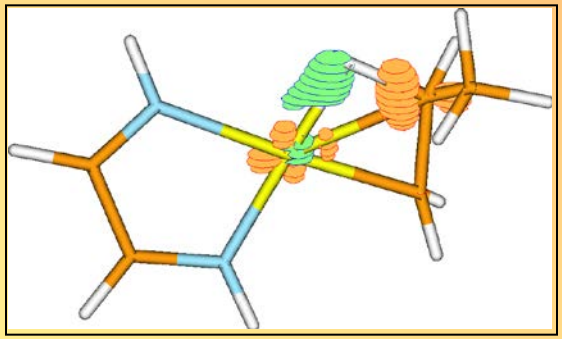
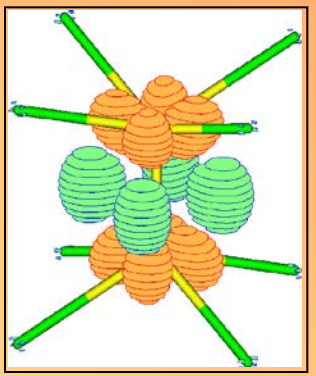
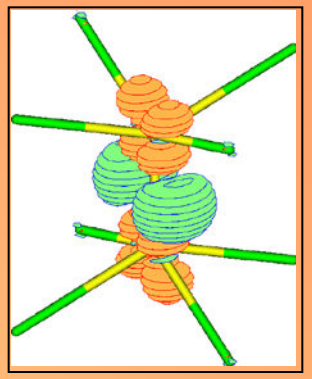
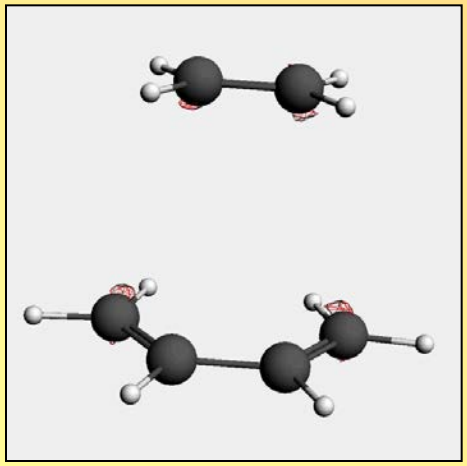
A Chemical Bond From the Natural Orbitals for Chemical Valence (NOCV) Perspective



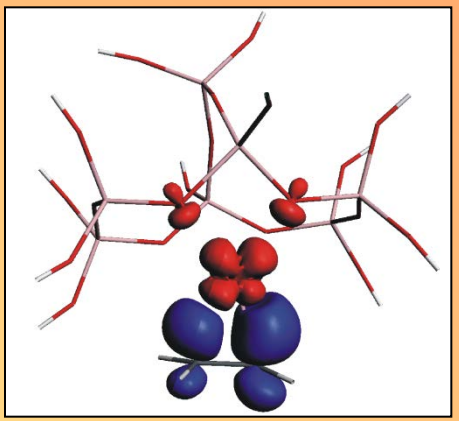


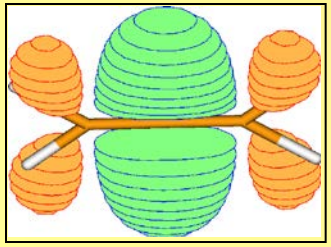


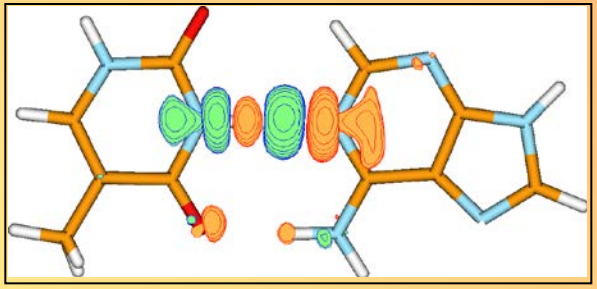


Mariusz P. Mitoraj

Jagiellonian University
Cracow, Poland
Department of Theoretical Chemistry

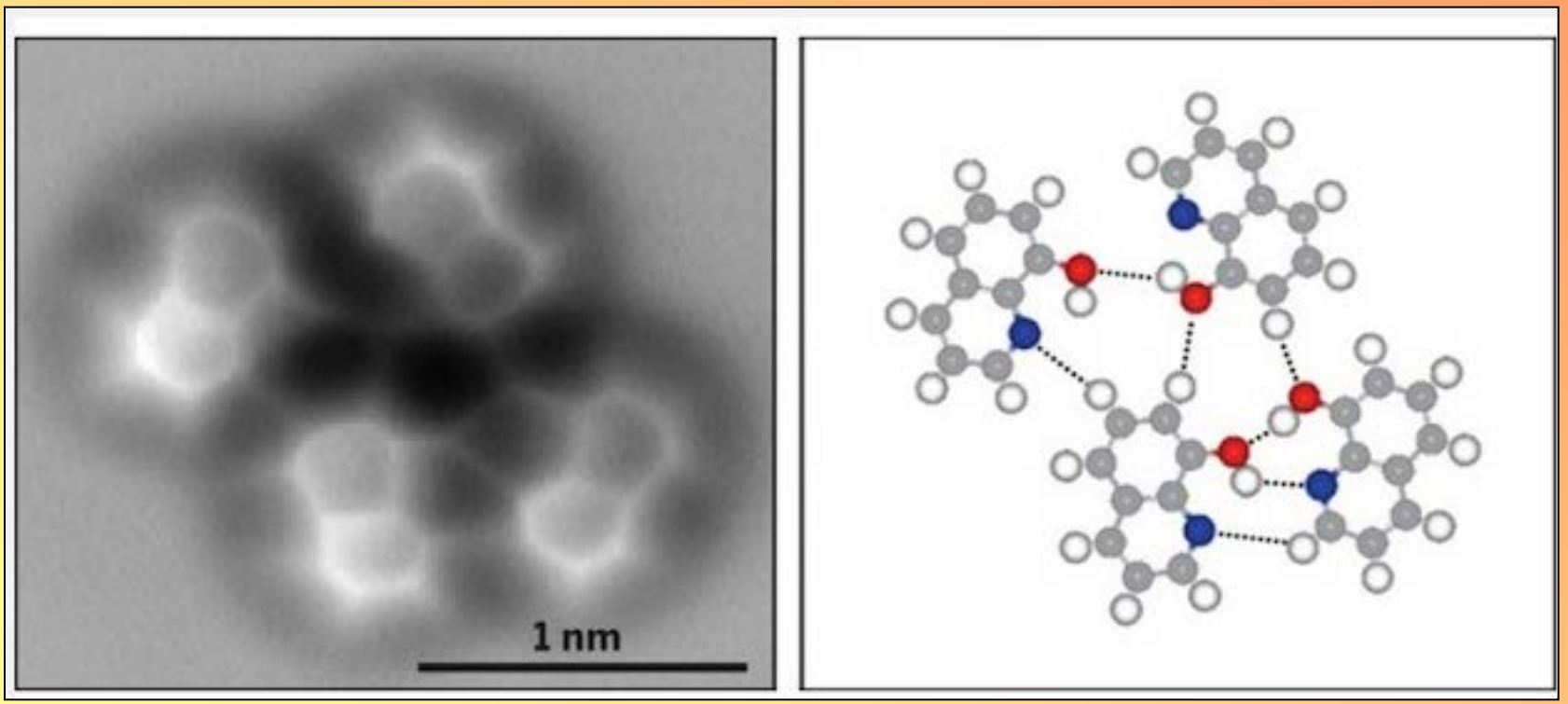






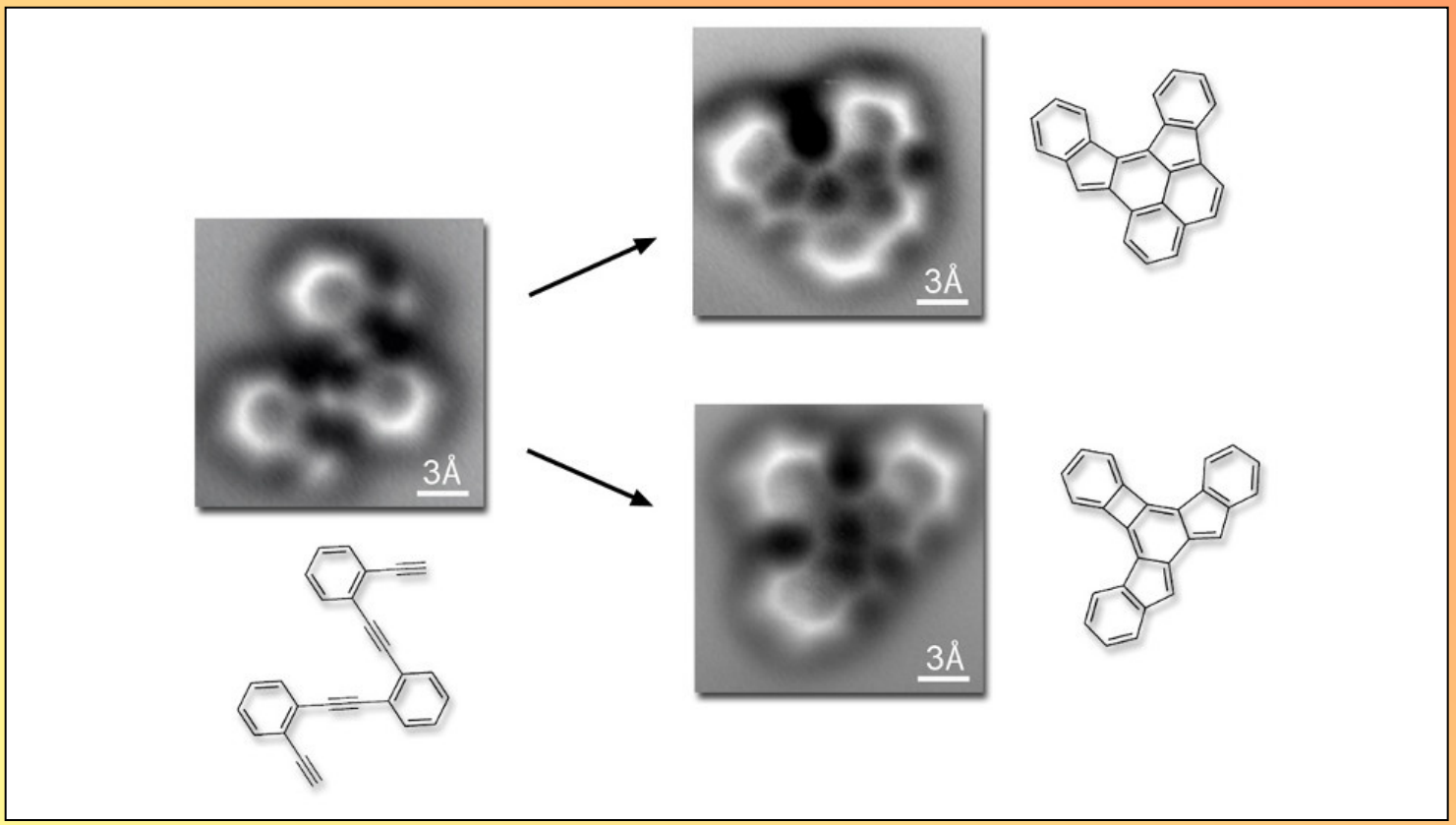
Experimental visualization chemical bond ?

Atomic Force Microscopy



„Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy"
J. Zhang et al., Science, 2013, 342, 611-614 .

Experimental seeing the chemical reaction at quantum level ?



REPORT

Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions

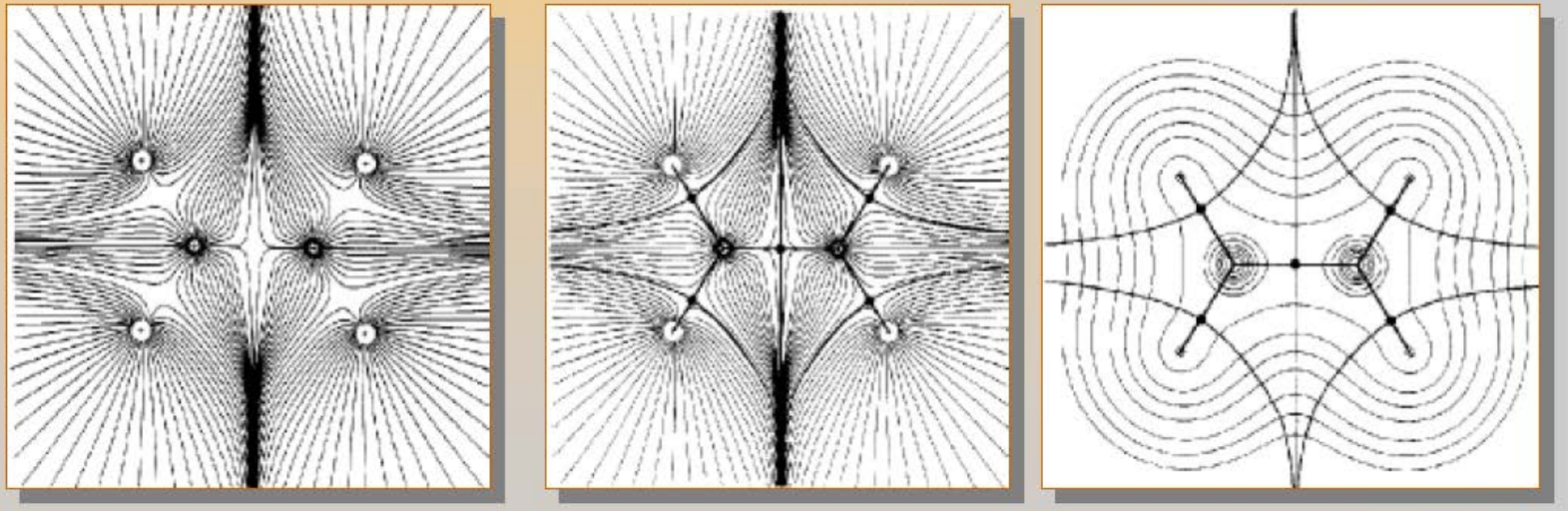
Dimas G. de Oteyza, Patrick Gorman, Yen-Chia Chen, Sebastian Wickenburg, Alexander Riss, Duncan J. Mowbray, Grisha Etkin, Zahra Pedramrazi, Hsin-Zon Tsai, Angel Rubio, Michael F. Crommie, and Felix R. Fischer

Science 21 June 2013: 1434-1437.Published online 30 May 2013

Examples of theoretical quantities for visualization of chemical bond

Bader theory of Atoms-in-Molecules

- electron density divided in physical space, based on derivatives and critical points of electron density



R.F.W. Bader, „*Theory of Atoms in Molecules*"
http://www.chemistry.mcmaster.ca/faculty/bader/aim/

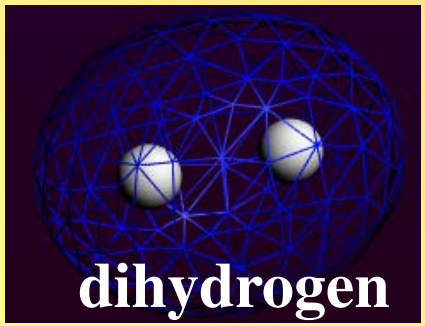
Quantum Theory of Atoms in Molecules (QTAIM) by Richard Bader

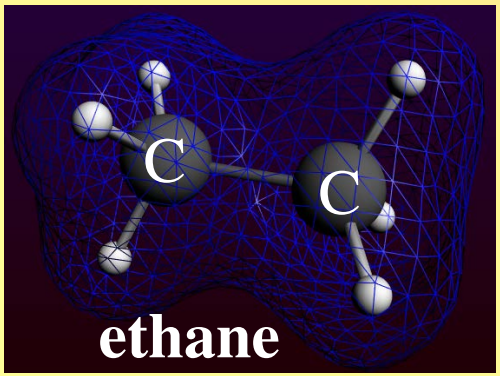
*start- electron (charge) density from wavefunction (ψ) (N electrons, with positions x_1, x_2, ….x_N):

$$\rho(\vec{r}) = N\int\cdots\int\left|\Psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N)\right|^2 ds_1 d\vec{x}_2 \ldots d\vec{x}_N$$

$$\rho(\vec{r} \rightarrow \infty) = 0$$

$$\int \rho(\vec{r})\, d\vec{r}_1 = N$$





charge density is delocalized over the whole molecule,

how then extract any information about bonding between selected atoms C-C or C-H ?

Quantum Theory of Atoms in Molecules (QTAIM) by Richard Bader

*construct the Hessian matrix (second derivatives of density) and perform diagonalization to obtain various „critical points".

Critical points of $\rho(r)$: maximum, minimum or saddle where the gradient of $\rho(r)$ vanish ($\nabla\rho(r_c) = 0$), where

$$\nabla\rho(\mathbf{r}) = \frac{\partial\rho(\mathbf{r})}{\partial x}\mathbf{u}_x + \frac{\partial\rho(\mathbf{r})}{\partial y}\mathbf{u}_y + \frac{\partial\rho(\mathbf{r})}{\partial z}\mathbf{u}_z$$

Hessian of ρ at a critical point:

$$A(r_c) = \begin{pmatrix} \frac{\partial^2\rho}{\partial x^2} & \frac{\partial^2\rho}{\partial x\partial y} & \frac{\partial^2\rho}{\partial x\partial z} \\ \frac{\partial^2\rho}{\partial y\partial x} & \frac{\partial^2\rho}{\partial y^2} & \frac{\partial^2\rho}{\partial y\partial z} \\ \frac{\partial^2\rho}{\partial z\partial x} & \frac{\partial^2\rho}{\partial z\partial y} & \frac{\partial^2\rho}{\partial z^2} \end{pmatrix}_{r=r_c}$$

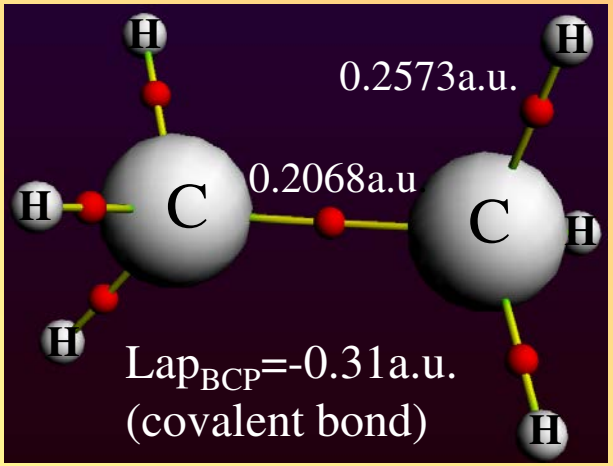
The Hessian matrix is real and symmetric
=> we can put it in a diagonal form:

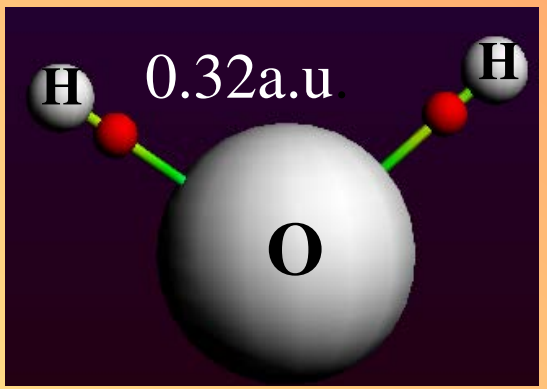
$$\Lambda = \begin{pmatrix} \frac{\partial^2\rho}{\partial x'^2} & 0 & 0 \\ 0 & \frac{\partial^2\rho}{\partial y'^2} & 0 \\ 0 & 0 & \frac{\partial^2\rho}{\partial z'^2} \end{pmatrix}_{r'=r_c} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}$$

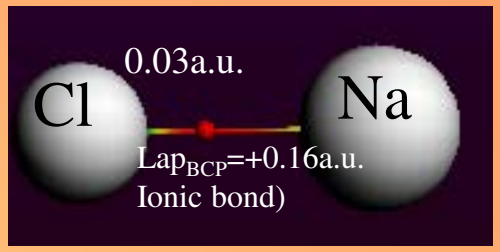
eigenvalues = curvatures of ρ

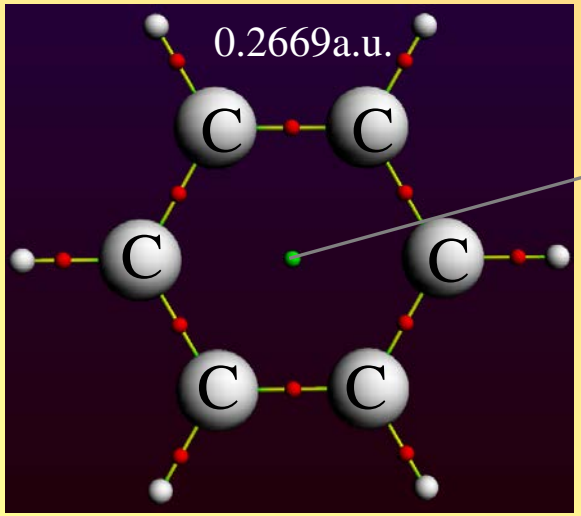
R.F.W. Bader, *Atoms in Molecules - A quantum theory*, Oxford University Press, New York, 1990.

Quantum Theory of Atoms in Molecules (QTAIM) by Richard Bader, ethane(C_2H_6) ,water(H_2O), sodium chloride (NaCl), benzene(C_6H_6) examples



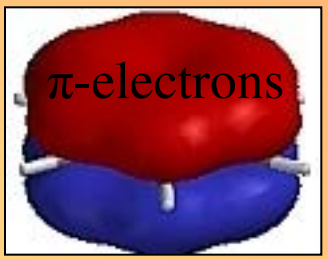






Ring-Critical-Point
RCP (3,+1)

Two eigenvalues positive
(in plane axes)
and one negative (perpendicular)



Examples of theoretical quantities for visualization of chemical bond

Differential density (deformation density)

$$\Delta\rho(r) = \rho^{mol.}(r) - \sum_{i=1}^{N_{at}} \rho_i^{at.}(r)$$

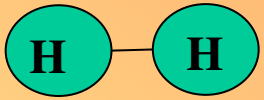
Positive values describe the point of density accumulation in the molecule (relative to isolated atoms). When the molecule is formed from atoms the density flows from the area of negative value towards the area with positive value.

Formation of chemical bond in H_2 – $\Delta\rho$ based picture

1. Start from promolecular state (atom/fragments)

$\rho_H = 1s^2$

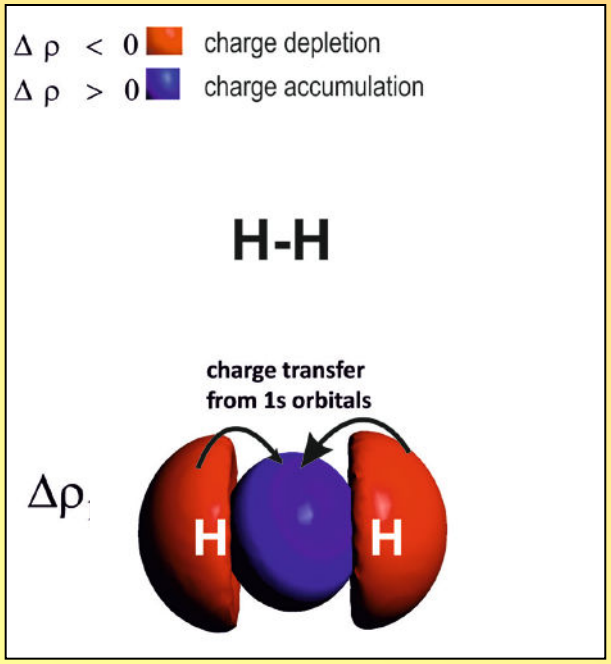
ρ_{H2}



$\rho_H = 1s^2$

$$\Delta\rho = \rho_{H2} - 2\rho_H$$

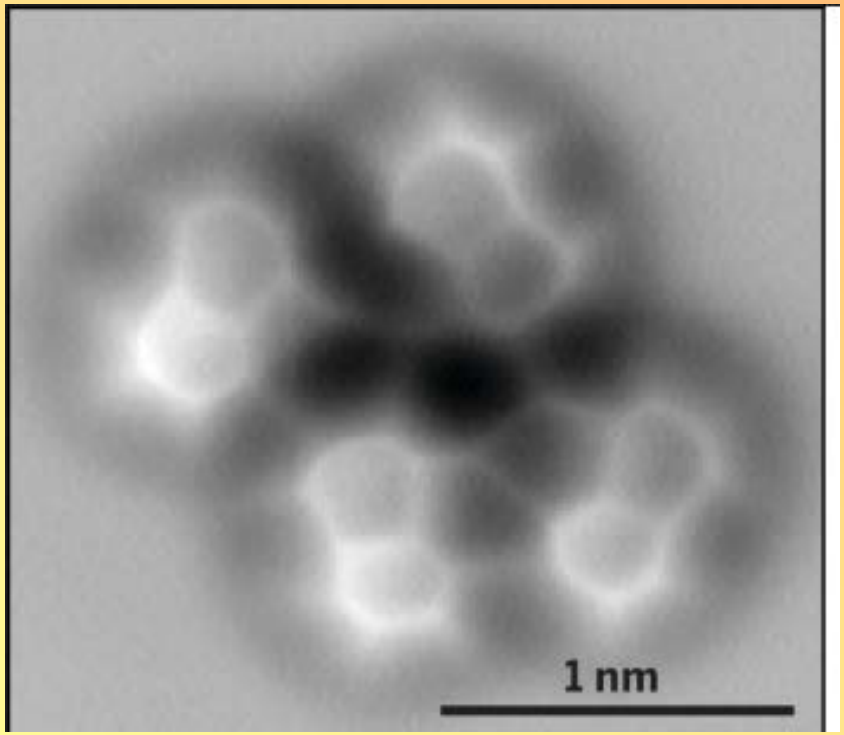
Deformation density (Differential density)



(1) qualitative data
by inspection of the sign
of $\Delta\rho$: negative (outflow),
positive (inflow) of density
due to bond formation

Experimental visualization of chemical bond vs calculated Δρ

Tetramer of 8-hydroxyquinoline connected via hydrogen bonds



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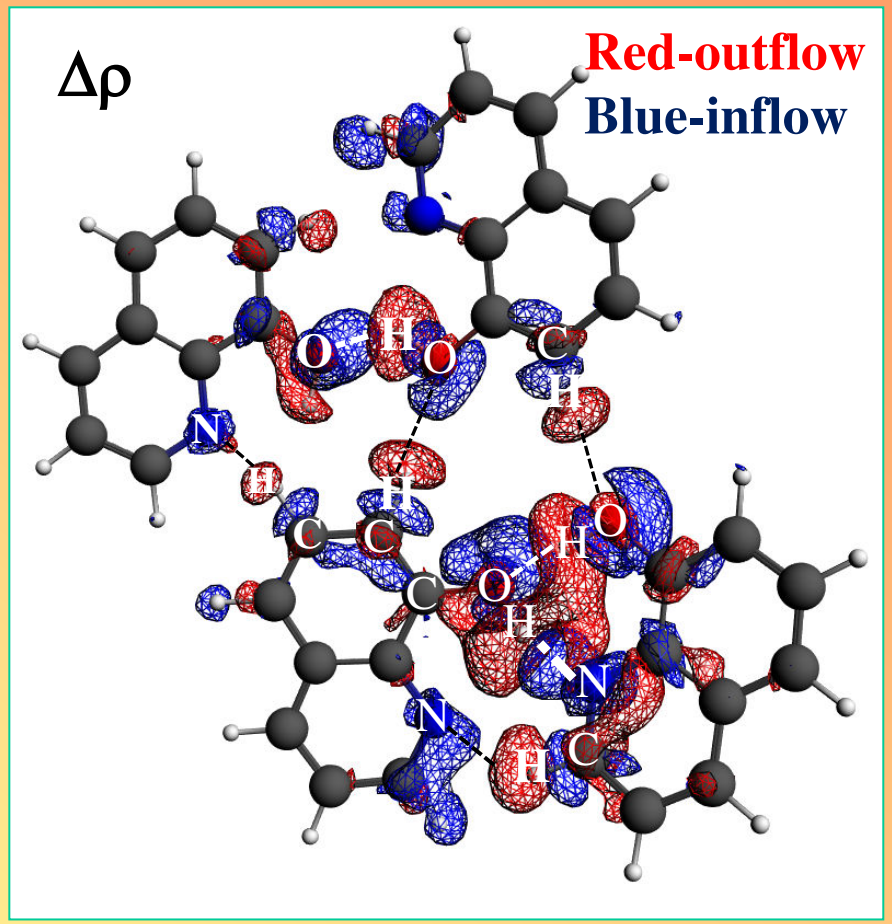
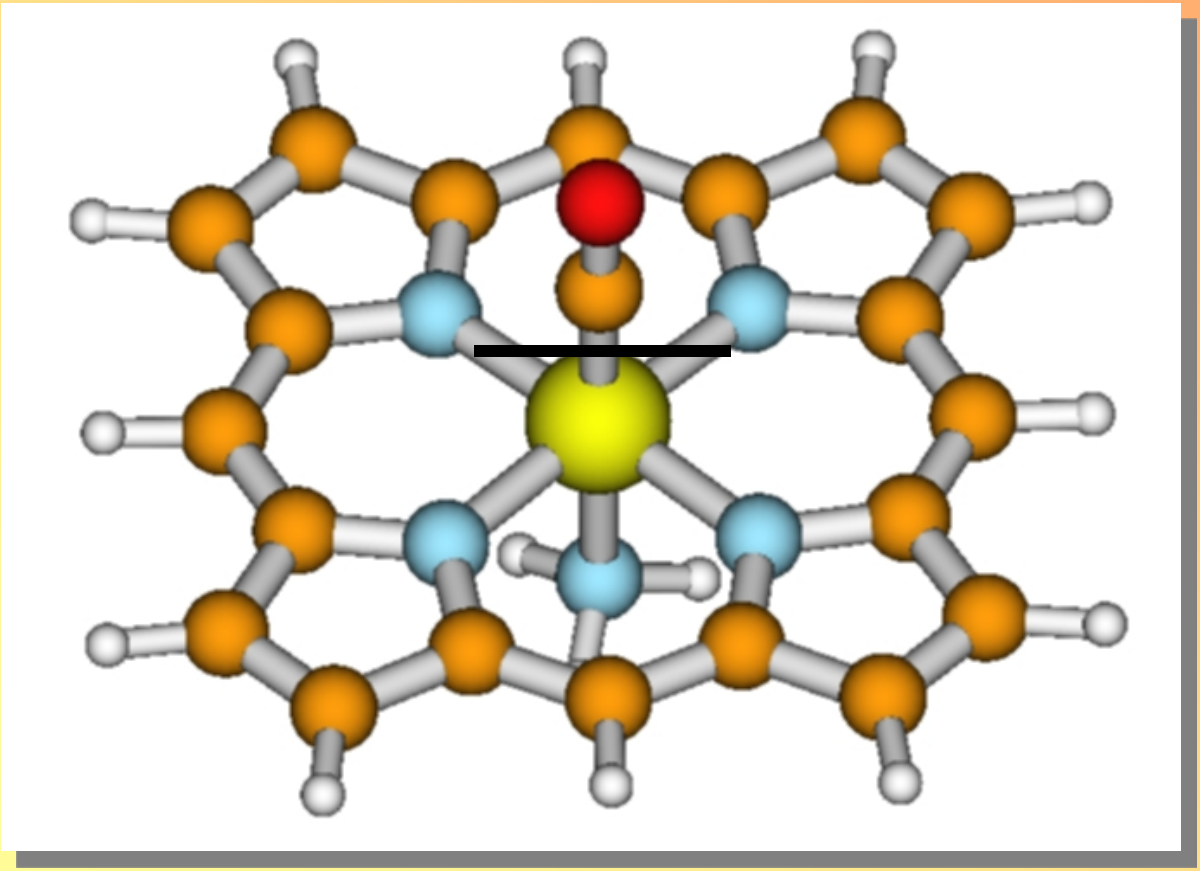


$\Delta\rho=\rho_{molecule}-\rho_1-\rho_2-\rho_3-\rho_4$

Formation of chemical bond in hem-CO; Δρ based picture

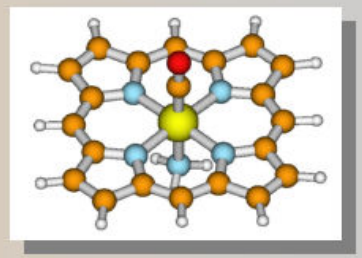
In the A/B resolution (fragment / ligand) :

$$\Delta\rho = \Delta\rho_{AB}(r) - \rho_A(r) - \rho_B(r)$$

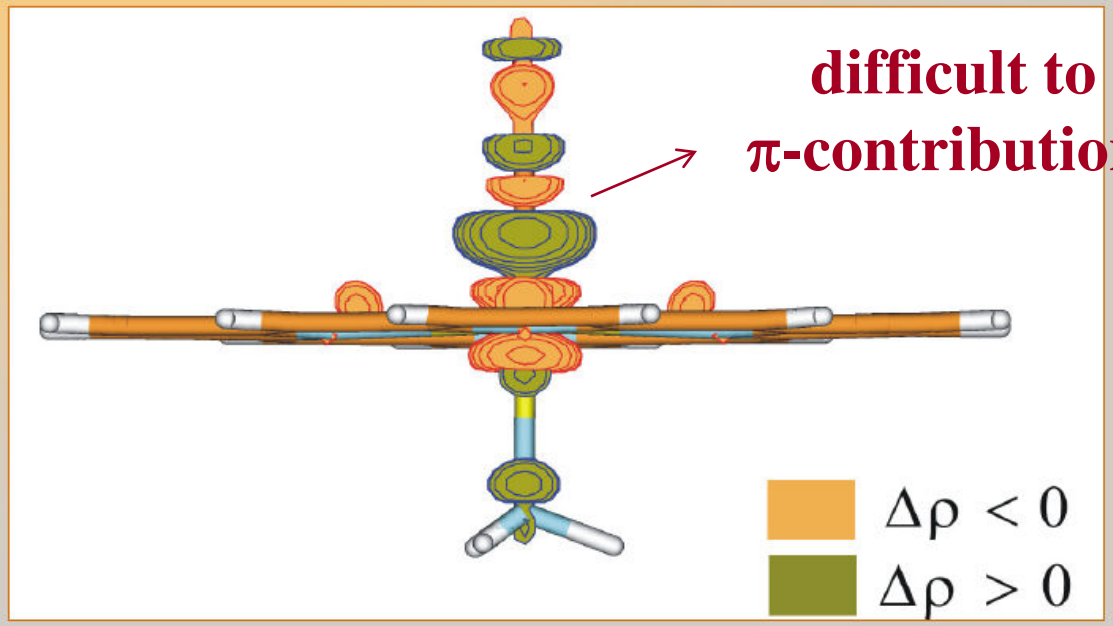


Formation of chemical bond in hem-CO; Δρ based picture

Heme - CO



Deformation density description



difficult to extract σ- or π-contributions of Fe-C bond

M.Mitoraj, A.Michalak, J.Mol.Model. 2007, 13, 347-355.

The Natural Orbitals for Chemical Valence (NOCV)

NOCV's ($\psi_i = \sum_i C_{ij} * \lambda_i$) diagonalize the deformation density matrix:

$$\Delta P C_i = v_i C_i \quad ; \quad i = 1, M$$

where **$\Delta P = P - P_0$, density matrix of the combined molecule,**
P_0- density matrix of the considered molecular fragments.

NOCV's also decompose the deformation density Δρ:

$$\Delta\rho(r) = \sum_{k=1}^{M} v_k \psi_k^2(r)$$

useful qualitative data by inspection of the sign of Δρ: negative (outflow), positive (inflow) of density

NOCV's are in pairs:

$$\Delta\rho(r) = \sum_{k=1}^{M/2} v_k[-\psi_{-k}^2(r) + \psi_k^2(r)] = \sum_{k=1}^{M/2} \Delta\rho_k(r)$$

Radoń, M. Theor Chem Account 2008, 120,337.

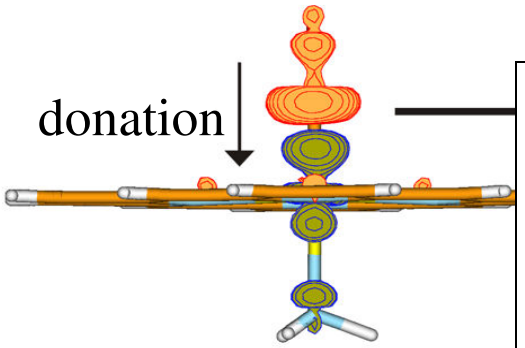
Mitoraj, M.; Michalak, A. *Organometallics* 2007, 26(26); 6576., Michalak, A.; Mitoraj, M.; Ziegler, T. *J. Phys. Chem. A.* 2008, 112 (9), 1933, Mitoraj, M.; Michalak, A. J. Mol. Model., 2008, 14, 681, Mitoraj, M.; Zhu, H.; Michalak, A.; Ziegler, T. 2008, *International Journal of Quantum Chemistry*, DOI: 10.1002/qua.21910., Mitoraj, M.; Michalak, A. *J. Mol. Model.* 2008, *14*, 681.

The contours of the deformation density (Δρ) and the contributions from the pairs of complementary orbitals for the heme/CO system

$$\Delta\rho(r) = \sum_{i=1}^{n} \nu_i \varphi_i^2(r)$$

$\Delta\rho_1 = -0.74 * \varphi_{-1}^2 + 0.74 * \varphi_1^2$

donation

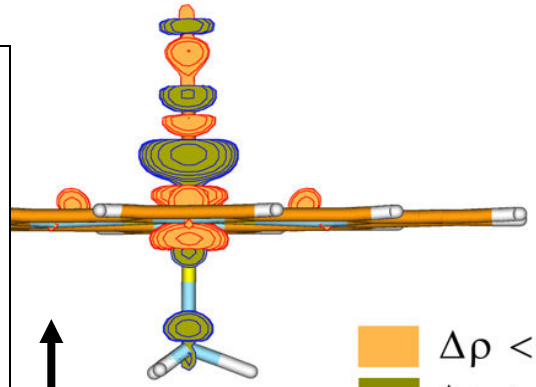


NOCV's

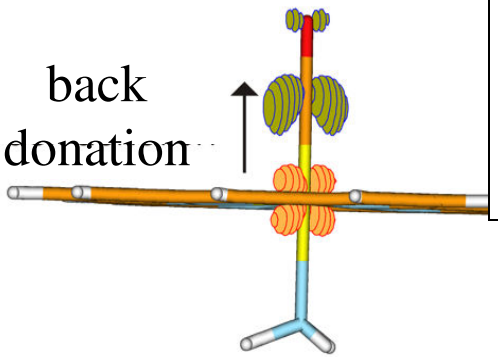
☹

No energetic estimation !

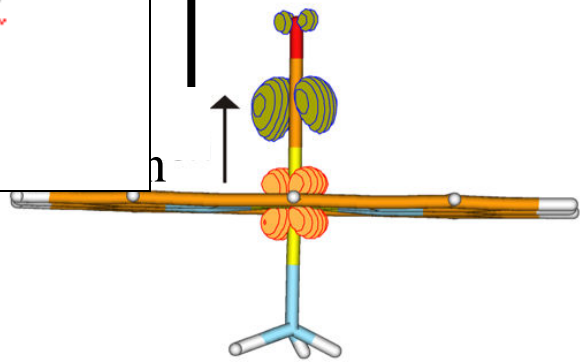
$\Delta\rho = \Delta\rho_1 + \Delta\rho_2 + \Delta\rho_3$



back donation



$\Delta\rho_2 = -0.52 * \varphi_{-2}^2 + 0.52 * \varphi_2^2$



$\Delta\rho_3 = -0.52 * \varphi_{-3}^2 + 0.52 * \varphi_3^2$

A combination of ETS/EDA and NOCV - (ETS-NOCV)

ETS/EDA: $-D_e=\Delta E_{total}= \Delta E_{dist} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$

$$\Delta E_{orb} = \sum_{\lambda}\sum_{\mu} \Delta P^{orb}_{\lambda\mu} F^{TS}_{\lambda\mu}$$

electronic factor

NOCV: $$\Delta\rho^{orb}(r) = \sum_{k=1}^{N/2} v_k[-\psi^2_{-k}(r) + \psi^2_k(r)] = \sum_{k=1}^{N/2} \Delta\rho_k(r)$$

ETS-NOCV:

$$\Delta E_{orb} = Tr(\Delta P^{orb} F^{TS}) = Tr(C^{+}\Delta P^{orb} C C^{+} F^{TS} C) = \sum_{k=1}^{N/2} v_k[-F^{TS}_{-k,-k} + F^{TS}_{k,k}] = \sum_{k=1}^{N/2} \Delta E^{orb}_k$$

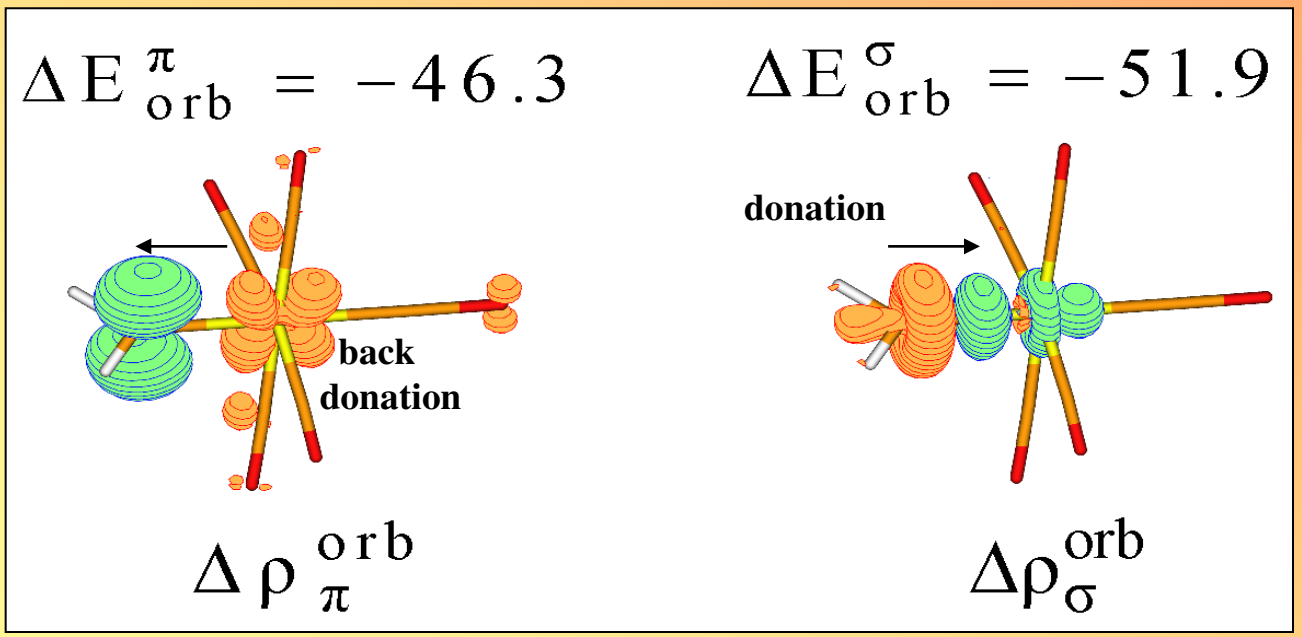
$$\Delta E_{orb} = \sum_{k=1}^{M/2} v_k[-F^{TS}_{-k} + F^{TS}_{-k}] = \sum_{k} \Delta E^{k}_{orb}$$

Energetic estimation of $\Delta\rho_k$

Mariusz P. Mitoraj, Artur Michalak and Tom Ziegler „A combined charge and energy decom-Position scheme for bond analysis" *J. Chem. Theory Comput.*, 2**009**, *5* (4), pp 962–975.

Dative bonds – systems with symmetry

$(CO)_5Cr{=}CH_2$



Donor/acceptor properties of ligands for $Ni(NH_3)_3X$ complexes:

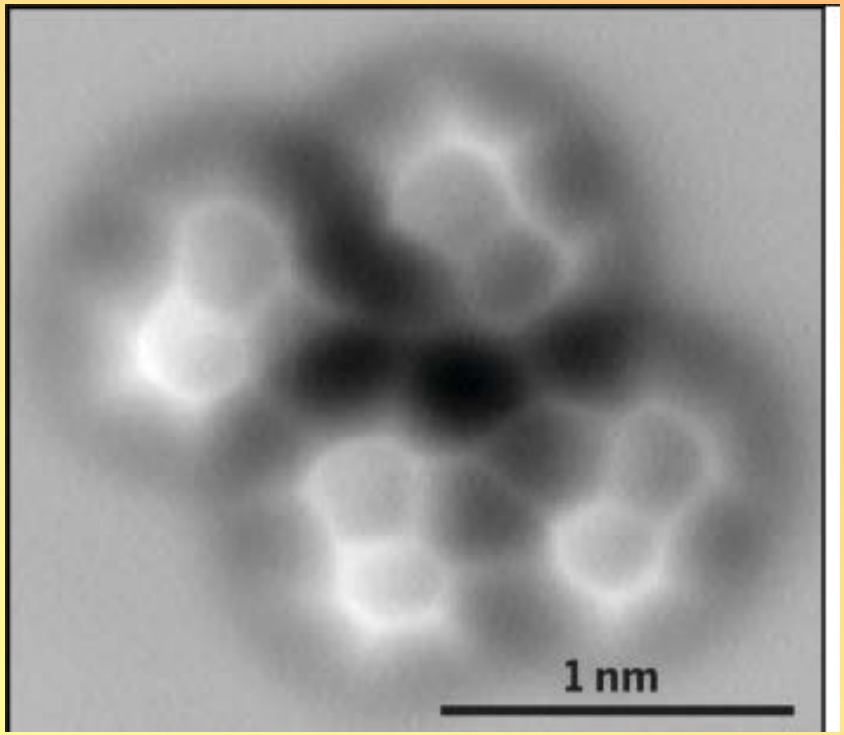
σ: $CN^- > PH_3 > NH_3 > C_2H_4 > CS > CO > N_2 > NO^+$

π: $NO^+ > CS > CO > N_2 > C_2H_4 > PH_3 > CN^- > NH_3$

Mitoraj Mariusz, Michalak A (2007) „ Donor-Acceptor Properties of Ligands from the Natural Orbitals for Chemical Valence” *Organometallics*, 26, 6576-6580

Experimental visualization of chemical bond vs calculated Δρ

Tetramer of 8-hydroxyquinoline connected via hydrogen bonds



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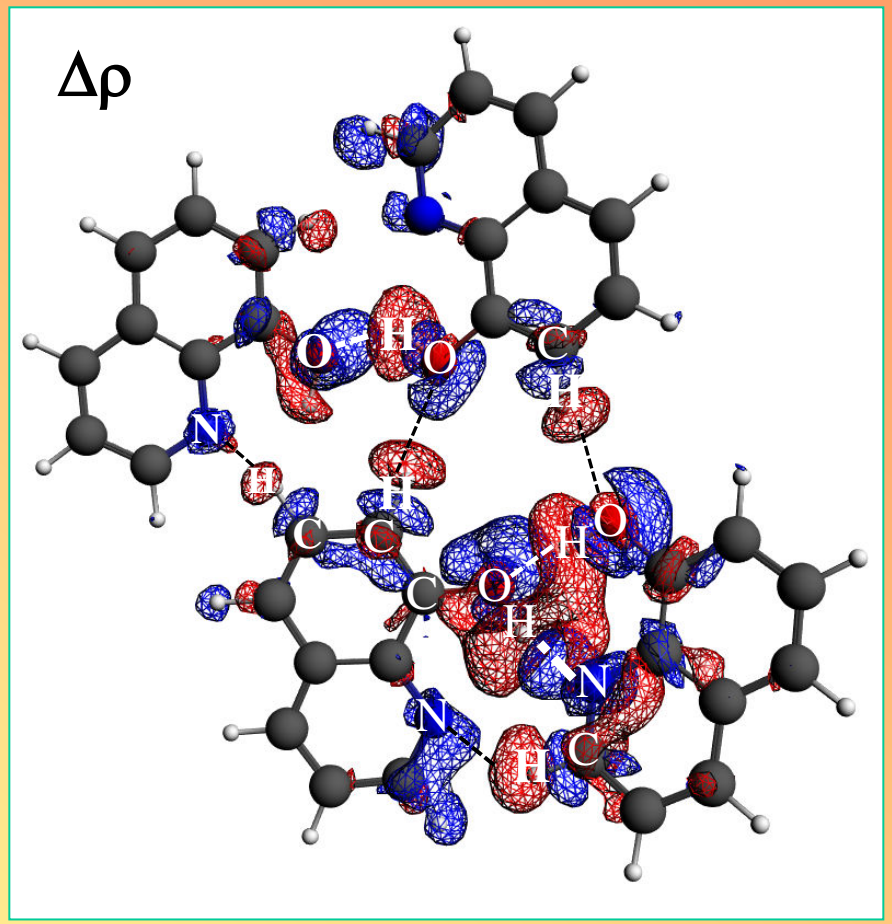
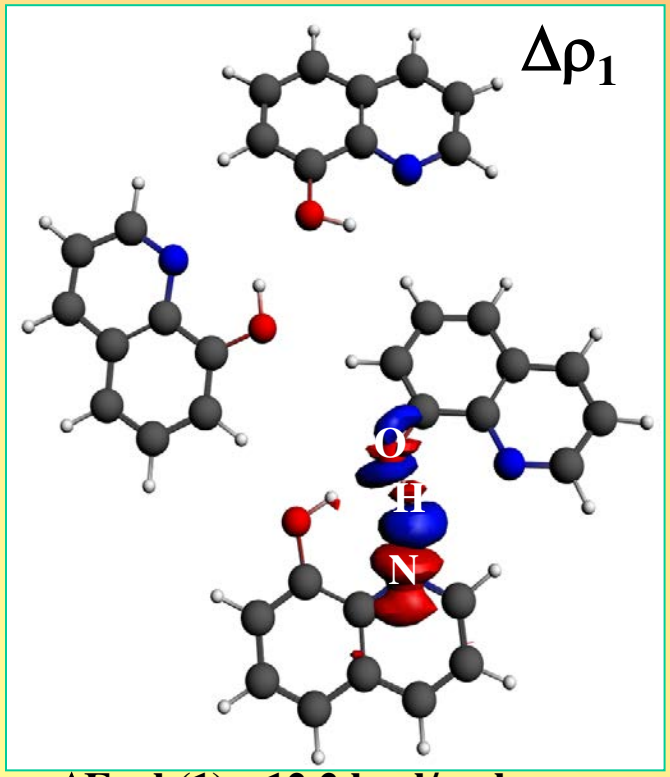
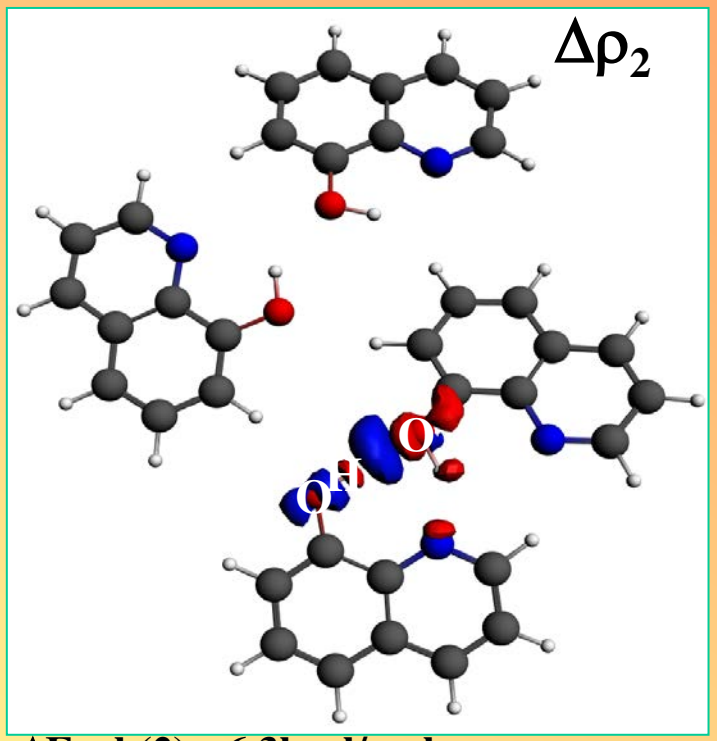


$\Delta\rho=\rho_{molecule}-\rho_1-\rho_2-\rho_3-\rho_4$

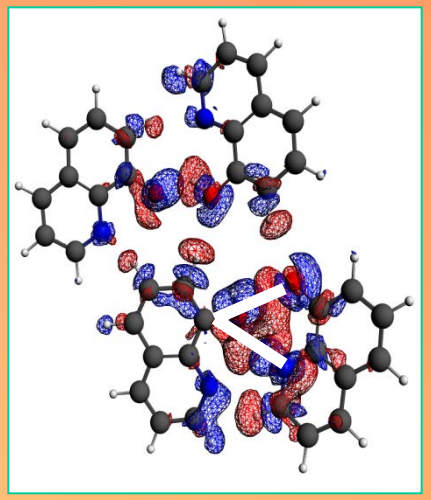
ETS-NOCV- tetra-8-hydroxyquinoline



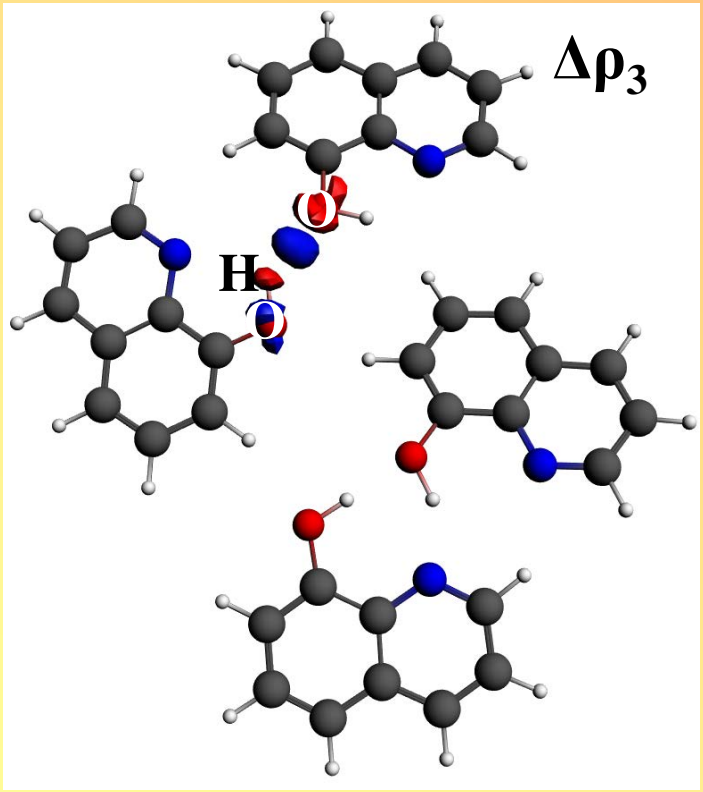
ΔEorb(1)=-12.2 kcal/mol



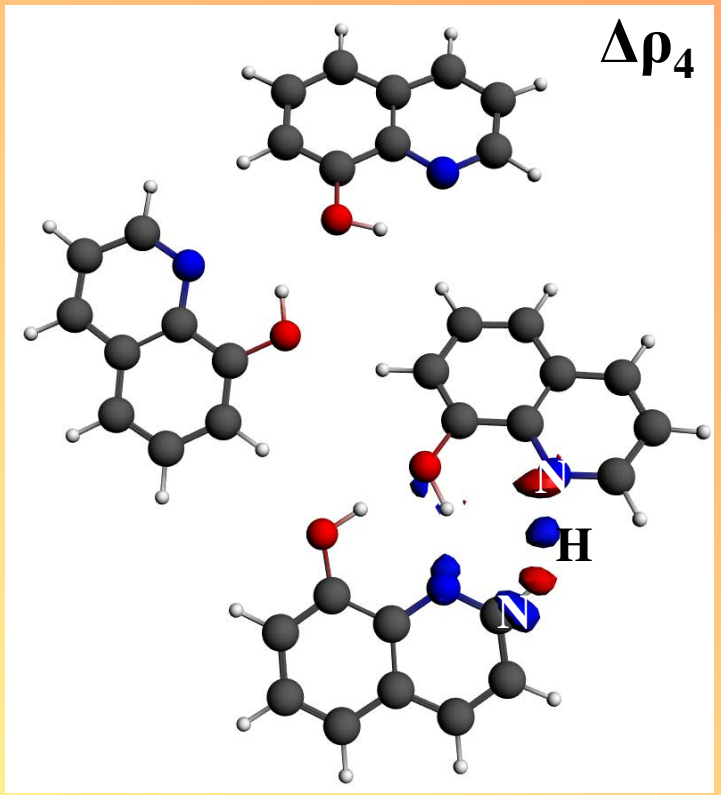
ΔEorb(2)=-6.3kcal/mol



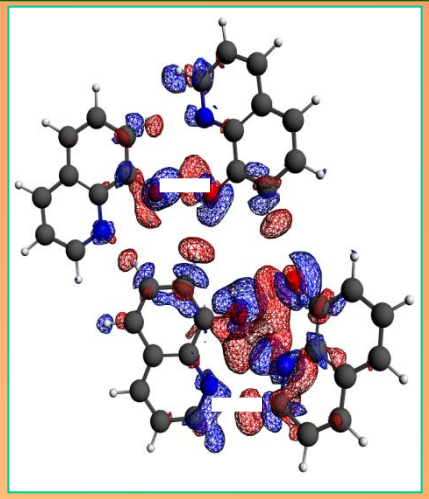
ETS-NOCV- tetra-8-hydroxyquinoline



ΔEorb(3)=-2.0 kcal/mol



ΔEorb(4)=-1.0 kcal/mol



Dative Bond $NH_3 \rightarrow BH_3$ - Calculations

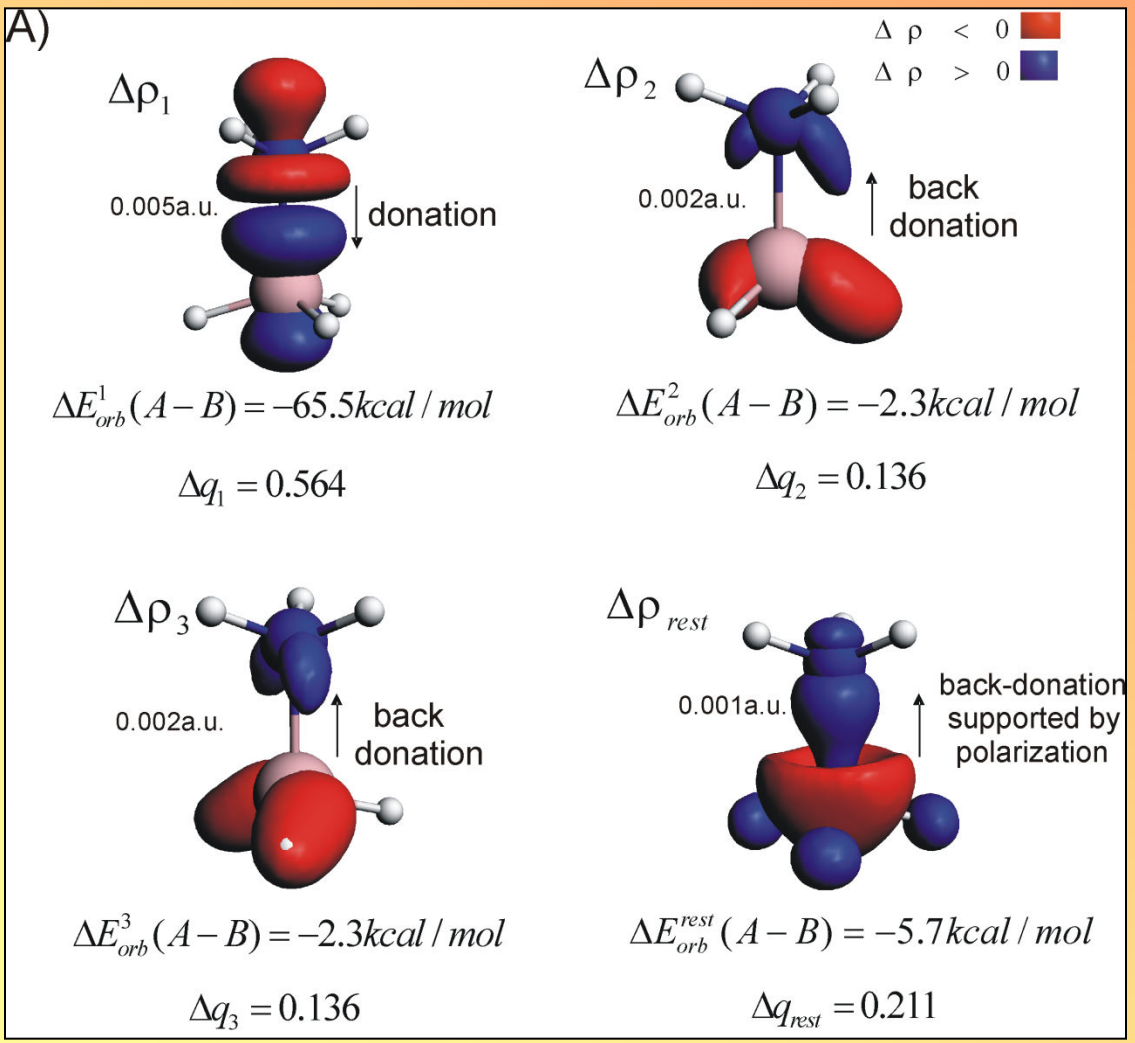
- Define closed shell fragments, NH_3 and BH_3
- Run SP calculations to get the fragment MO's
- Run SP ETS-NOCV calculations for whole molecule in the basis of previously calculated fragment MO's

In order to perform EDA/ETS in NOCV resolution one must add the keywords:

ETSNOCV
PRINT ETSLOWDIN

and **NOSYM** must be used

Dative Bond $NH_3 \rightarrow BH_3$ - Calculations



$\Delta E^{1}_{orb}(A-B) = -65.5 kcal/mol$

$\Delta q_1 = 0.564$

$\Delta E^{2}_{orb}(A-B) = -2.3 kcal/mol$

$\Delta q_2 = 0.136$

$\Delta E^{3}_{orb}(A-B) = -2.3 kcal/mol$

$\Delta q_3 = 0.136$

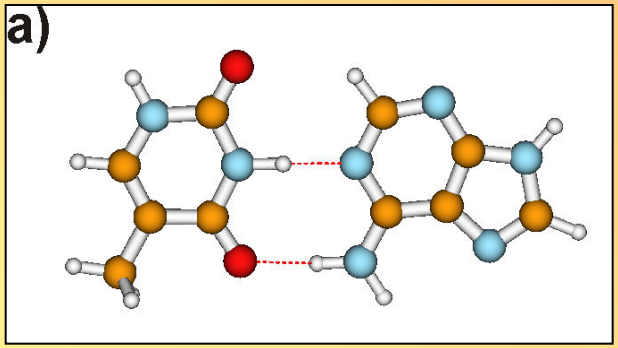
$\Delta E^{rest}_{orb}(A-B) = -5.7 kcal/mol$

$\Delta q_{rest} = 0.211$

M.Mitoraj *J. Phys. Chem. A*, 2011, 115 (51), pp 14708–14716

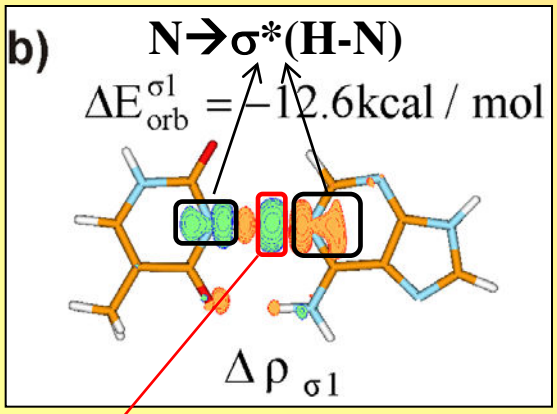
Inter-Molecular-Hydrogen Bonds

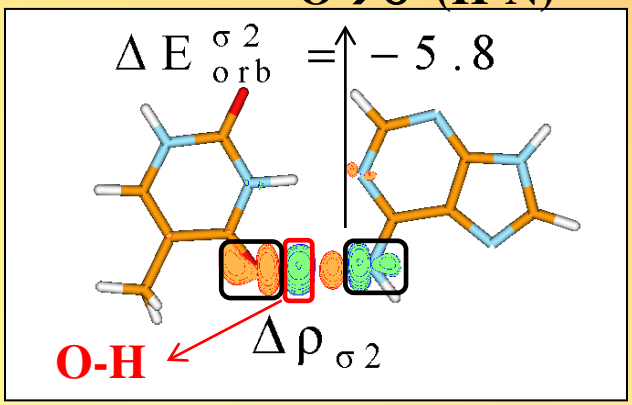
Adenine-Thymine

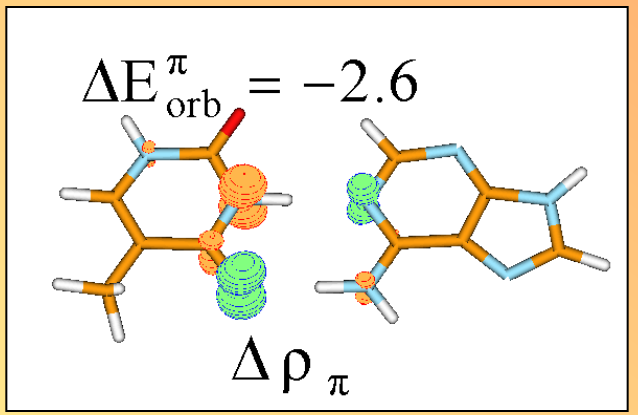


kcal/mol, (BP86/TZ2P)	A-T
ΔE_{int}	-13.0
ΔE_{orb}	**-22.0**
ΔE_{Pauli}	38.7
ΔE_{prep}	2.1
ΔE_{elstat}	-31.9
ΔH_{total}- experiment[99]	-12.1
ΔE_{total} – other theoretical results	-13.2

ΔE_{orb}=-22.0







H-N covalency!

Rafał Kurczab, Mariusz P. Mitoraj, Artur Michalak and Tom Ziegler
J. Phys. Chem. A,2010, 114, 8581.

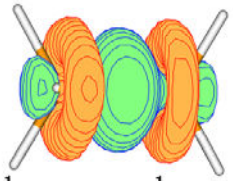
Hydrogen Bond A-T Calculations

- Define closed shell fragments, Adenine and Thymine
- Run SP calculations to get the fragment MO's
- Run SP ETS-NOCV calculations for whole molecule in the basis of previously calculated fragment MO's

Covalent bonds

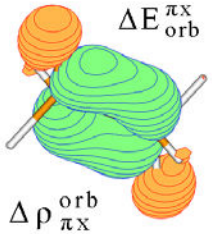
CH_3-CH_3

$\Delta E^{\sigma}_{orb} = -173.4 kcal/mol$



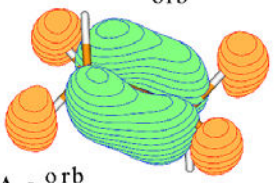
$\Delta\rho^{orb}_{\sigma} = \Delta\rho^{orb}_{\sigma,\alpha} + \Delta\rho^{orb}_{\sigma,\beta}$

$\Delta E^{\pi x}_{orb} = -7.2 kcal/mol$



$\Delta\rho^{orb}_{\pi x}$

$\Delta E^{\pi y}_{orb} = -7.2 kcal/mol$

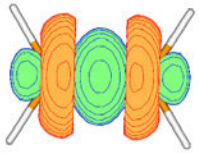


$\Delta\rho^{orb}_{\pi y}$

CH_2=CH_2

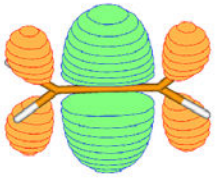
ΔE^{σ}_{orb} -220.6 kcal/mol

$\Delta\rho^{orb}_{\sigma}$



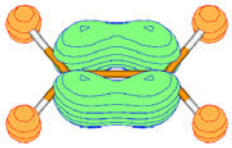
$\Delta E^{\pi 1}_{orb}$ -67.8

$\Delta\rho^{orb}_{\pi 1}$



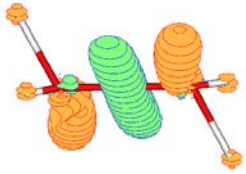
$\Delta E^{\pi 2}_{orb}$ -5.7

$\Delta\rho^{orb}_{\pi 2}$

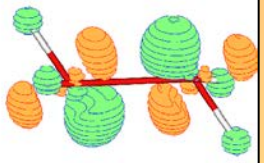


GeH_2=GeH_2

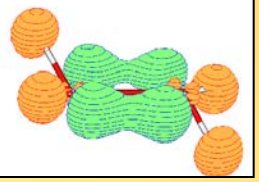
-75.2 kcal/mol



-37.0



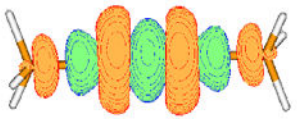
-2.6



$H_3CC{\equiv}CCH_3$

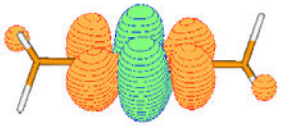
ΔE^{σ}_{orb} -209.7 kcal/mol

$\Delta\rho^{orb}_{\sigma}$



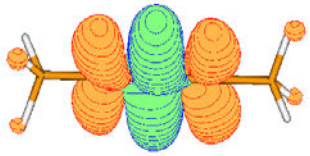
$\Delta E^{\pi 1}_{orb}$ -88.8

$\Delta\rho^{orb}_{\pi 1}$



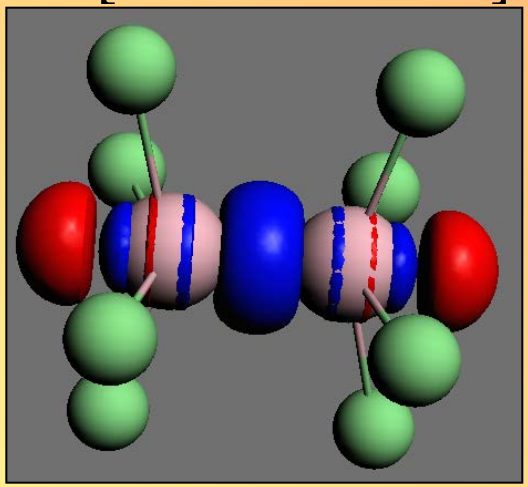
$\Delta E^{\pi 2}_{orb}$ -88.8

$\Delta\rho^{orb}_{\pi 2}$

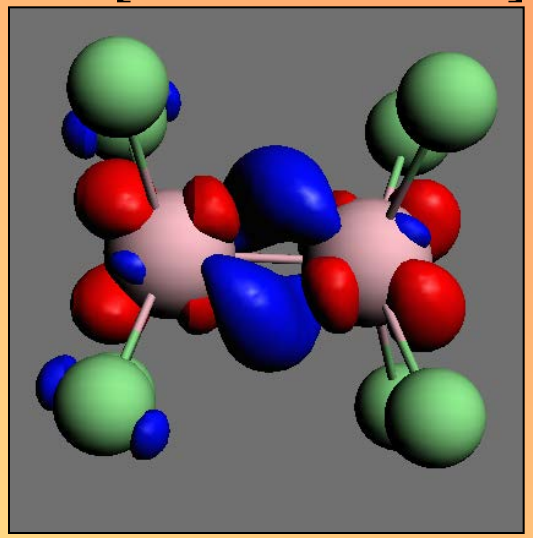


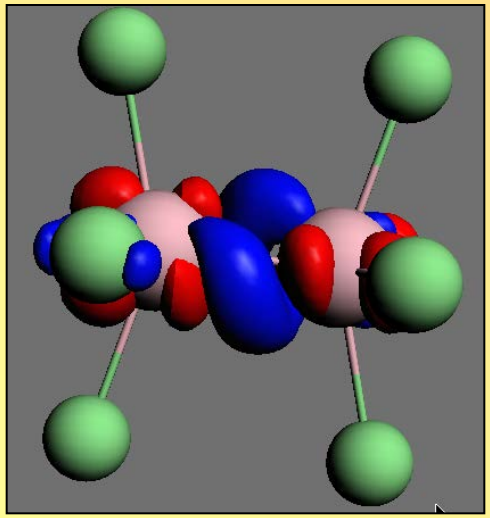
Quadruple bond; $Re_2Cl_8^{2-}$

σ[-84.3 kcal/mol]

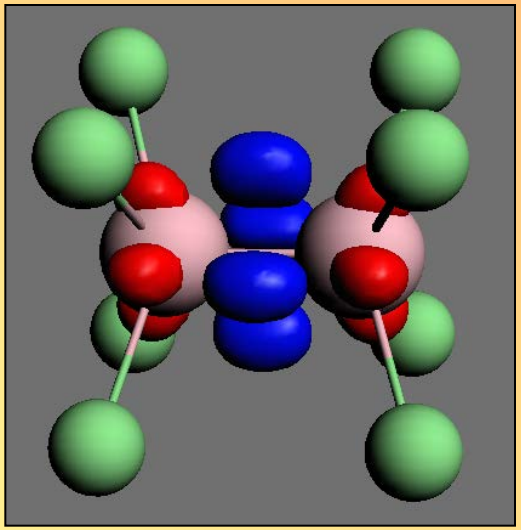


π1[-65.5 kcal/mol]





π2[-65.5 kcal/mol]



δ[-1.3 kcal/mol]

Ethane Built from two methyl radicals

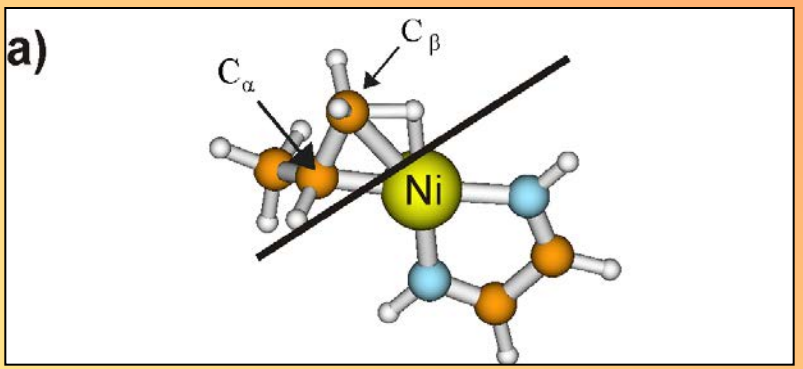
1. Define CH_3 regions (uneven number of electrons);
2. Run SP RESTRICTED ! Calculations for CH_3 fragments
   to get the fragment MO's; ($1/2\alpha + 1/2\beta$ electrons for SOMO of CH_3)
3. Use **fragoccupations** keyword in order to keep the right occupations
   for each CH_3

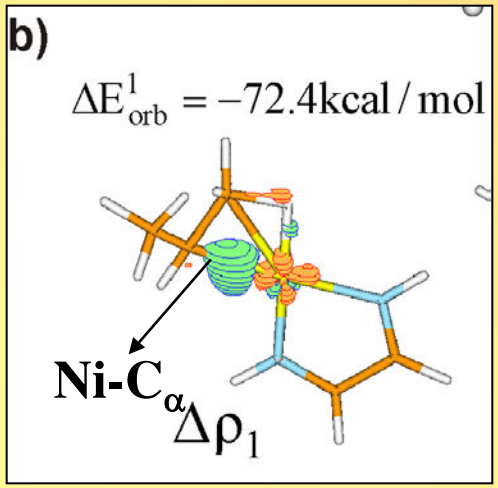
```
fragoccupations
f1 A 5 // 4
subend
f2 A 4 // 5
subend
End
```

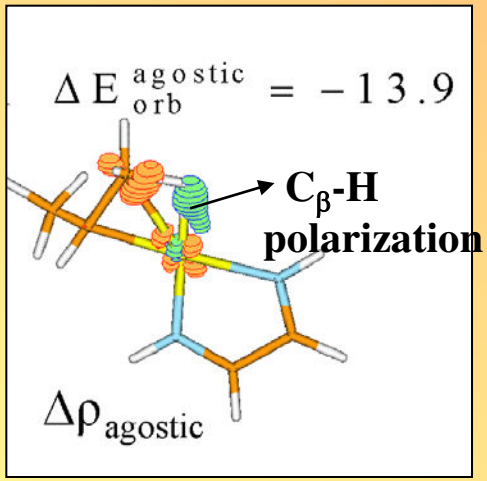
4. Run SP ETS-NOCV calculations for whole molecule in the basis
   of previously calculated fragment MO's **-alpha-and beta-NOCV's**

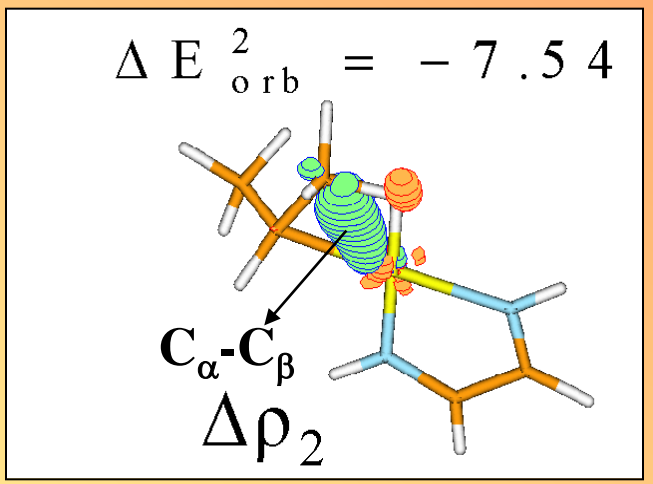
Agostic intramolecular RH---Metal interaction

Ni-diimine cationic Brookhart model catalyst





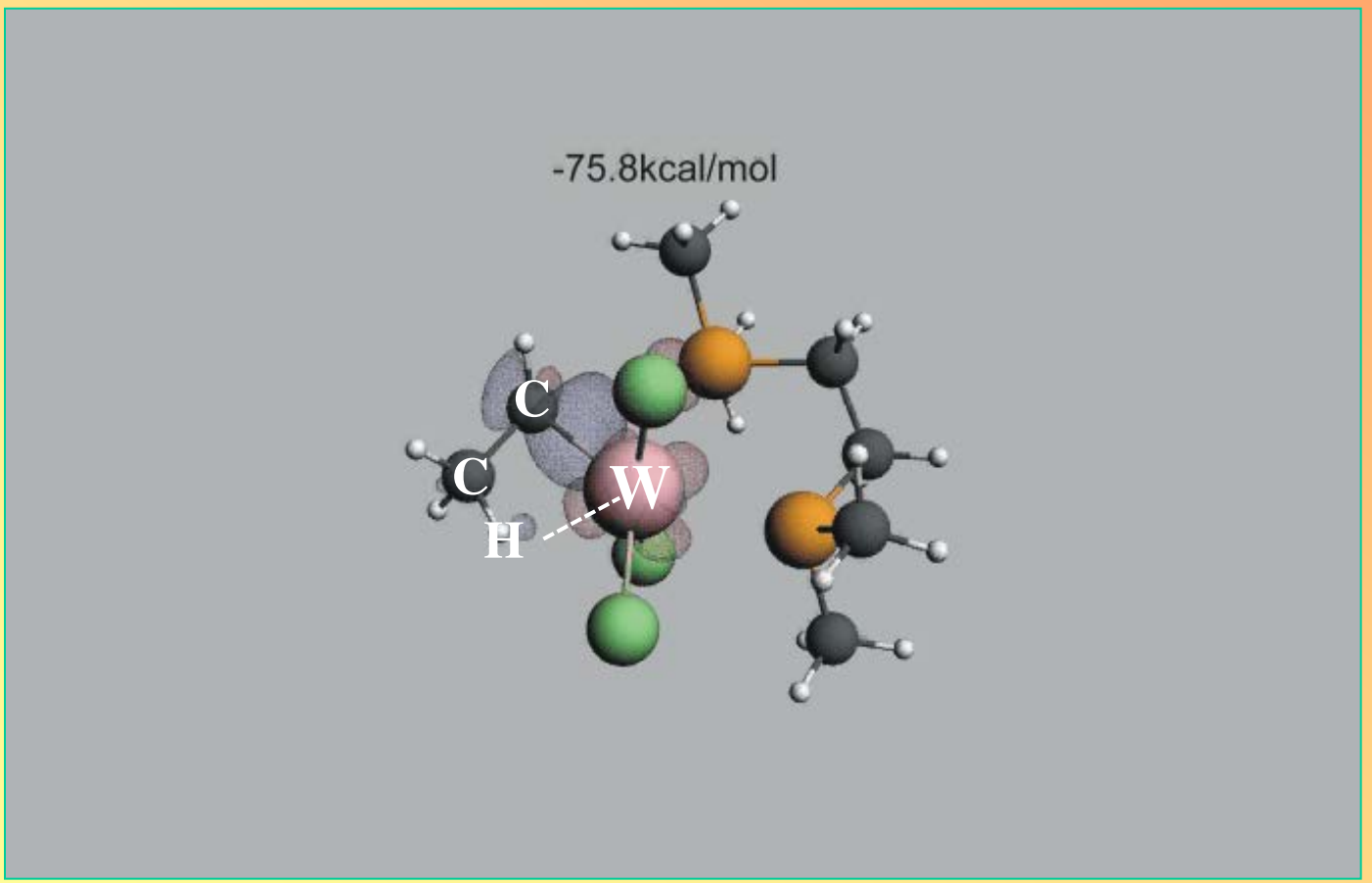




Mariusz P. Mitoraj, Artur Michalak and Tom Ziegler „On the Nature of the Agostic Bond between Metal Centers and β-Hydrogen Atoms in Alkyl Complexes. An Analysis Based on the Extended Transition State Method and the Natural Orbitals for Chemical Valence Scheme (ETS-NOCV)"

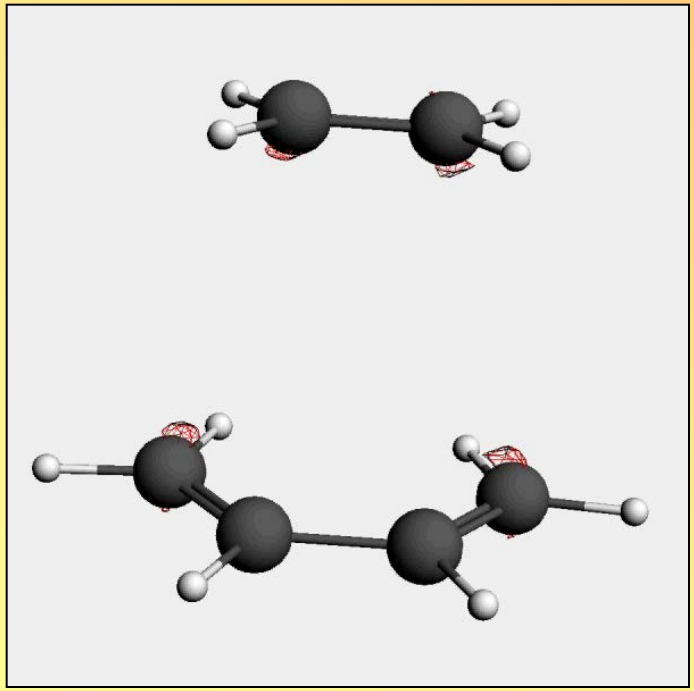
Organometallics, 2009, *28* (13), pp 3727

Role of Agostic Interaction in Hydride Transfer – Release of Ethene Molecule

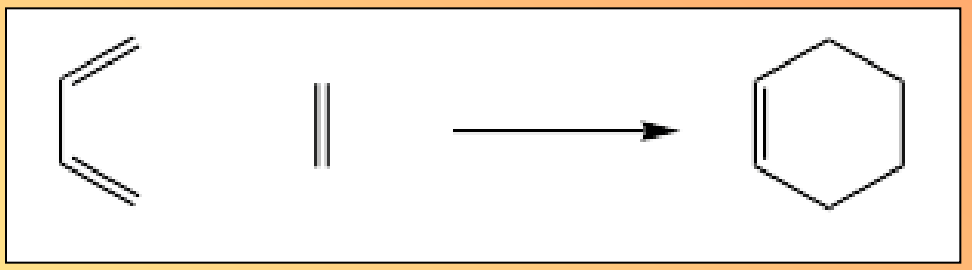


ETS-NOCV in a description chemical reactions

Diels – Alder cycloaddition: ethene + 1,3-butadiene



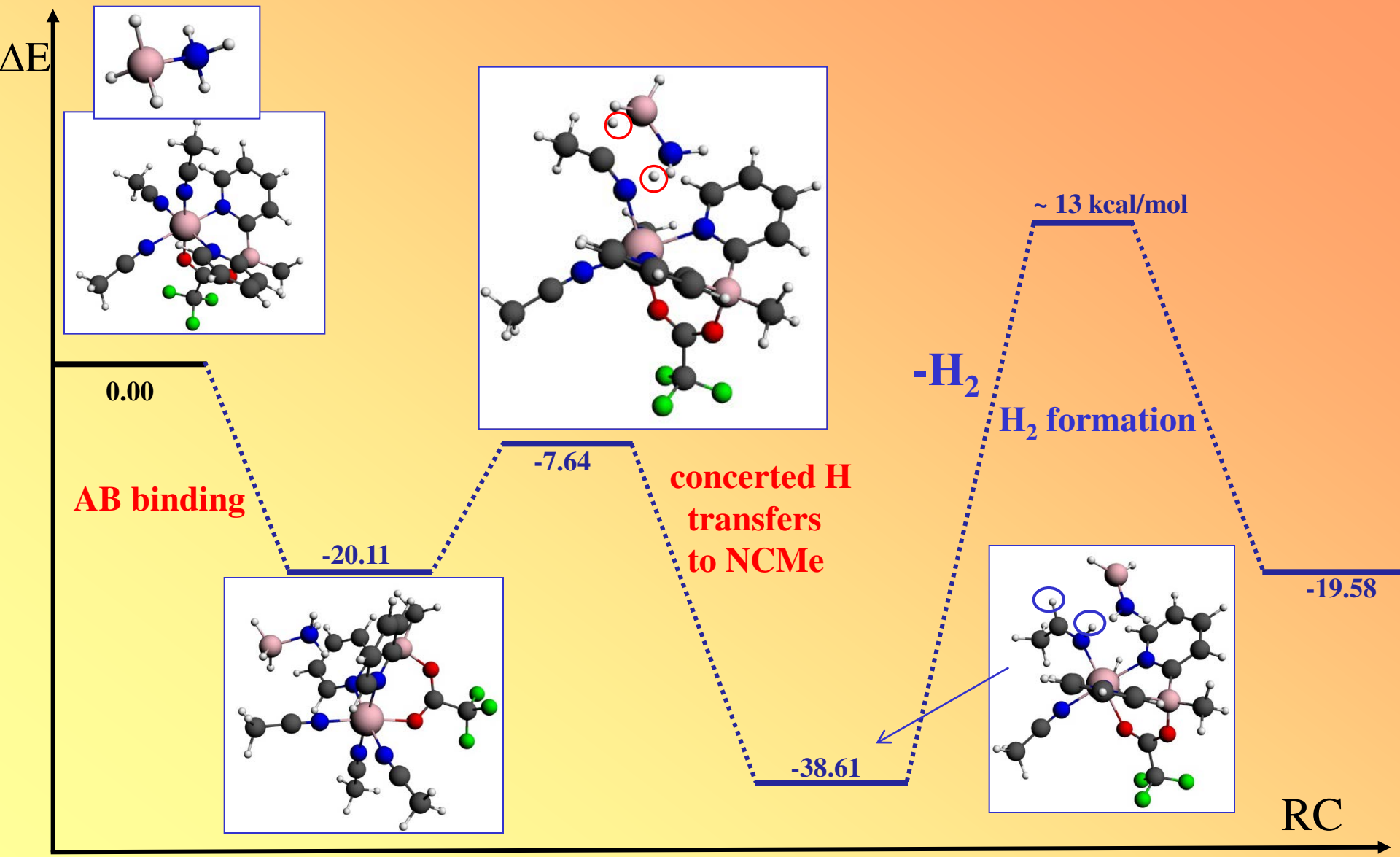
$\Delta\rho_1$ trajectory



Mitoraj MP, Parafiniuk M, Srebro M, Handzlik M, Buczek, A, Michalak A JMolModel, 2011, 17, 2337-2352.

Dehydrogenation of Ammonia Borane by Ru-complex

Mechanism obtained from DFT/CPMD calculations



Organometallics, 2013, 32, 4103-4113

Ammonia Borane binding to the Ru-catalyst

AB binds to NCMe of the catalyst by BH-HC and BH-π interactions

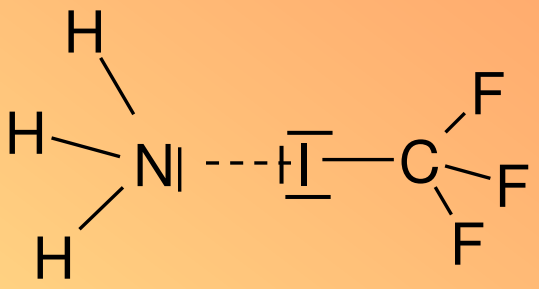
Halogen Bonding CF_3I---NH_3 from ETS-NOCV perspective

ΔE_{total}=-7.4kcal/mol

ΔE_{orb}=-9.2

ΔE_{elstat}=-15.2

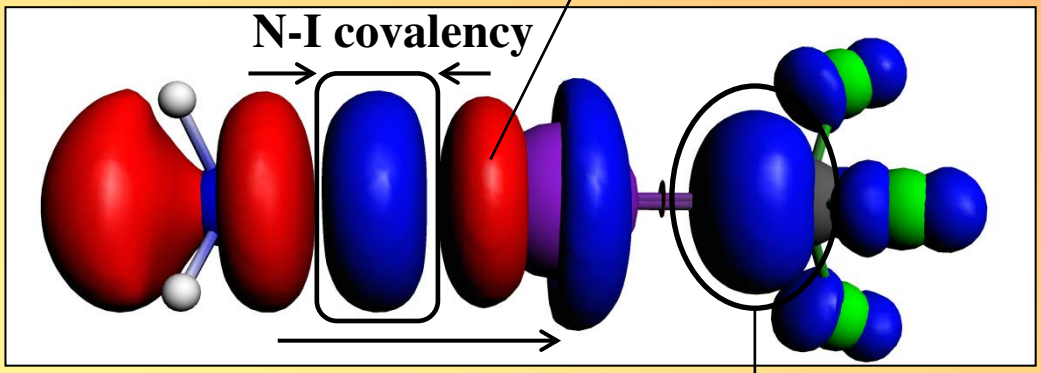
ΔE_{Pauli}=18.3



Charge outflow, increase positive charge

ETSNOCV(red-outflow,blue-inflow)

-8.3 kcal/mol



$N \rightarrow \sigma^*(C\text{-}F)$

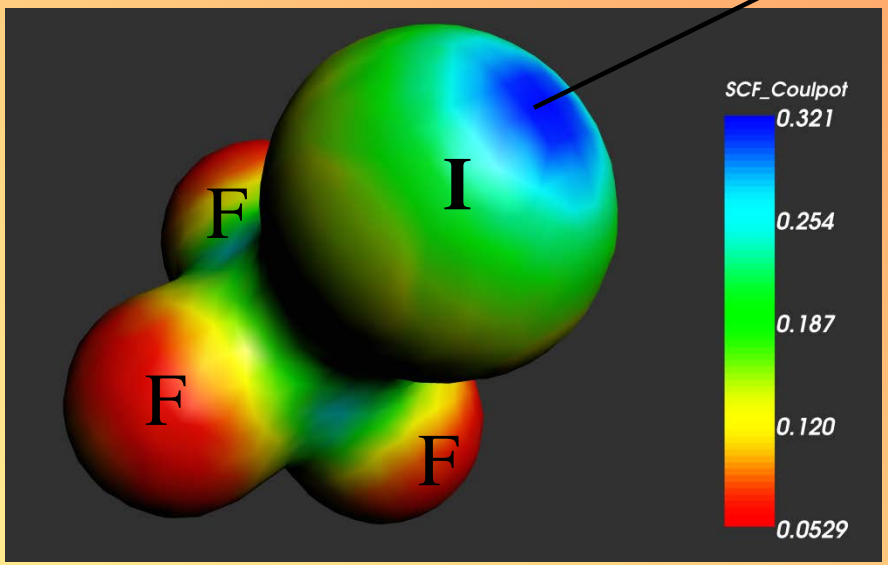
charge accumulation, increase s-character
(pointed out by prof. Grabowski)

Grabowski S. *Chem. Rev.*, 2011, 111 (4), pp 2597–2625

Halogen Bonding CF_3I---NH_3 from ETS-NOCV perspective

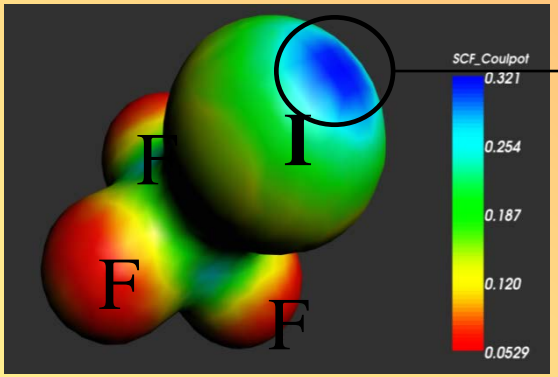
Domination of the electrostatic factor is due to the presense of σ-hole on iodine atom:

ΔE_{total}=-7.4kcal/mol
ΔE_{orb}=-9.2
ΔE_{elstat}=-15.2
ΔE_{Pauli}=18.3

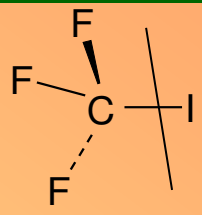


(Politzer P, Lane P, Concha MC, Ma Y, Murray J (2007) JMolModel, 13, 305, „An Overview of Halogen Bonding”

ETS-NOCV perspective, σ-hole

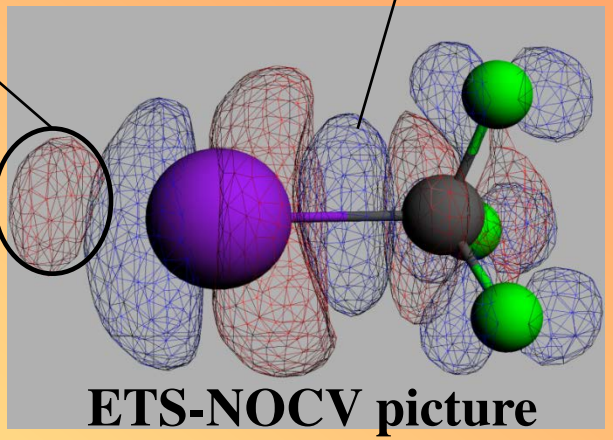


Electrostatic potential picture

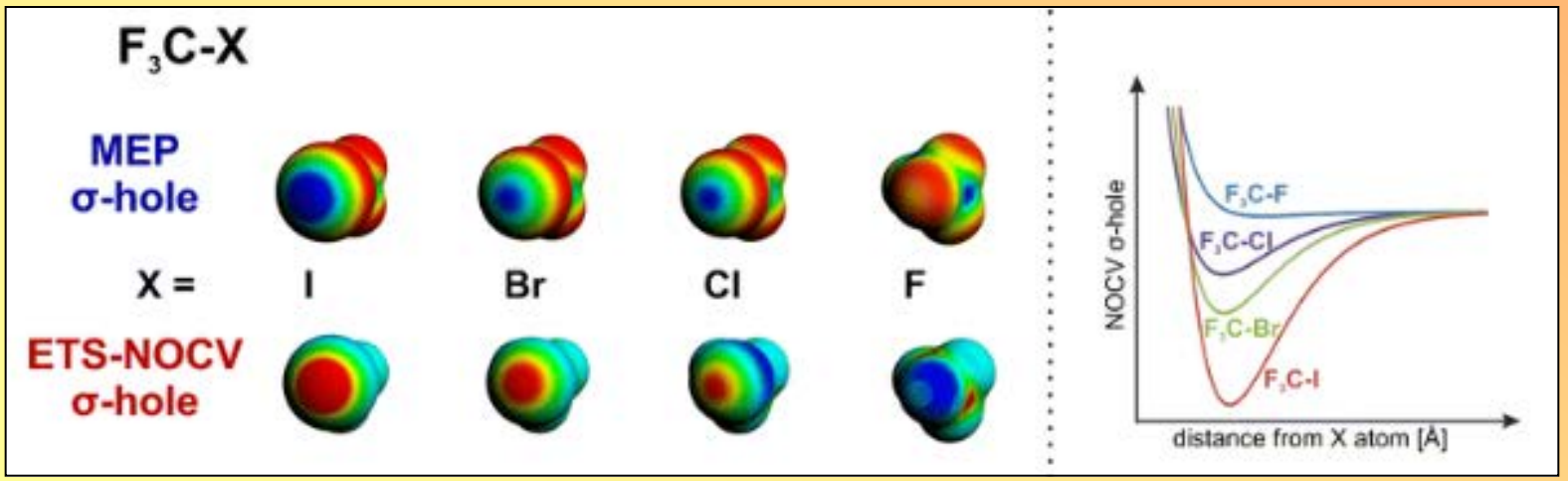


σ-hole

σ(C-F) bond



ETS-NOCV picture



Mitoraj M, Michalak A JMolModel, 2013, DOI 10.1007/s00894-012-1474-4, Dyduch K., Mitoraj M, Michalak A, JMolModel, 2013, 19, 2747.

Hands-on-session agenda

Exercise1. Getting started with the simple bond formed between ammonia and borane – typical *donor–acceptor* bond $H_3N \rightarrow BH_3$.

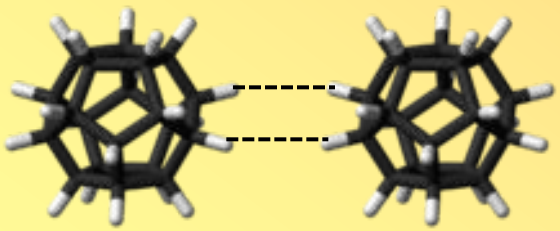
Exercise2. Why ammonia (with one lone electron pair) can form the bond with iodine (containing three lone pairs)? ($H_3N\cdots ICF_3$)

Exercise4. Analysis of carbon–carbon bond in ethane $H_3C\uparrow + \downarrow CH_3$.

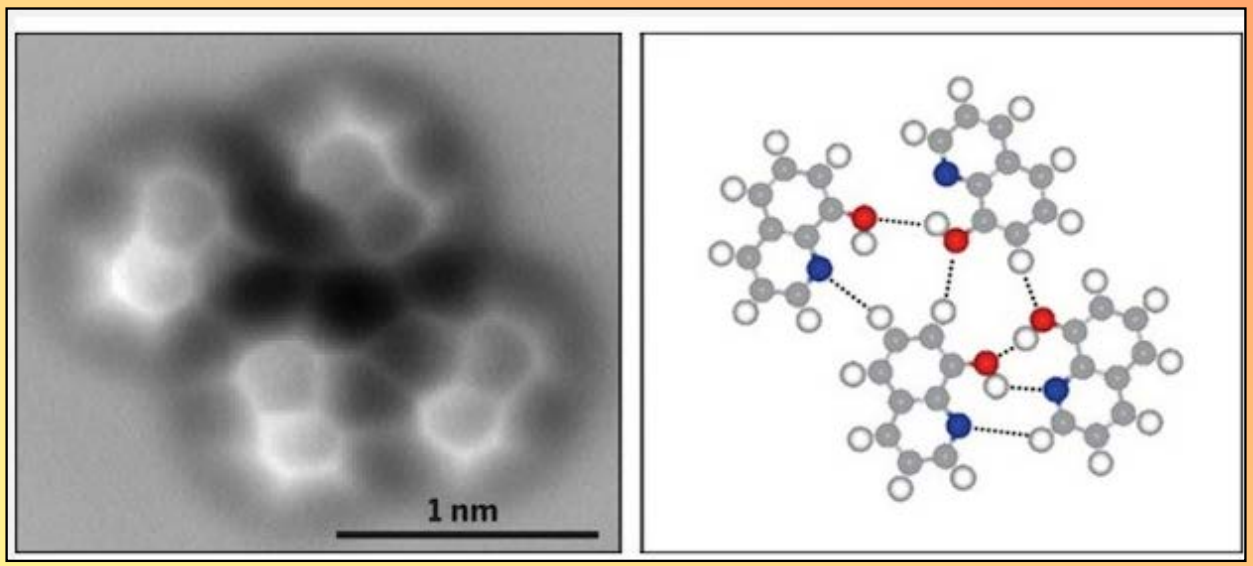
Exercise 5. Analysis of C=C bond in ethene $H_2C\uparrow\uparrow+\downarrow\downarrow CH_2$

Exercise 6. Analysis of quadruple bond between Re atoms in $[Cl_4ReReCl_4]^{2-}$ ($Cl_4Re\uparrow\uparrow\uparrow\uparrow+\downarrow\downarrow\downarrow\downarrow Re\ Cl_4$) (Cotton Re complex).

Exercise7. Analysis of weak homopolar dihydrogen interaction CH···HC formed between closed shell two dodecahedran hydrocarbon units:



Exercise8. Interaction between four monomers of tetra-hydroxoquinoline bonded via O···HO hydrogen bonds. All necessary input files (quin1.in, quin2.in, quin3.in, quin4.in and Quin-tetramer-NOCV.in) are in the directory /home/baw/baw-workshop/mitoraj/Exercise8. Compare the most important NOCV-deformation density channels to the experimental picture of bonding emerging from the tunneling microscope:



(Science, 2013, 342, 611-614)

TZ2p+/BP86/kcal/mol	ΔE_{int}	ΔE_{orb}	ΔE_{elstat}	ΔE_{Pauli}	$\Delta E_{dispersion}$
$H_3N \rightarrow BH_3$					
$H_3N \cdots ICF_3$					
$F_3C\uparrow + \downarrow I$					
$H_3C\uparrow + \downarrow CH_3$					
$H_2C\uparrow\uparrow + \downarrow\downarrow CH_2$					
$LRe\uparrow\uparrow\uparrow\uparrow + \downarrow\downarrow\downarrow\downarrow ReL$					
dimer-dodekahedran					

Thank You very much for Your Attention!