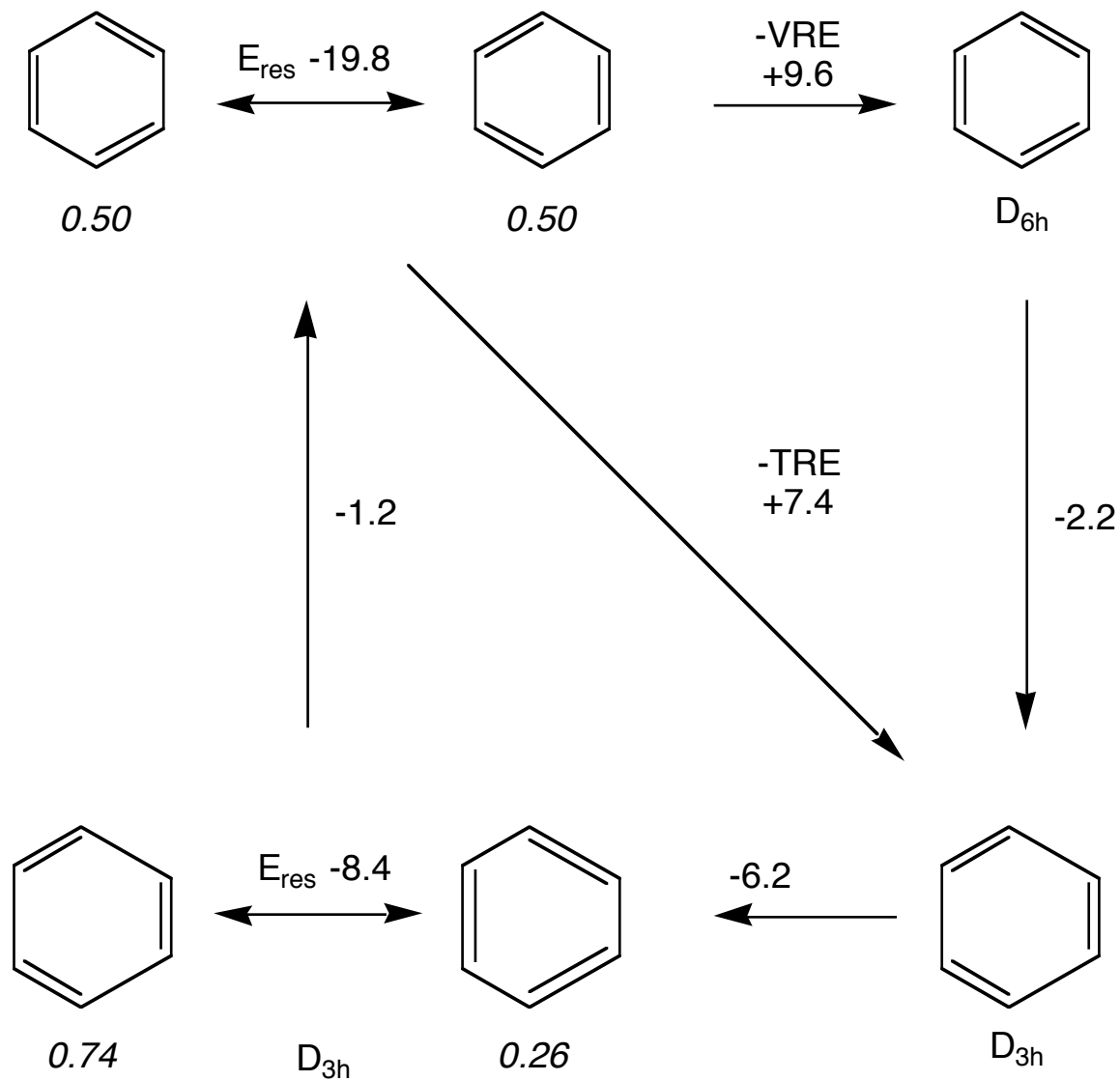
65	(Shaik(2001))
62.8	(D_{6h})
48.95	(BLW-res)
86.61	(BLW-HF)

D_{6h}

Spin overlap : 0.25; Overlap between separate-opt structures 0.89

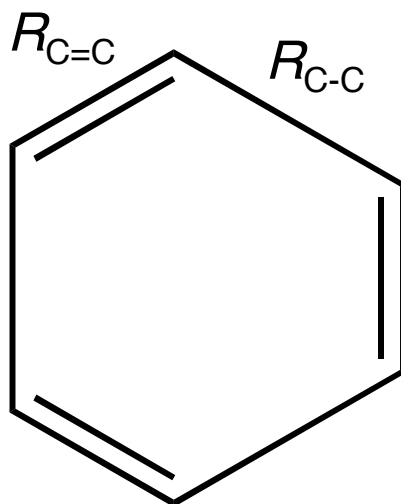
Overlap between together-opt breathing structures 0.55

Benzene and hexatriene



1,3,5-Cyclohexatriene geometries

6-31G basis set



Model	$R_{C=C}$ (Å)	R_{C-C} (Å)
VB-Atomic	1.368	1.509
VB-Partial	1.343	1.512
VB-Delocal	1.369	1.433
BLW	1.322	1.511

Delocal benzene (not shown) in excellent agreement with the experimental value

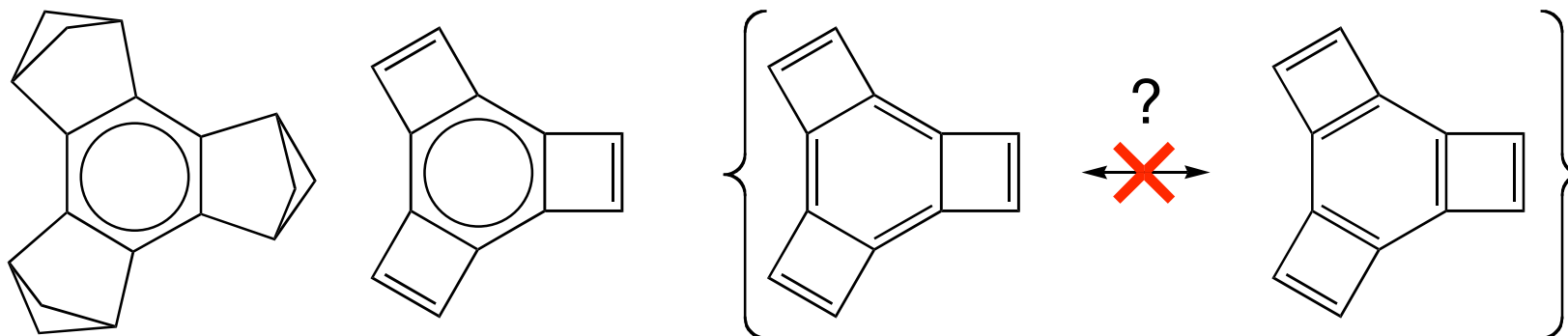
Delocal cyclohexatriene looks like linear polyenes (1.368 Å and 1.458 Å)

Unfortunately “accepted” resonance energy is say 60 Kcal/mol

Clamped benzenes

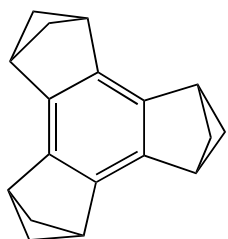
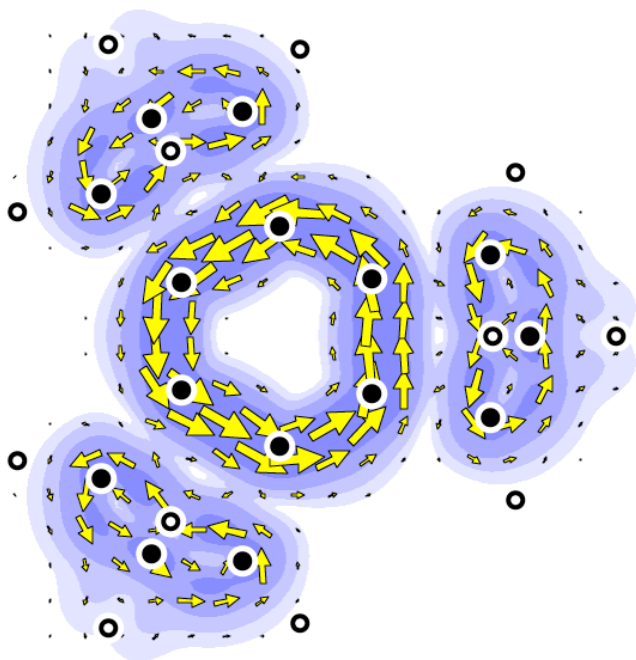
Does clamping lead to electron localisation?

- Inspired by aromaticity studies



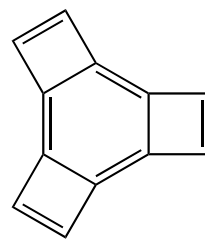
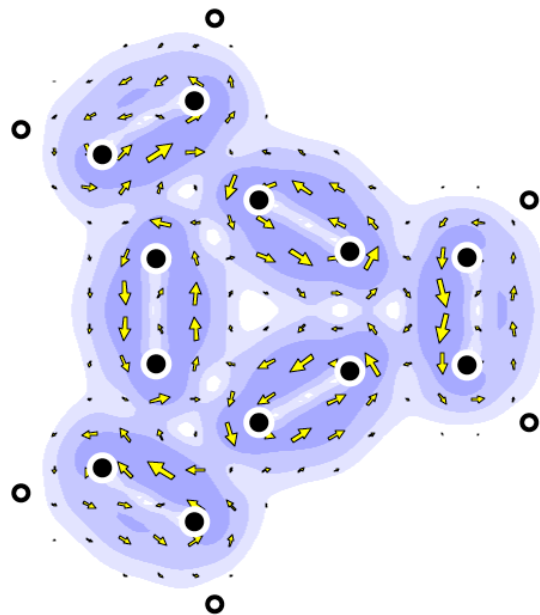
- Aromaticity criteria
 - Ability to sustain an induced, diatropic ring current
 - Extra stabilisation: Pauling resonance energy

Ring current



$$\Delta R = 0.096 \text{ \AA}$$

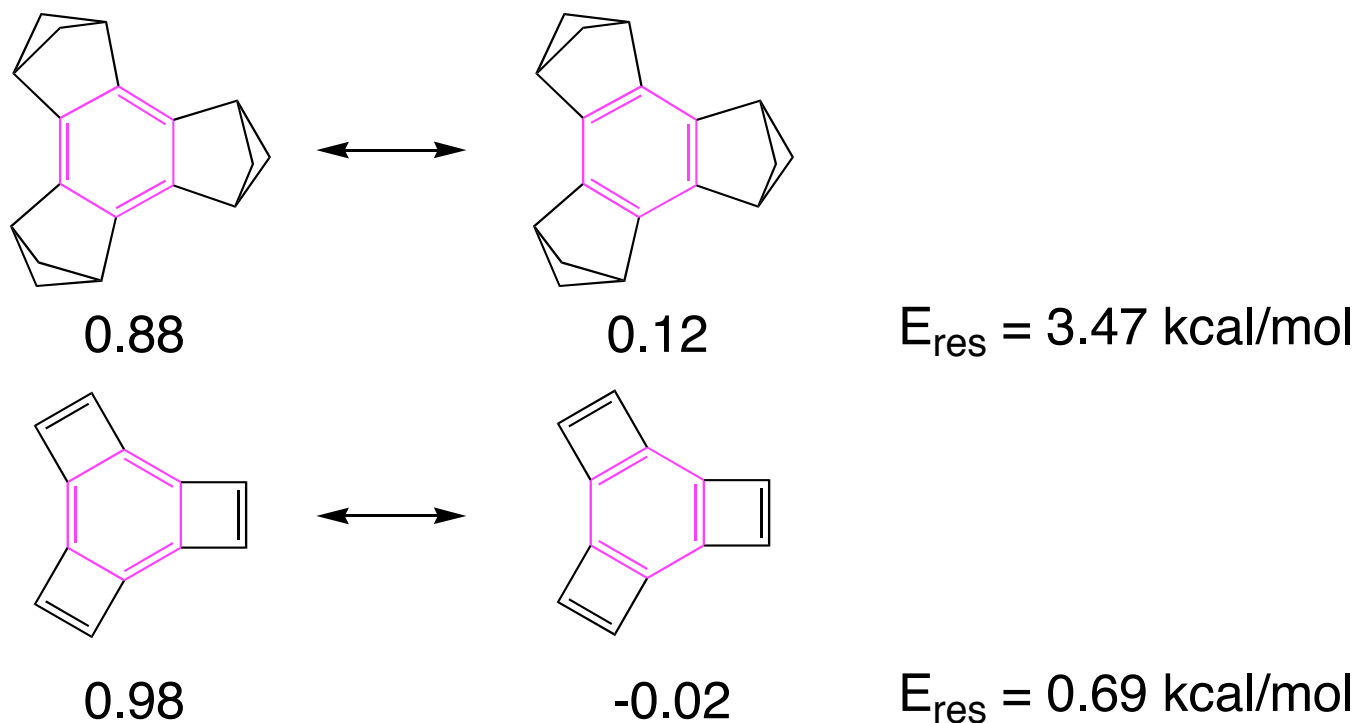
survival



$$\Delta R = 0.182 \text{ \AA}$$

extinction

Pauling resonance energies

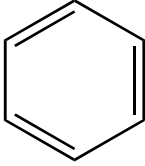
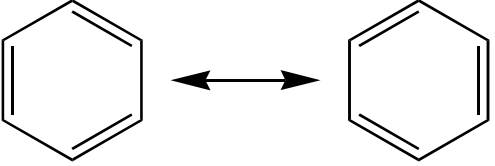


cf. benzene: $E_{\text{res}} = 20$ kcal/mol

Perceived discrepancy between magnetic and energy criterion

see also: J. G. Hill, P. B. Karadakov, D. L. Cooper, *Mol. Phys.*, **104** (2006), 677-680.

Properties of 1,3,5-cyclohexatriene and benzene

	One-structure			Two-structure		
						
Property	P_{xx}	P_{yy}	P_{zz}	P_{xx}	P_{yy}	P_{zz}
Polarisability	62.91	19.44	19.44	61.15	18.14	18.14
Magnetisability	-40.57	-53.00	-53.00	-40.63	-52.83	-52.83

Similar response for benzene and 1,3,5-cyclohexatriene!

CI space:

$$\psi_0 = \phi_1 + \phi_2 \quad (A_{1g})$$

$$\psi_1 = \phi_1 - \phi_2 \quad (B_{2u})$$

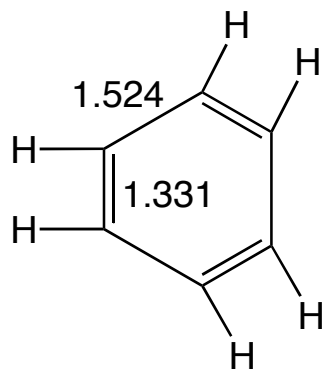
\hat{O} symmetries:

$$(x, y) \quad E_{1u}$$

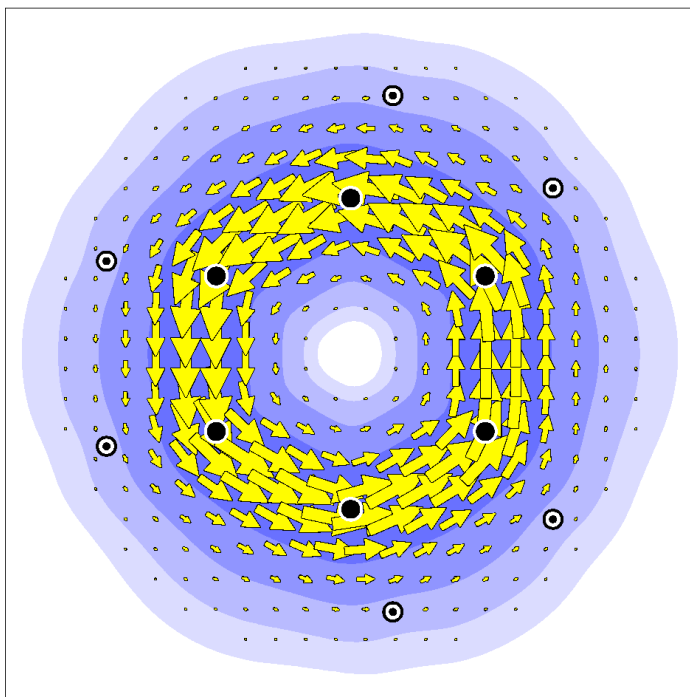
$$z \quad A_{2u}$$

CI response:

$$\sim \left\langle \psi_0 \left| \begin{matrix} (x, y) \\ z \end{matrix} \right| \psi_1 \right\rangle = 0$$

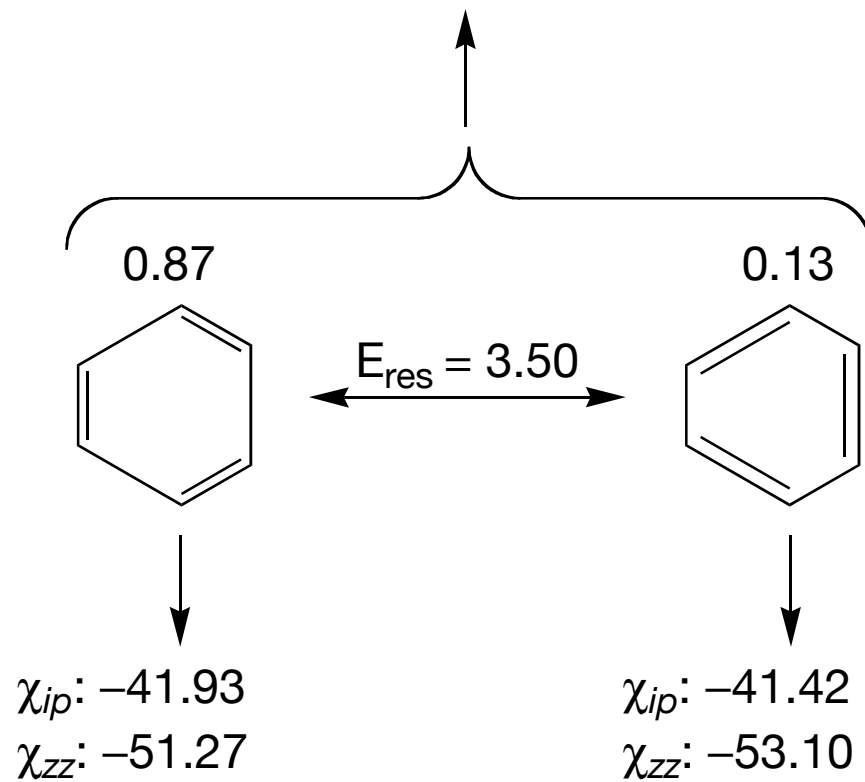


Deformed benzene



$$\chi_{ip}: -41.88$$

$$\chi_{zz}: -51.56$$



Conclusions

- Chemical concepts can be explored by the application of orbital restrictions in valence bond theory
- No causal relationship between Pauling resonance energy and considered response properties
- Nature of the bonds in a valence bond structure are determined by the whole molecular environment: spin-coupled bonds are not independent, localised bonds