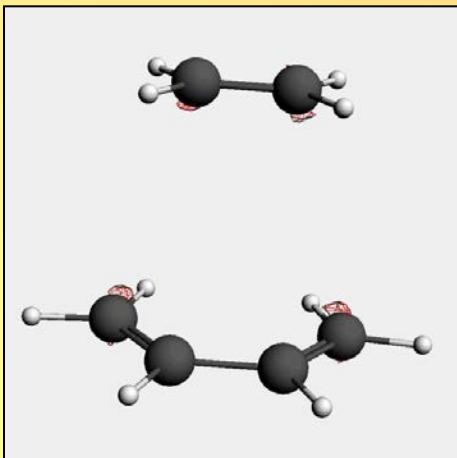
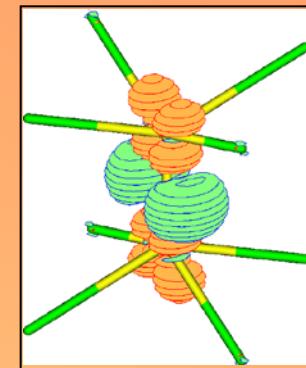
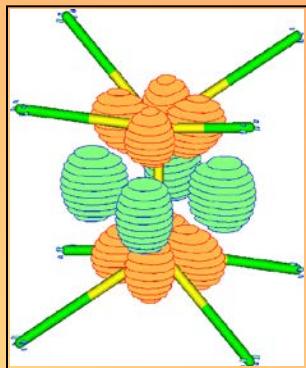
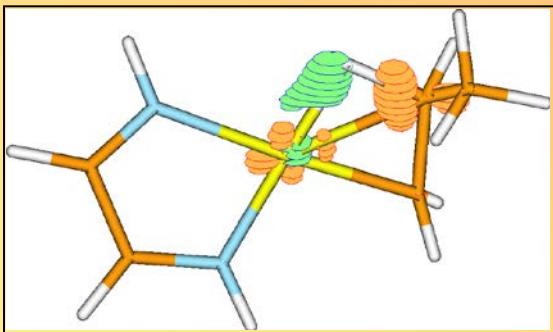
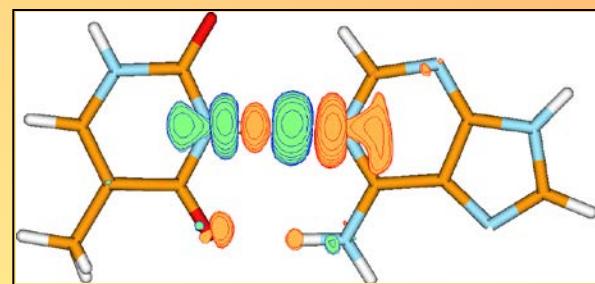
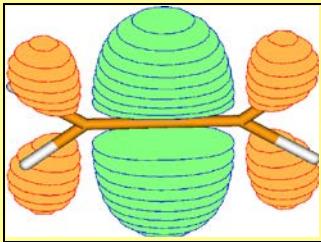
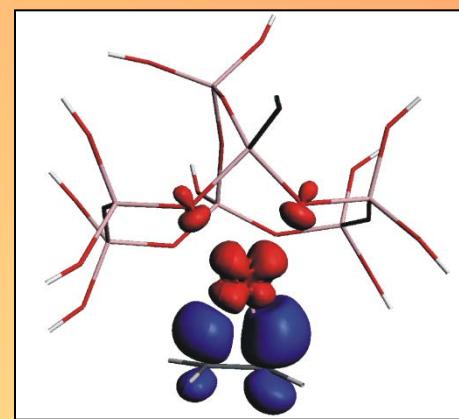


A Chemical Bond From the Natural Orbitals for Chemical Valence (NOCV) Perspective



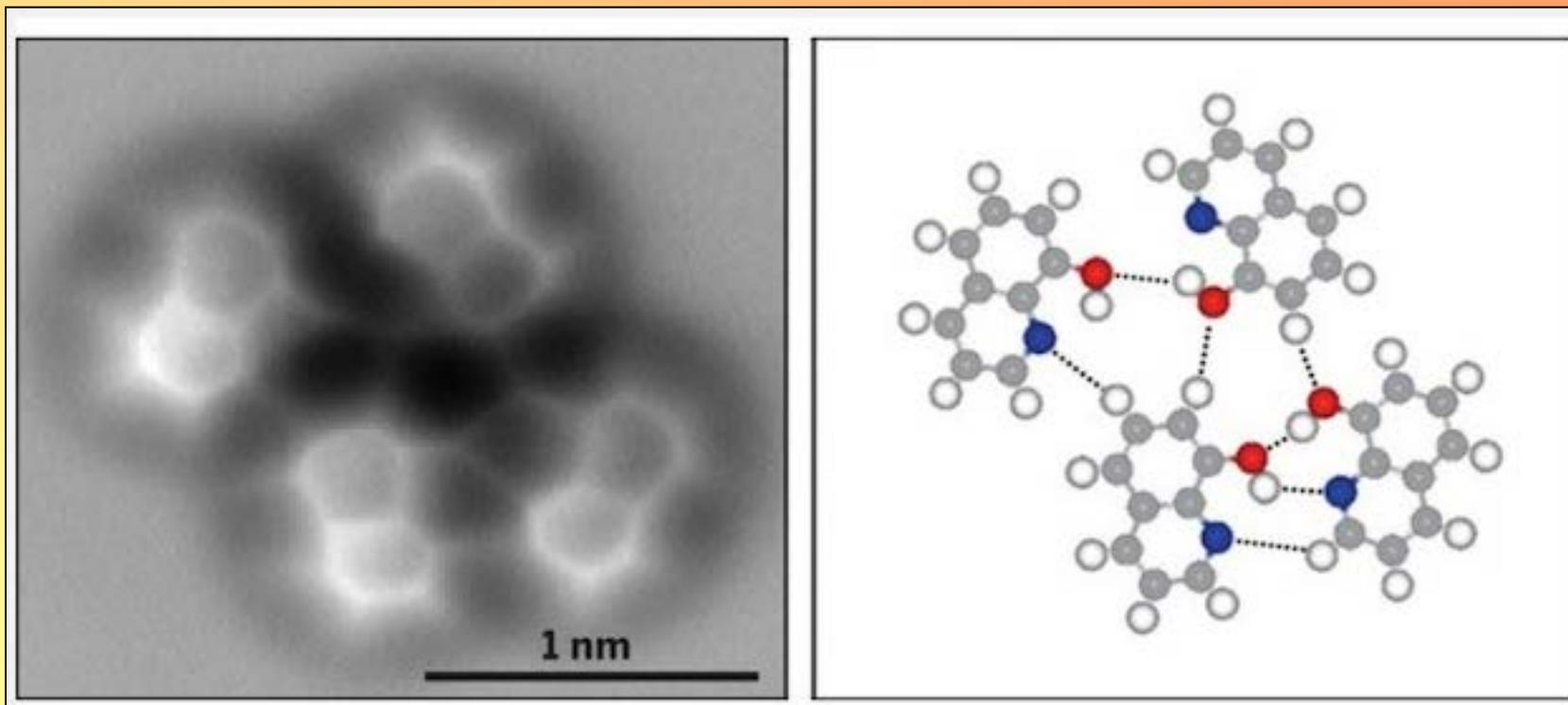
Mariusz P. Mitoraj

Jagiellonian University
Cracow, Poland
Department of Theoretical Chemistry



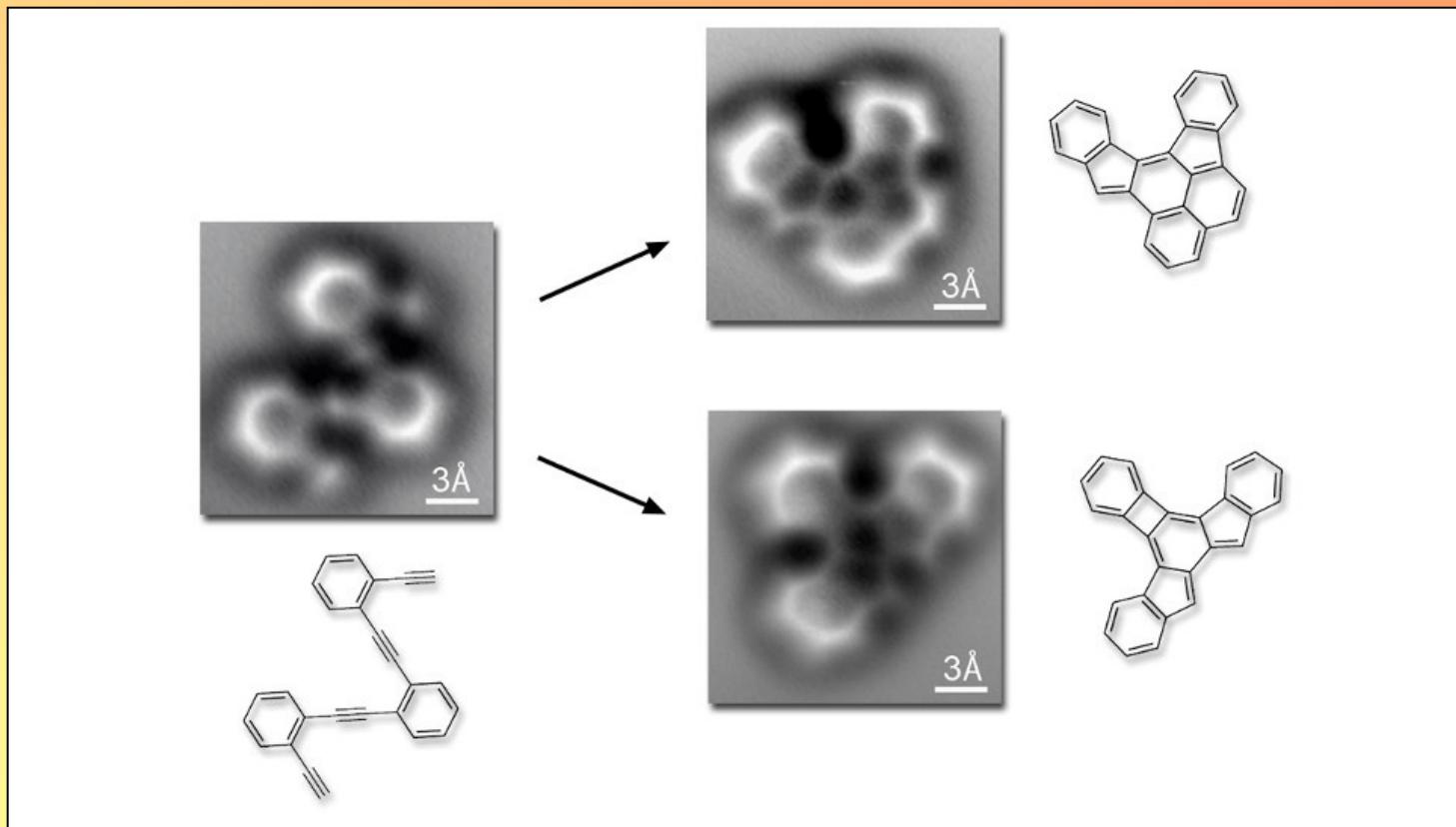
Experimental visualization chemical bond ?

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

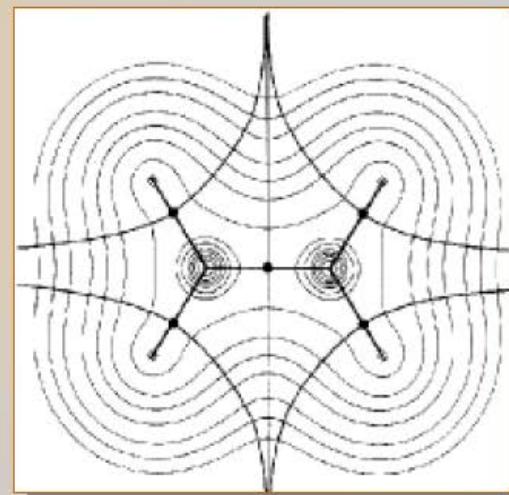
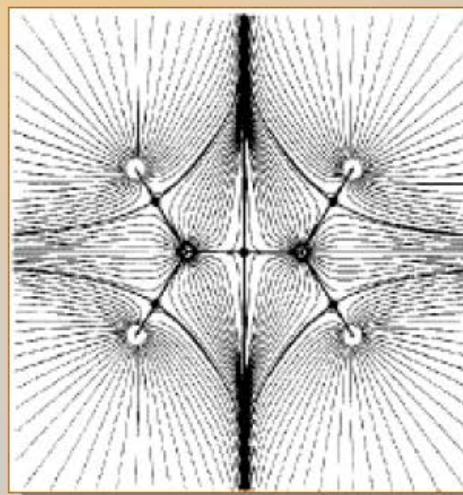
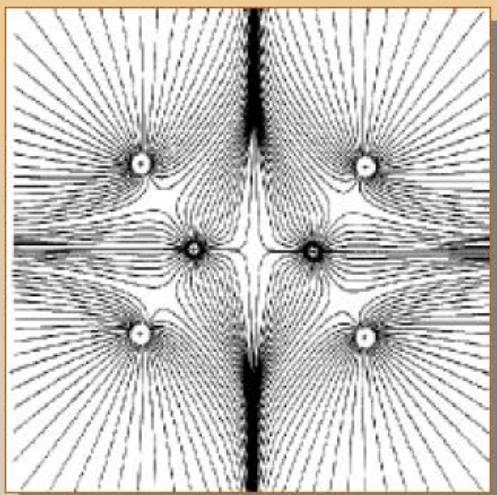
Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions

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

Bader theory of Atoms-in-Molecules

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

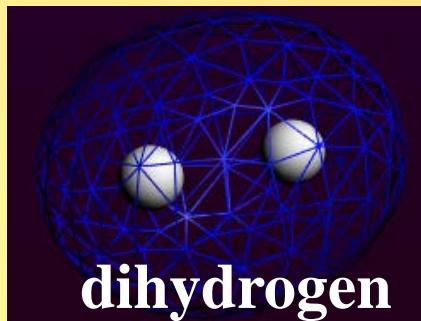


Quantum Theory of Atoms in Molecules (QTAIM) by Richard Bader

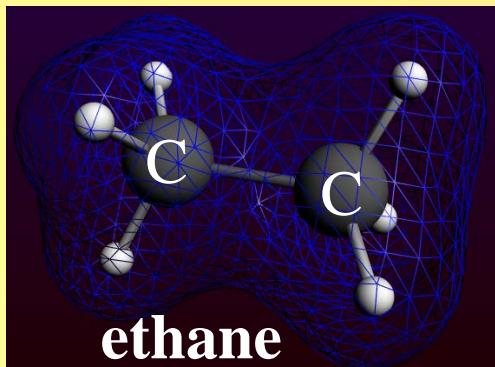
*start- electron (charge) density from wavefunction (ψ)
(N electrons, with positions x_1, x_2, \dots, x_N):

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

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



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 $\rho(\mathbf{r})$: maximum, minimum or saddle where the gradient of $\rho(\mathbf{r})$ vanish ($\nabla \rho(\mathbf{r}_c) = 0$), 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:

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

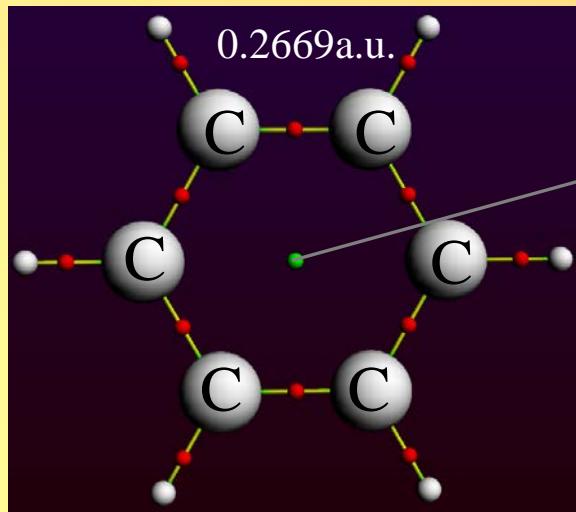
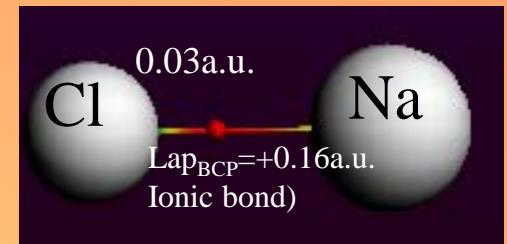
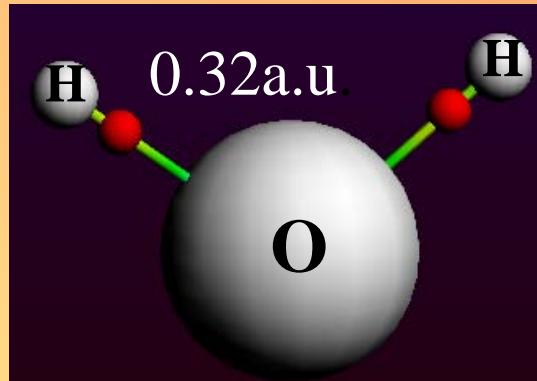
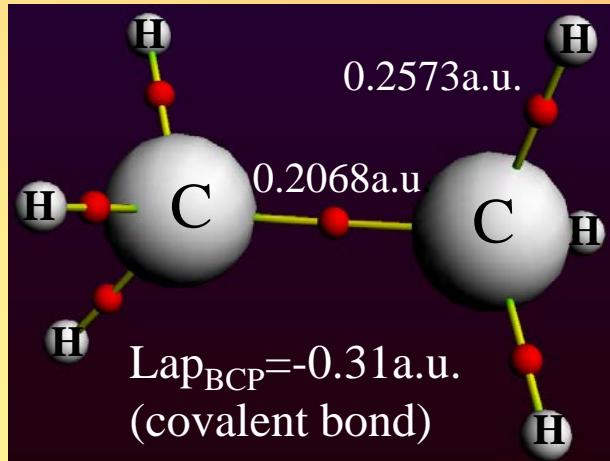
The Hessian matrix is real and symmetric

=> we can put it in a diagonal form:

eigenvalues = curvatures of ρ

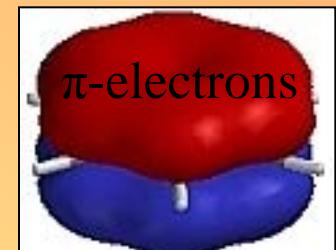
$$A = \begin{pmatrix} \frac{\partial^2 \rho}{\partial x'^2} & 0 & 0 \\ 0 & \frac{\partial^2 \rho}{\partial y'^2} & 0 \\ 0 & 0 & \frac{\partial^2 \rho}{\partial z'^2} \end{pmatrix}_{r'=r_c} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}$$

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

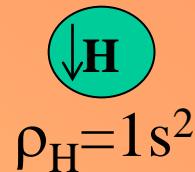
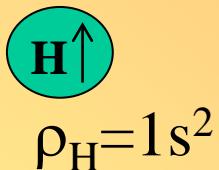
Differential density (deformation density)

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

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.

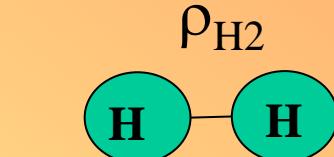
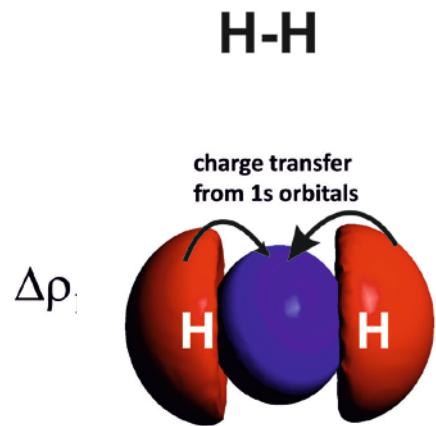
Formation of chemical bond in H_2 – $\Delta\rho$ based picture

1. Start from promolecular state (atom/fragments)



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

$\Delta\rho < 0$ charge depletion
 $\Delta\rho > 0$ charge accumulation

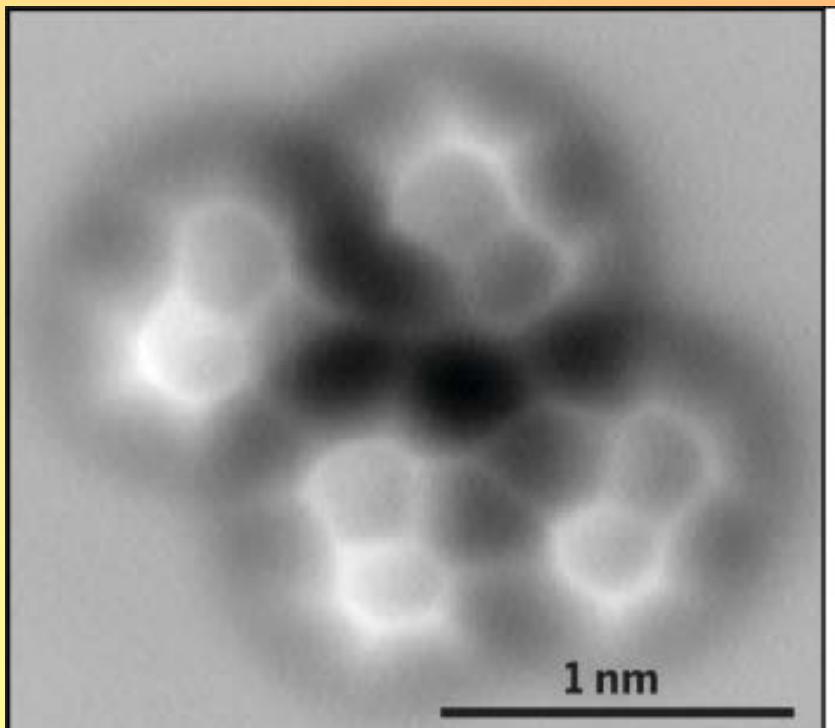


Deformation density (Differential density)

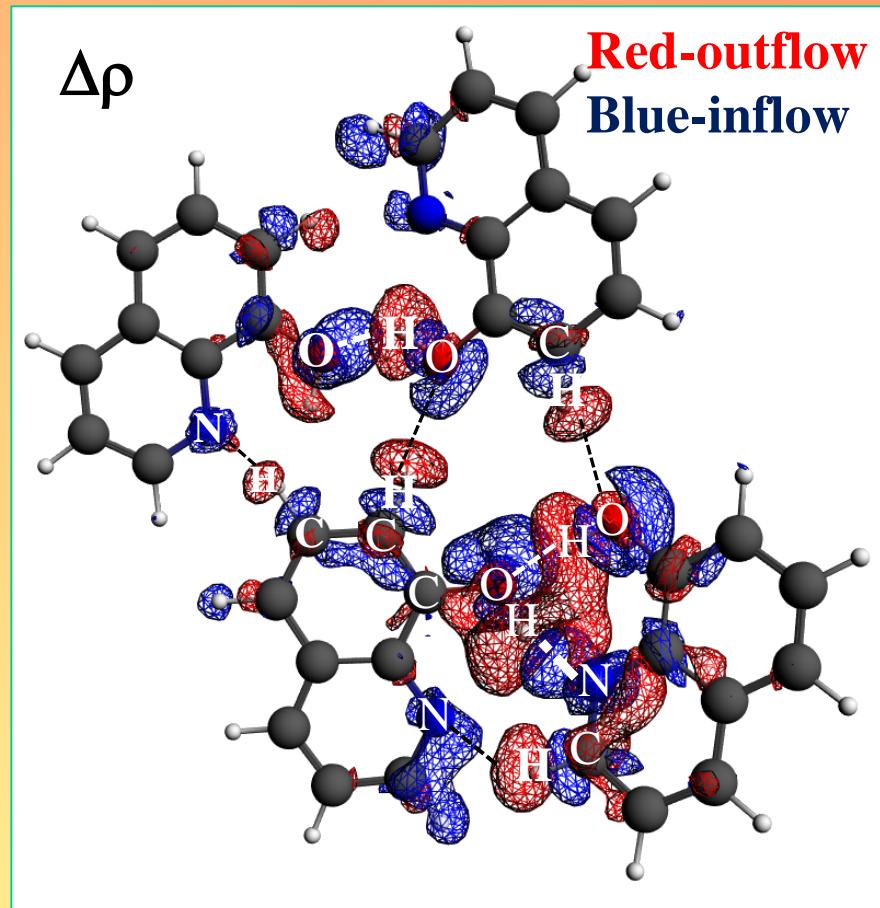
(1) qualitative data
by inspection of the sign
of $\Delta\rho$: negative (outflow),
positive (inflow) of density
due to bond formation

Experimental visualization of chemical bond vs calculated $\Delta\rho$

Tetramer of 8-hydroxyquinoline connected via hydrogen bonds



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

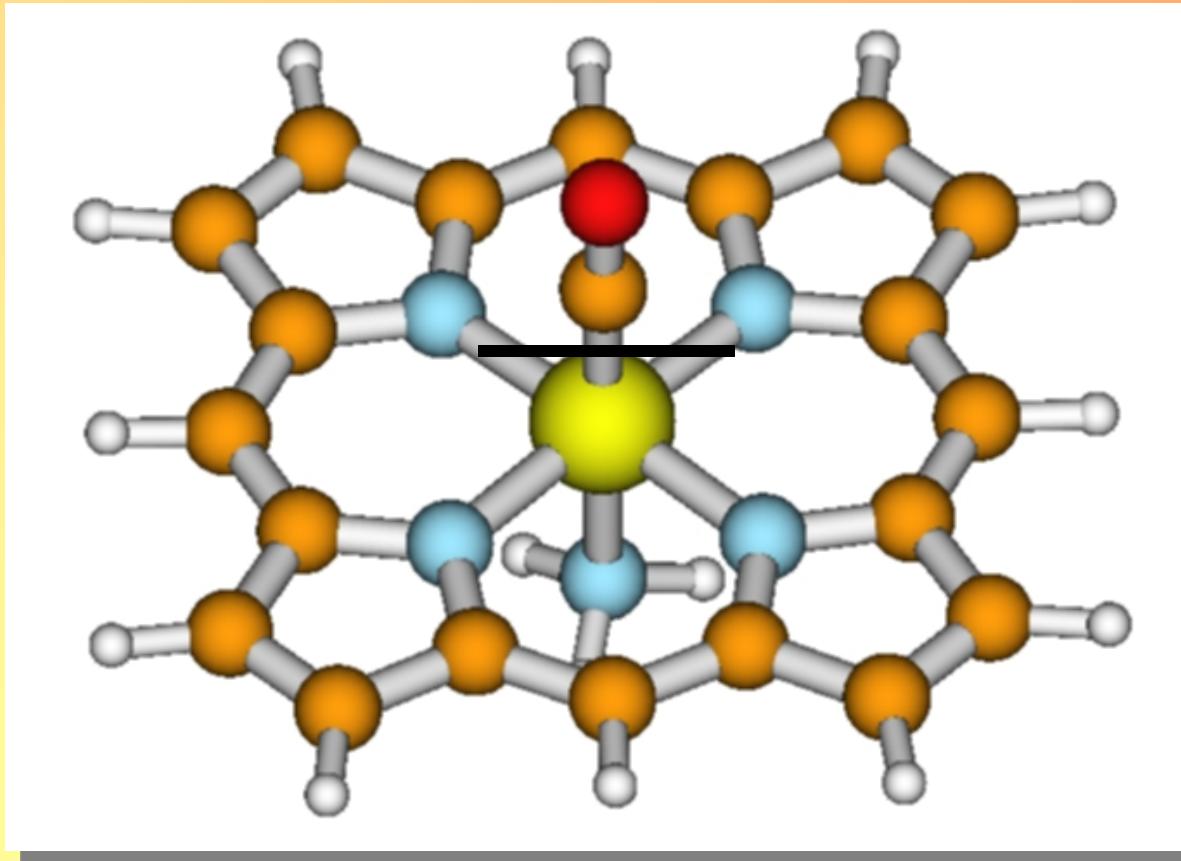


$$\Delta\rho = \rho_{\text{molecule}} - \rho_1 - \rho_2 - \rho_3 - \rho_4$$

Formation of chemical bond in hem-CO; $\Delta\rho$ based picture

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

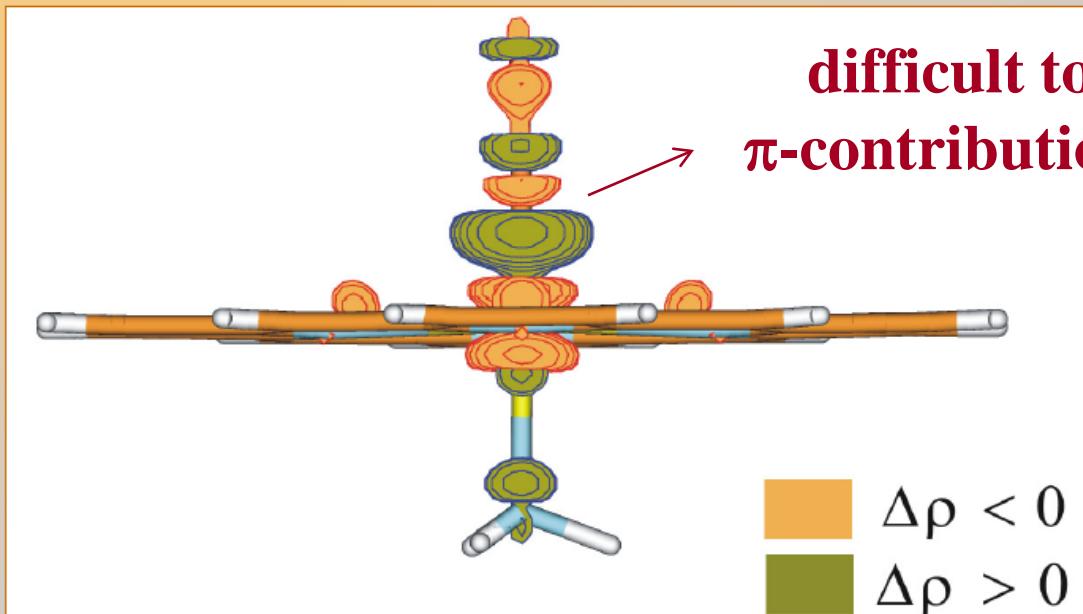
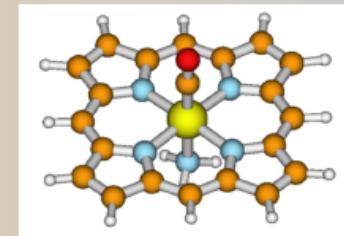
$$\Delta\rho = \Delta\rho_{AB}(r) - \rho_A(r) - \rho_B(r)$$



Formation of chemical bond in hem-CO; $\Delta\rho$ based picture

Heme - CO

Deformation density description



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 $\Delta\rho$:

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

useful qualitative data
by inspection of the sign
of $\Delta\rho$: negative (outflow),
positive (inflow) of density

NOCV's are in pairs:

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

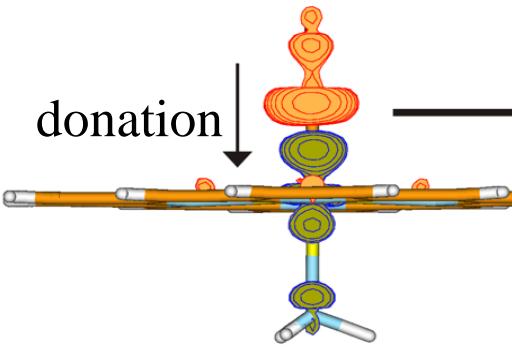
Radoń, M. Theor Chem Account 2008, 120,337.

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 ($\Delta\rho$) and the contributions from the pairs of complementary orbitals for the heme/CO system

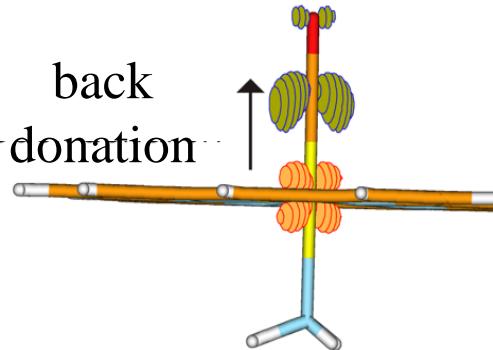
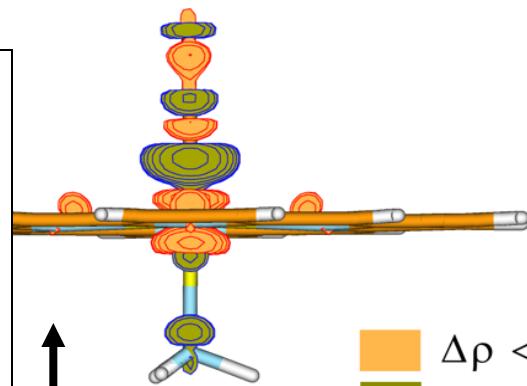
$$\Delta\rho(r) = \sum_{i=1}^n v_i \varphi_i^2(r)$$

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



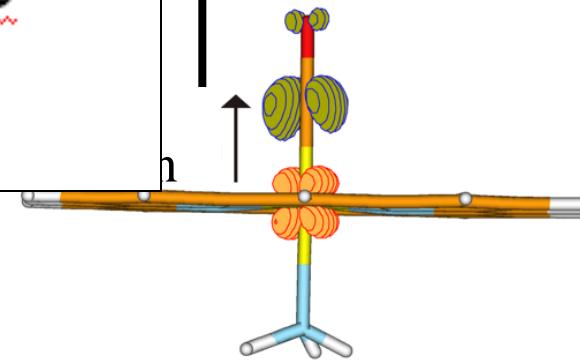
$$\Delta\rho = \Delta\rho_1 + \Delta\rho_2 + \Delta\rho_3$$

NOCV's



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

No energetic estimation !



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

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

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

$$\Delta E_{\text{orb}} = \sum_{\lambda} \sum_{\mu} \Delta P_{\lambda\mu}^{\text{orb}} F_{\lambda\mu}^{\text{TS}}$$

↓
electronic
factor

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

ETS-NOCV:

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



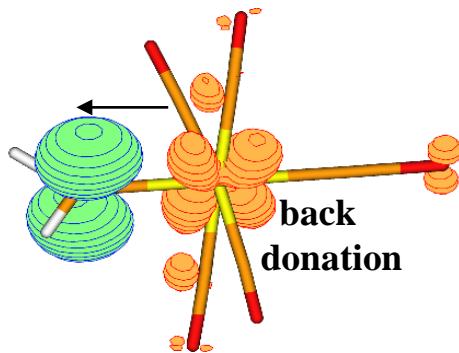
$$\Delta E_{\text{orb}} = \sum_{k=1}^{M/2} v_k [-F_{-k}^{\text{TS}} + F_{-k}^{\text{TS}}] = \sum_{k=1}^{M/2} \Delta E_k^{\text{orb}}$$

Energetic estimation
of $\Delta \rho_k$

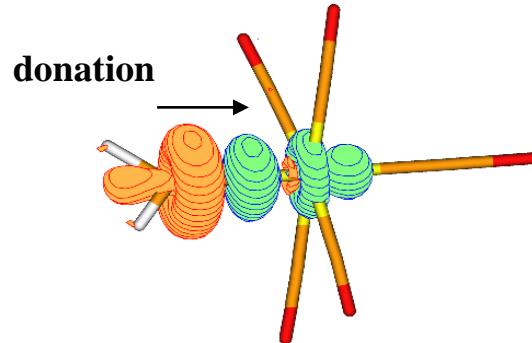
Dative bonds – systems with symmetry



$$\Delta E_{\text{orb}}^{\pi} = -46.3$$



$$\Delta E_{\text{orb}}^{\sigma} = -51.9$$

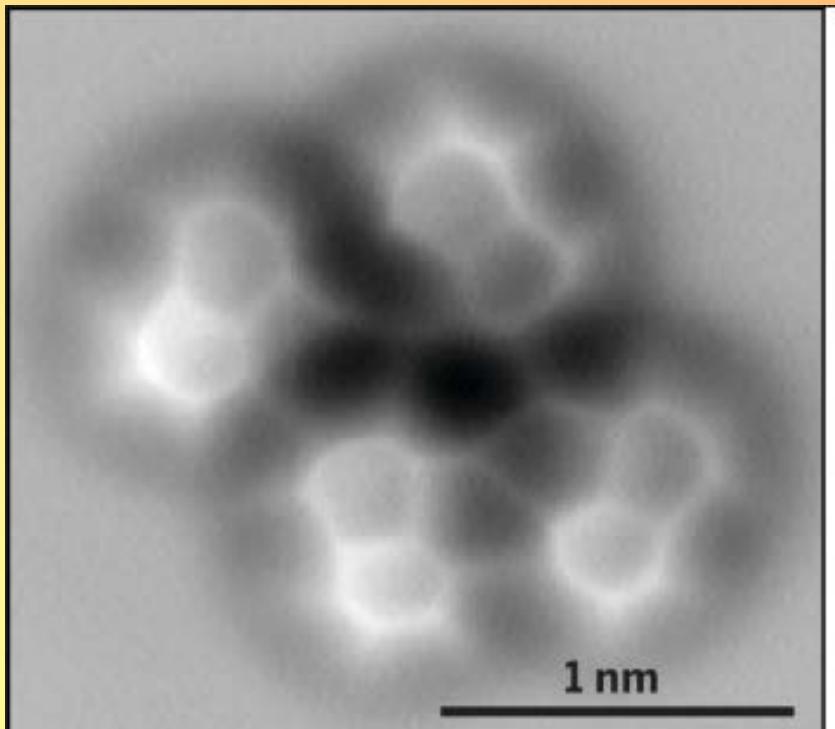


Donor/acceptor properties of ligands for $\text{Ni}(\text{NH}_3)_3 \text{X}$ complexes:

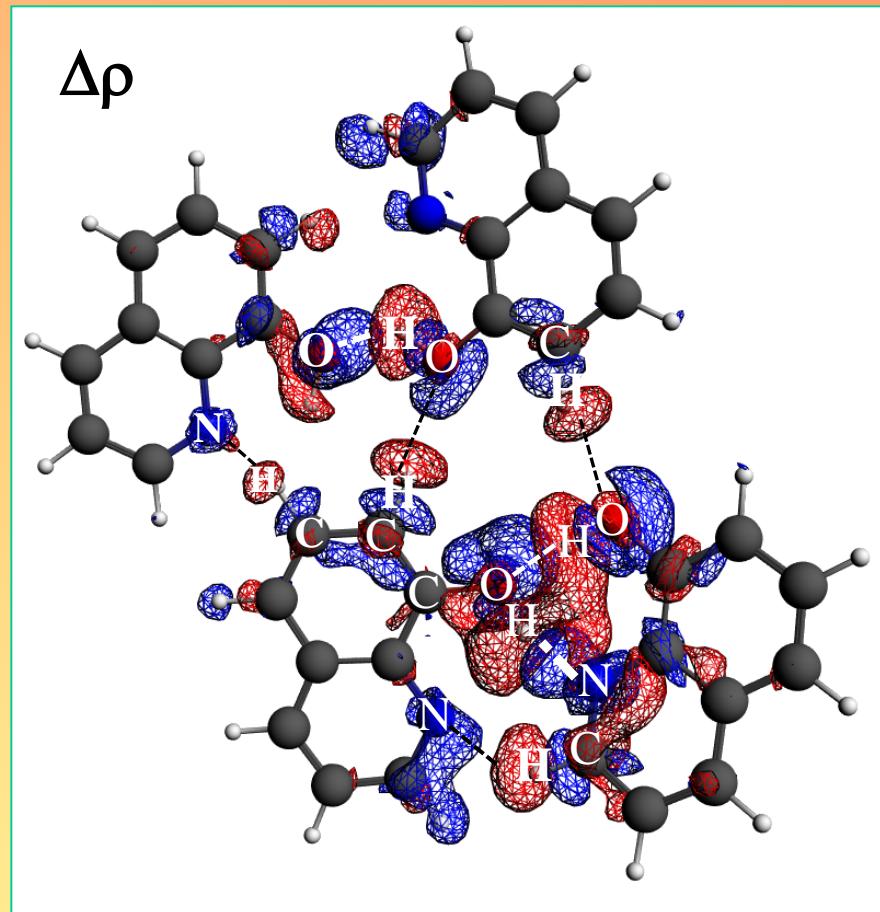
σ : $\text{CN}^- > \text{PH}_3 > \text{NH}_3 > \text{C}_2\text{H}_4 > \text{CS} > \text{CO} > \text{N}_2 > \text{NO}^+$
 π : $\text{NO}^+ > \text{CS} > \text{CO} > \text{N}_2 > \text{C}_2\text{H}_4 > \text{PH}_3 > \text{CN}^- > \text{NH}_3$

Experimental visualization of chemical bond vs calculated $\Delta\rho$

Tetramer of 8-hydroxyquinoline connected via hydrogen bonds

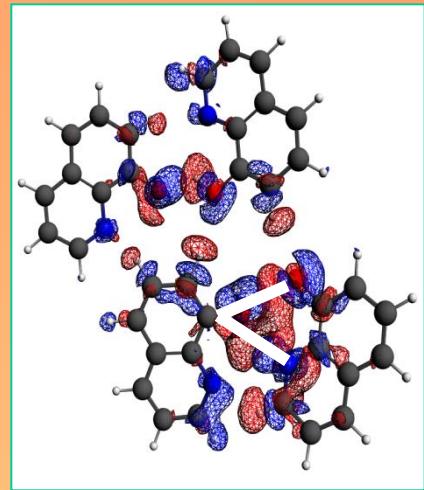
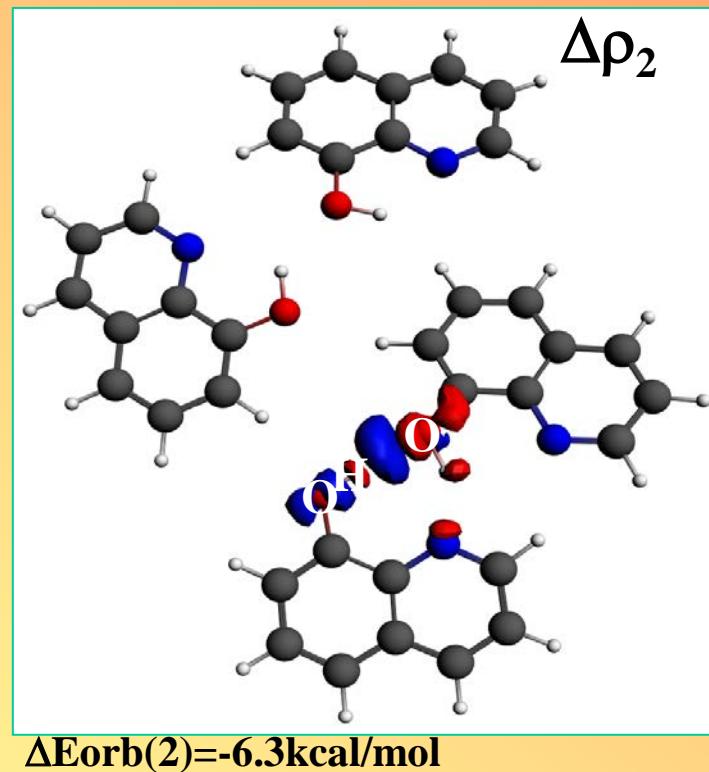
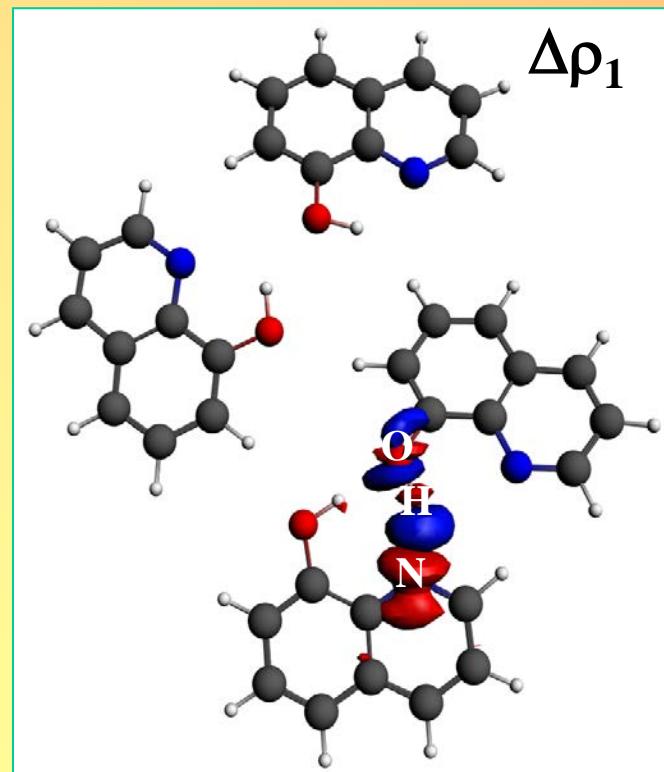


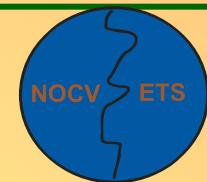
Real-Space Identification of Intermolecular Bonding
with Atomic Force Microscopy"
J. Zhang et al., Science, 2013, 342, 611-614 .



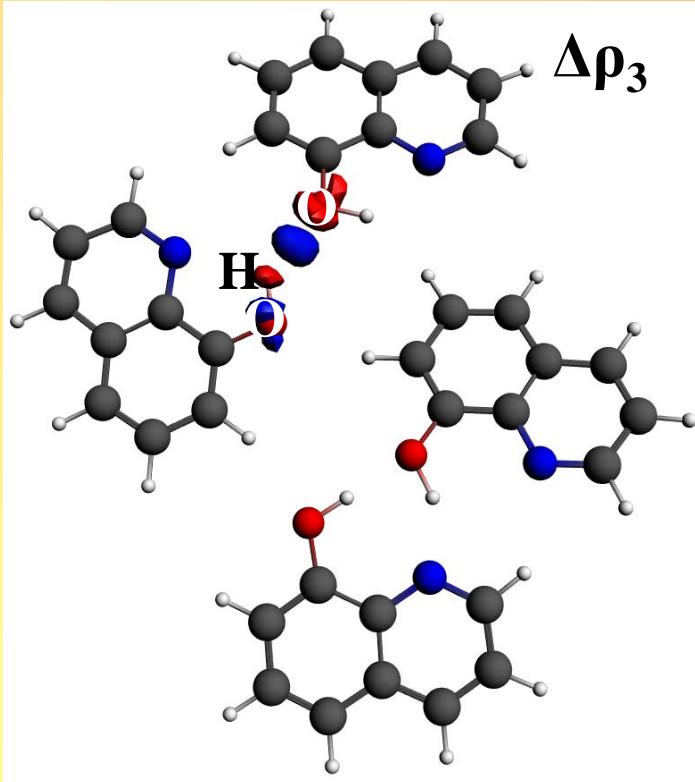
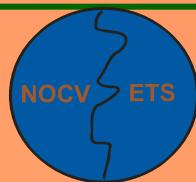
$$\Delta\rho = \rho_{\text{molecule}} - \rho_1 - \rho_2 - \rho_3 - \rho_4$$

ETS-NOCV- tetra-8-hydroxyquinoline

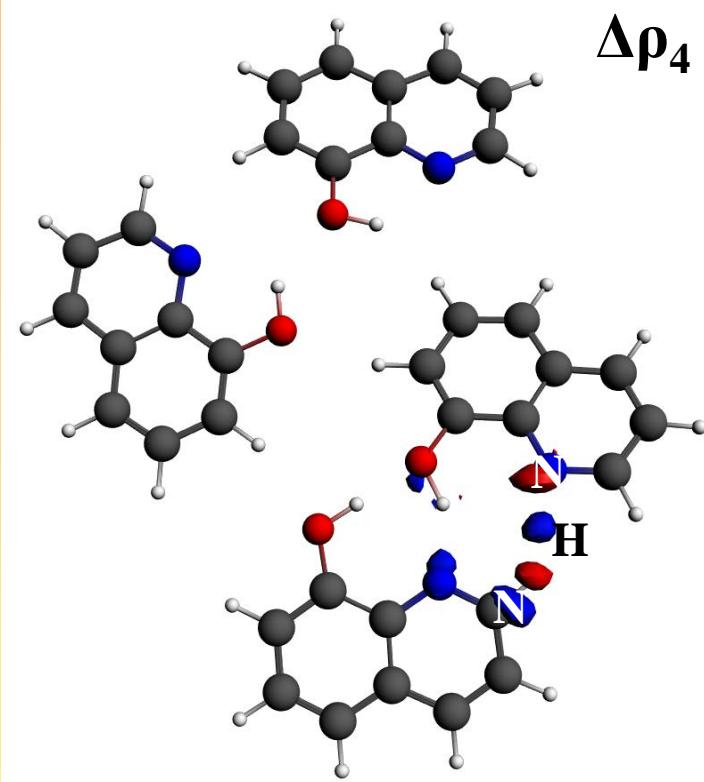




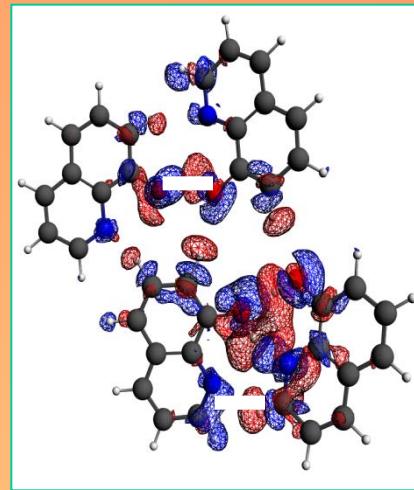
ETS-NOCV- tetra-8-hydroxyquinoline

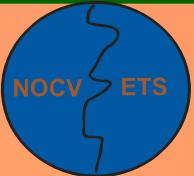


$\Delta E_{\text{orb}}(3) = -2.0 \text{ kcal/mol}$



$\Delta E_{\text{orb}}(4) = -1.0 \text{ kcal/mol}$





Dative Bond $\text{NH}_3 \rightarrow \text{BH}_3$ - 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:

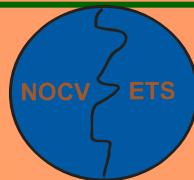
ETSNOCV

PRINT ETSLOWDIN

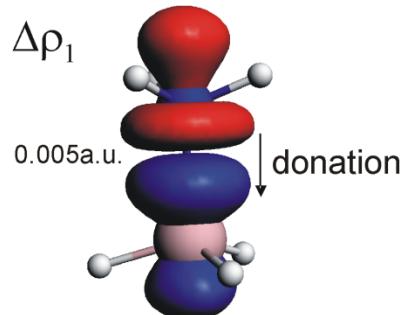
and **NOSYM** must be used



Dative Bond $\text{NH}_3 \rightarrow \text{BH}_3$ - Calculations

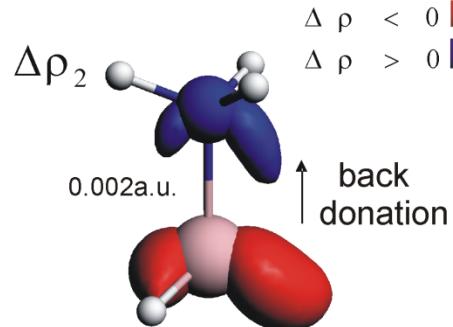


A)



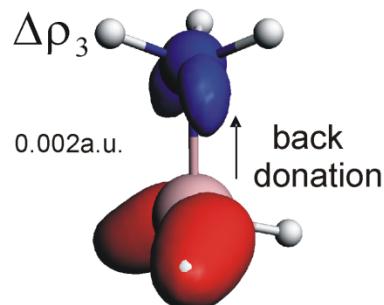
$$\Delta E_{orb}^1(A-B) = -65.5 \text{ kcal/mol}$$

$$\Delta q_1 = 0.564$$



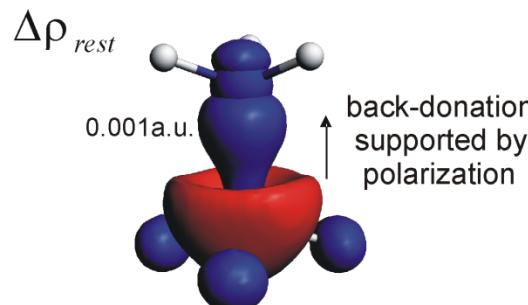
$$\Delta E_{orb}^2(A-B) = -2.3 \text{ kcal/mol}$$

$$\Delta q_2 = 0.136$$



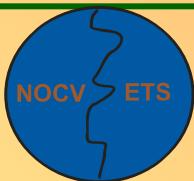
$$\Delta E_{orb}^3(A-B) = -2.3 \text{ kcal/mol}$$

$$\Delta q_3 = 0.136$$

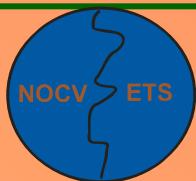


$$\Delta E_{orb}^{rest}(A-B) = -5.7 \text{ kcal/mol}$$

$$\Delta q_{rest} = 0.211$$

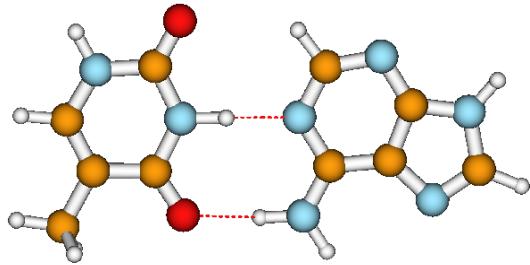


Inter-Molecular-Hydrogen Bonds



Adenine-Thymine

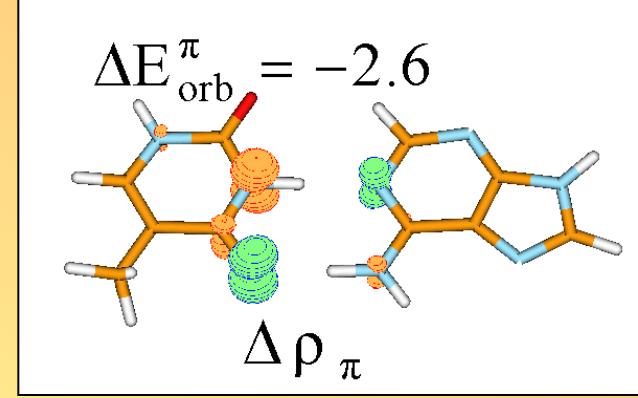
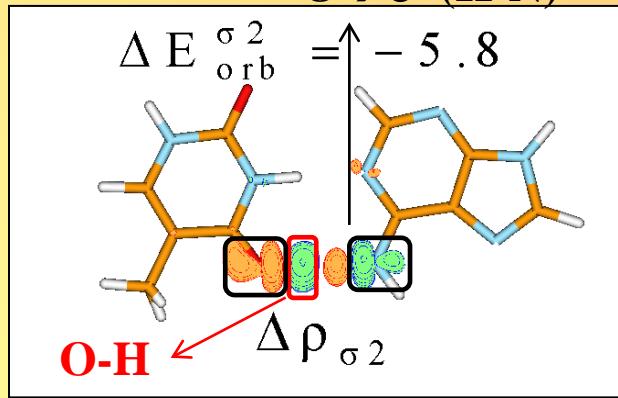
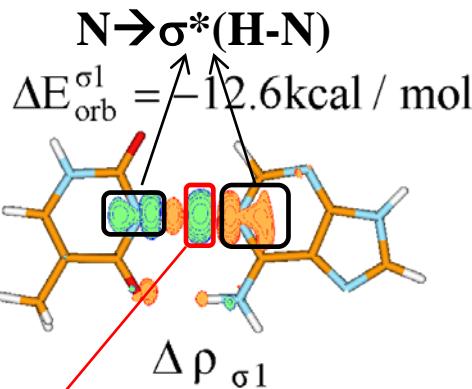
a)



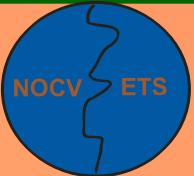
$$\Delta E_{\text{orb}} = -22.0$$

| | 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 | |
| $\Delta H_{\text{total}} - \text{experiment}^{99}$ | -12.1 | |
| $\Delta E_{\text{total}} - \text{other theoretical results}$ | -13.2 | |

b)



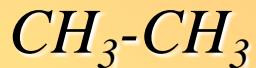
H-N covalency!



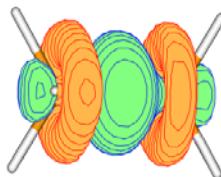
Hydrogen Bond A-T Calculations

- 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

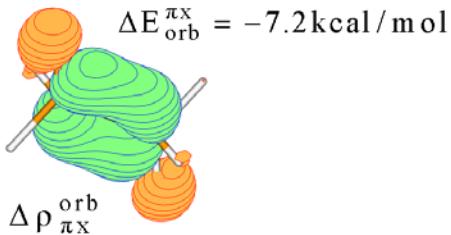
Covalent bonds



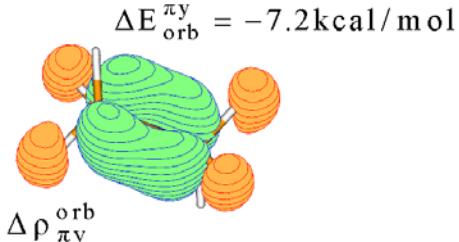
$$\Delta E_{\text{orb}}^{\sigma} = -173.4 \text{ kcal/mol}$$



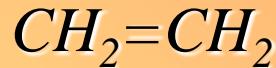
$$\Delta \rho_{\sigma}^{\text{orb}} = \Delta \rho_{\sigma,\alpha}^{\text{orb}} + \Delta \rho_{\sigma,\beta}^{\text{orb}}$$



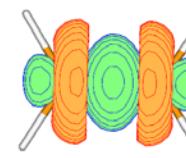
$$\Delta \rho_{\pi_X}^{\text{orb}}$$



$$\Delta \rho_{\pi_Y}^{\text{orb}}$$

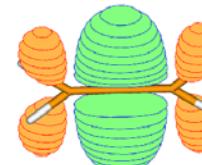


$$\Delta E_{\text{orb}}^{\sigma} = -220.6 \text{ kcal/mol}$$



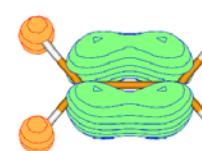
$$\Delta \rho_{\sigma}^{\text{orb}}$$

$$\Delta E_{\text{orb}}^{\pi_1} = -67.8 \text{ kcal/mol}$$

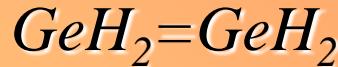


$$\Delta \rho_{\pi_1}^{\text{orb}}$$

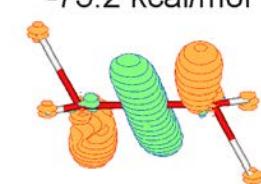
$$\Delta E_{\text{orb}}^{\pi_2} = -5.7 \text{ kcal/mol}$$



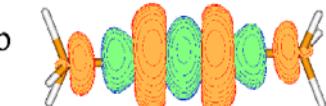
$$\Delta \rho_{\pi_2}^{\text{orb}}$$



$$-75.2 \text{ kcal/mol}$$

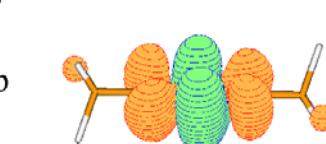


$$\Delta E_{\text{orb}}^{\sigma} = -209.7 \text{ kcal/mol}$$



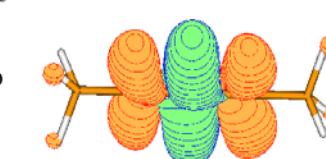
$$\Delta \rho_{\sigma}^{\text{orb}}$$

$$\Delta E_{\text{orb}}^{\pi_1} = -88.8 \text{ kcal/mol}$$



$$\Delta \rho_{\pi_1}^{\text{orb}}$$

$$\Delta E_{\text{orb}}^{\pi_2} = -88.8 \text{ kcal/mol}$$



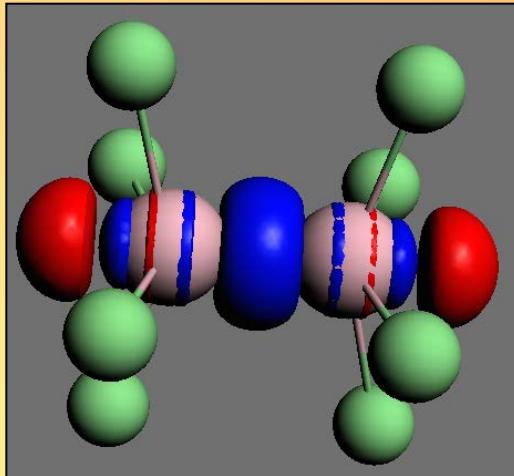
$$\Delta \rho_{\pi_2}^{\text{orb}}$$



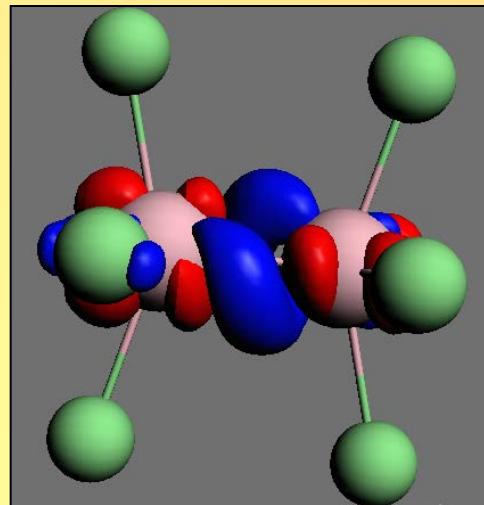
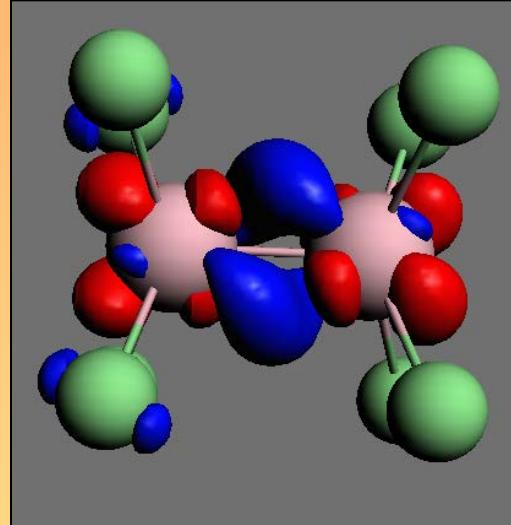
Quadruple bond; $\text{Re}_2\text{Cl}_8^{2-}$



σ [-84.3 kcal/mol]

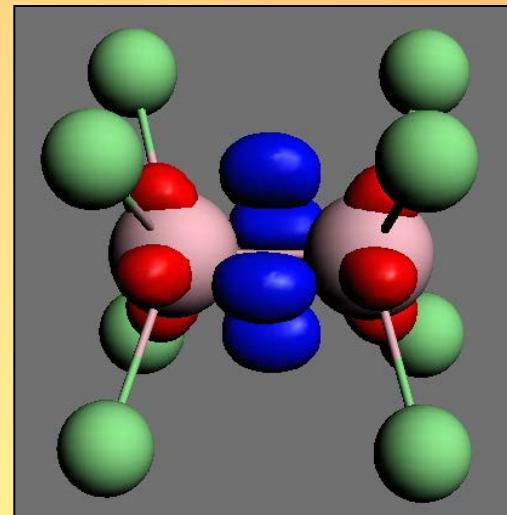


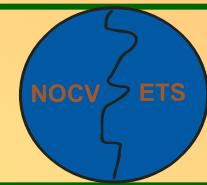
$\pi 1$ [-65.5 kcal/mol]



$\pi 2$ [-65.5 kcal/mol]

δ [-1.3 kcal/mol]





Ethane Built from two methyl radicals

1. Define CH₃ regions (uneven number of electrons);
2. Run SP RESTRICTED ! Calculations for CH₃ fragments
to get the fragment MO's; (1/2α + 1/2β electrons for SOMO of CH₃)
3. Use **fragoccupations** keyword in order to keep the right occupations
for each CH₃

fragoccupations

f1 A 5 // 4

subend

f2 A 4 // 5

subend

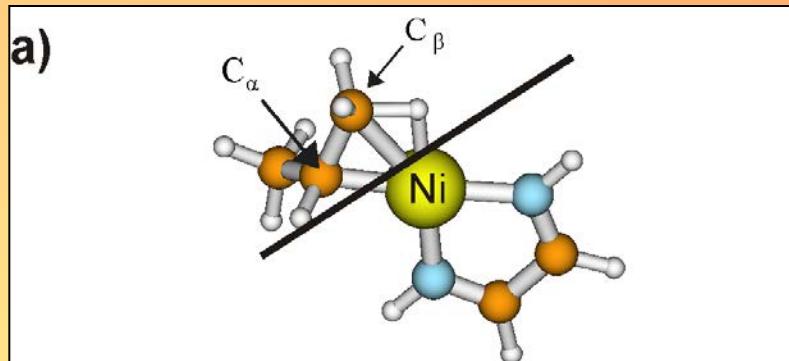
End

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



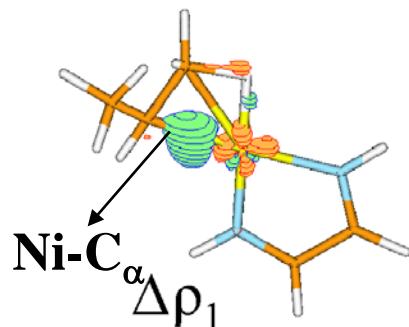
Agostic intramolecular RH---Metal interaction

Ni-diimine cationic Brookhart model catalyst

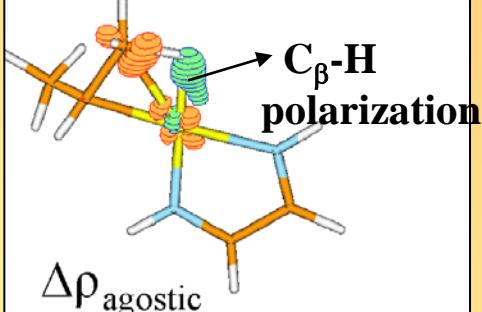


b)

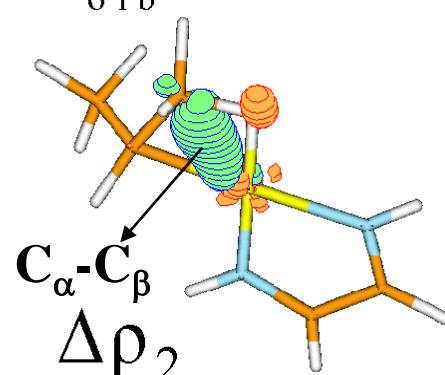
$$\Delta E_{\text{orb}}^1 = -72.4 \text{ kcal/mol}$$



$$\Delta E_{\text{orb}}^{\text{agostic}} = -13.9$$



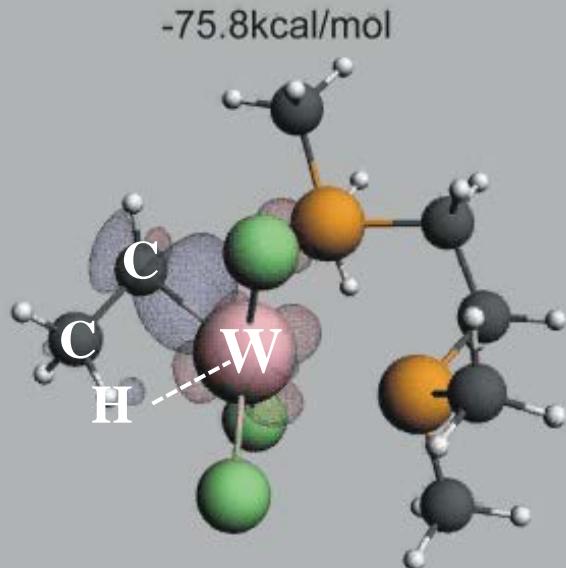
$$\Delta E_{\text{orb}}^2 = -7.54$$



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)”



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

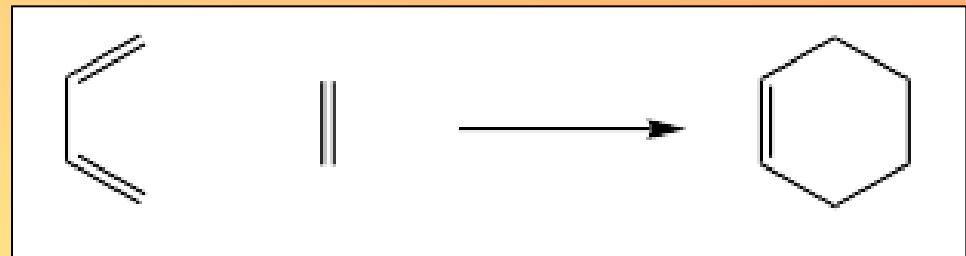
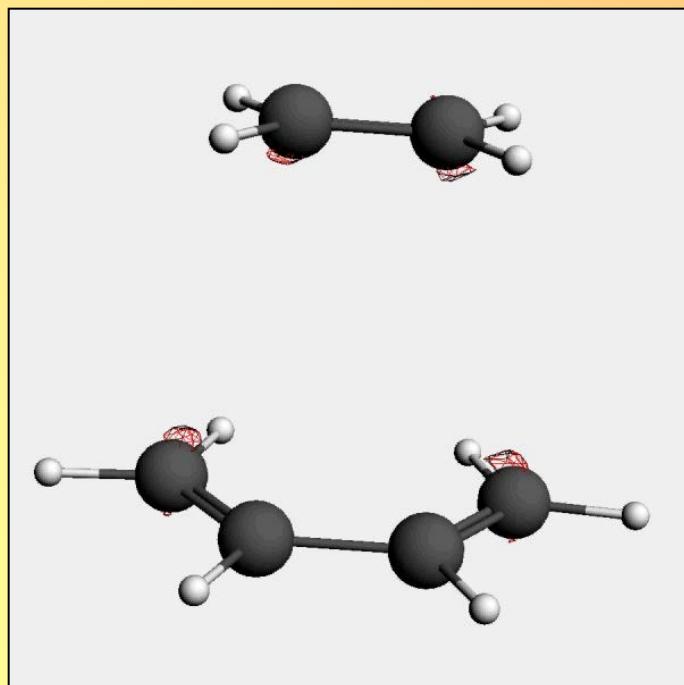




ETS-NOCV in a description chemical reactions



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

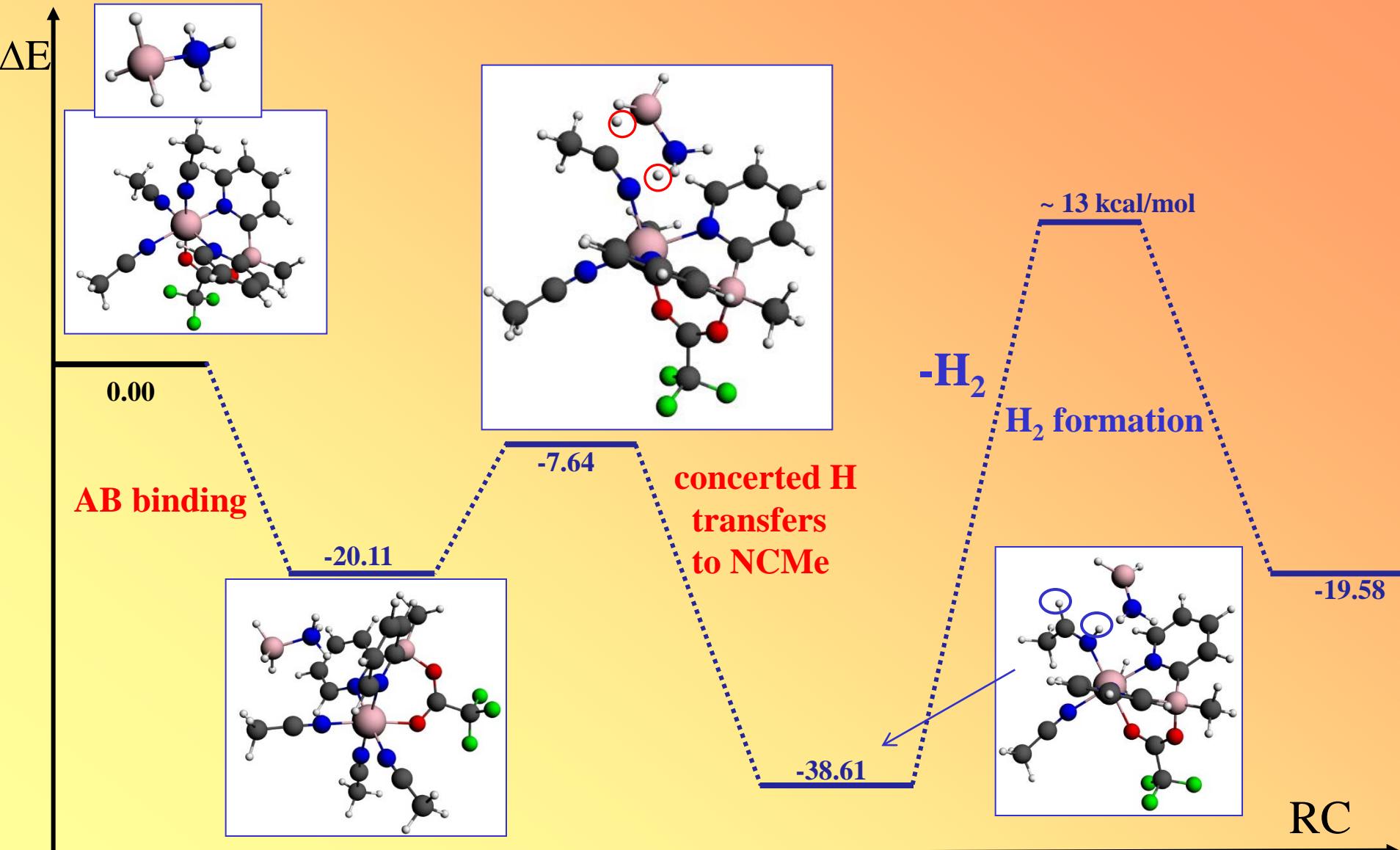


$\Delta\rho_1$ trajectory



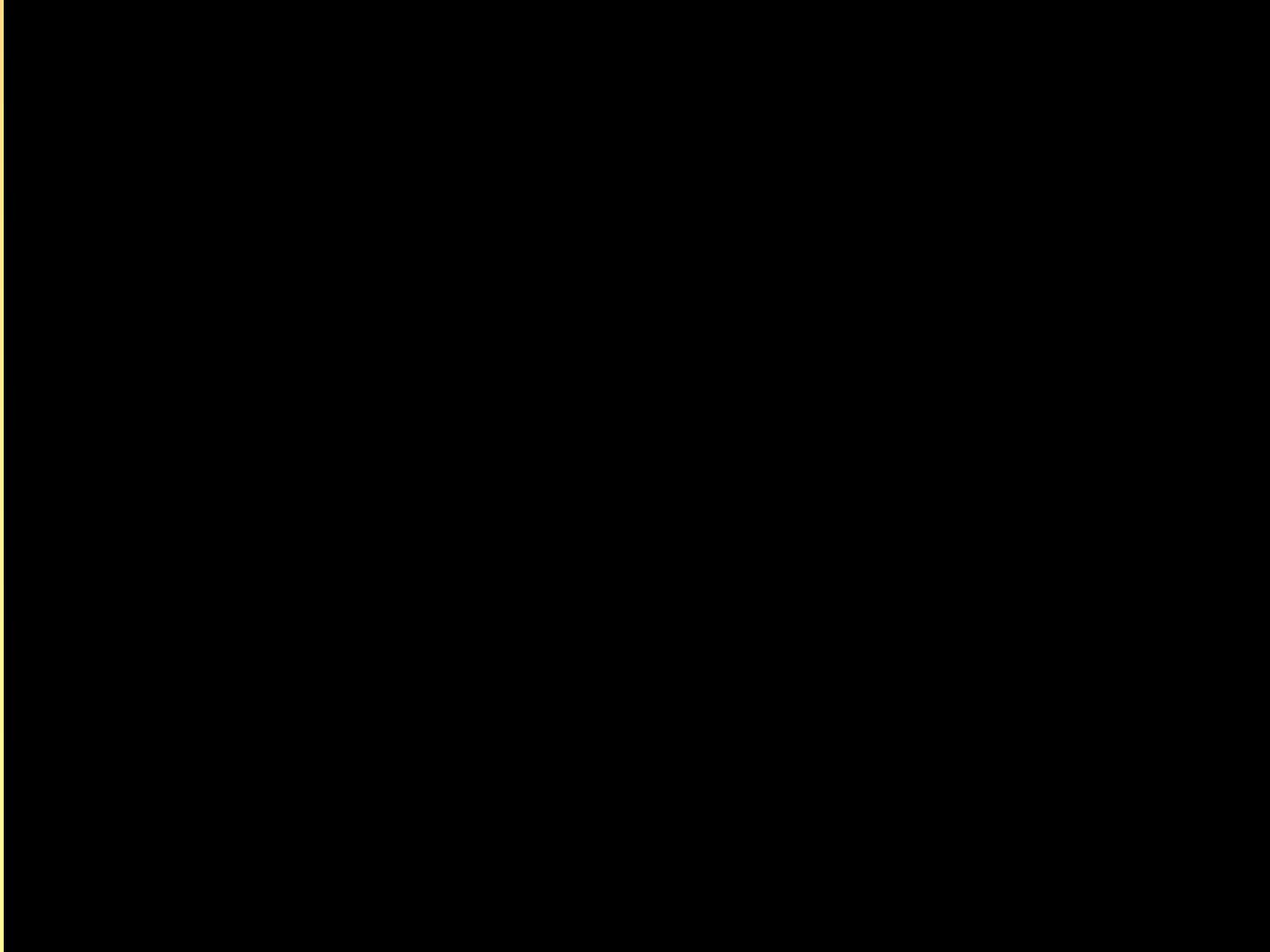
Dehydrogenation of Ammonia Borane by Ru-complex







Ammonia Borane binding to the Ru-catalyst



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

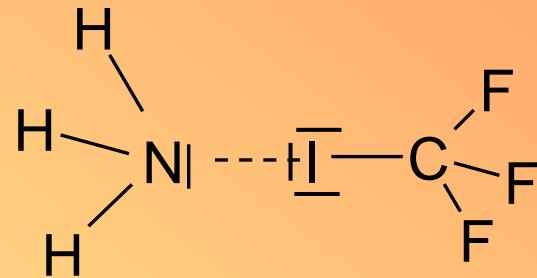
Halogen Bonding $\text{CF}_3\text{I} \cdots \text{NH}_3$ from ETS-NOCV perspective

$$\Delta E_{\text{total}} = -7.4 \text{ kcal/mol}$$

$$\Delta E_{\text{orb}} = -9.2$$

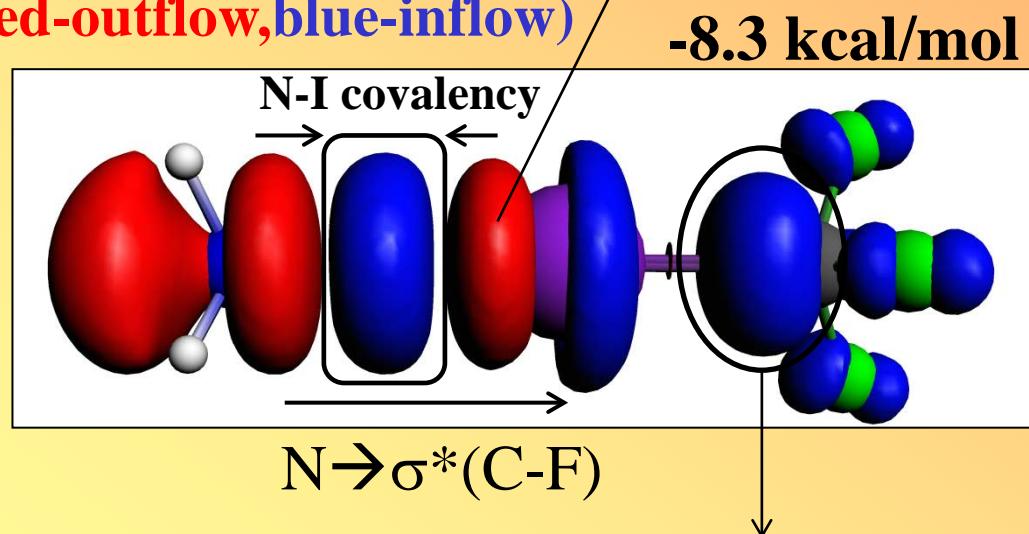
$$\Delta E_{\text{elstat}} = -15.2$$

$$\Delta E_{\text{Pauli}} = 18.3$$



Charge outflow, increase positive charge

$$-8.3 \text{ kcal/mol}$$



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

Halogen Bonding $\text{CF}_3\text{I} \cdots \text{NH}_3$ from ETS-NOCV perspective

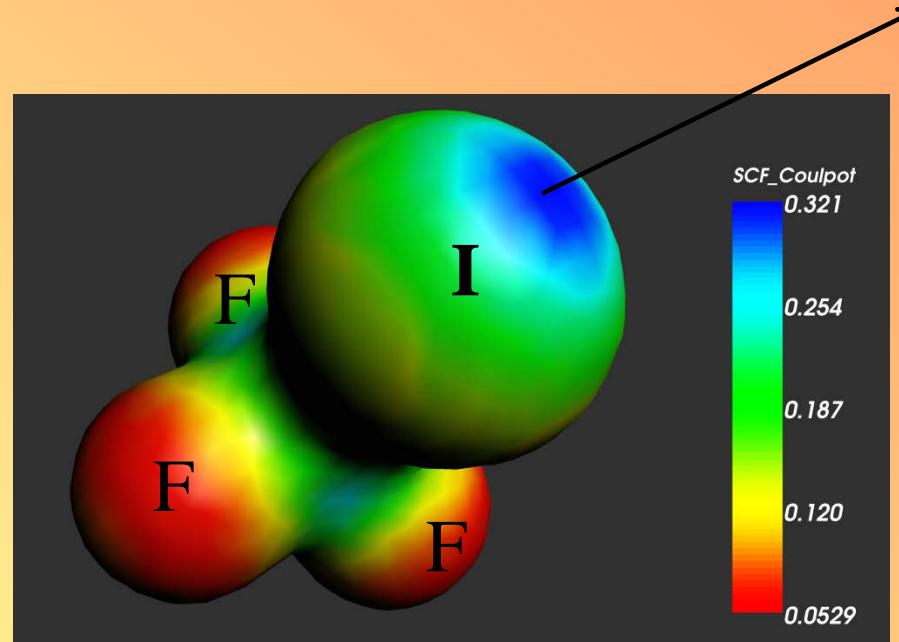
Domination of the electrostatic factor is due to the presence of σ -hole on iodine atom:

$$\Delta E_{\text{total}} = -7.4 \text{ kcal/mol}$$

$$\Delta E_{\text{orb}} = -9.2$$

$$\boxed{\Delta E_{\text{elstat}} = -15.2}$$

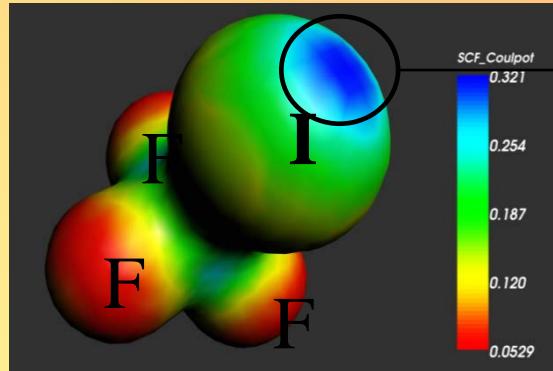
$$\Delta E_{\text{Pauli}} = 18.3$$



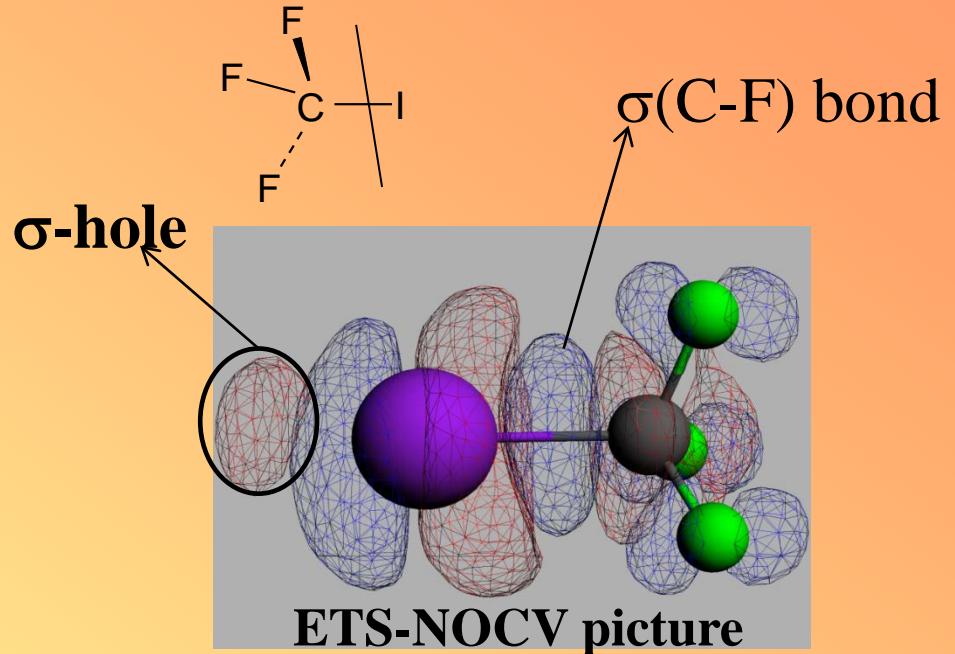
(Politzer P, Lane P, Concha MC, Ma Y, Murray J (2007) JMolModel, 13, 305, „An Overview of Halogen Bonding”



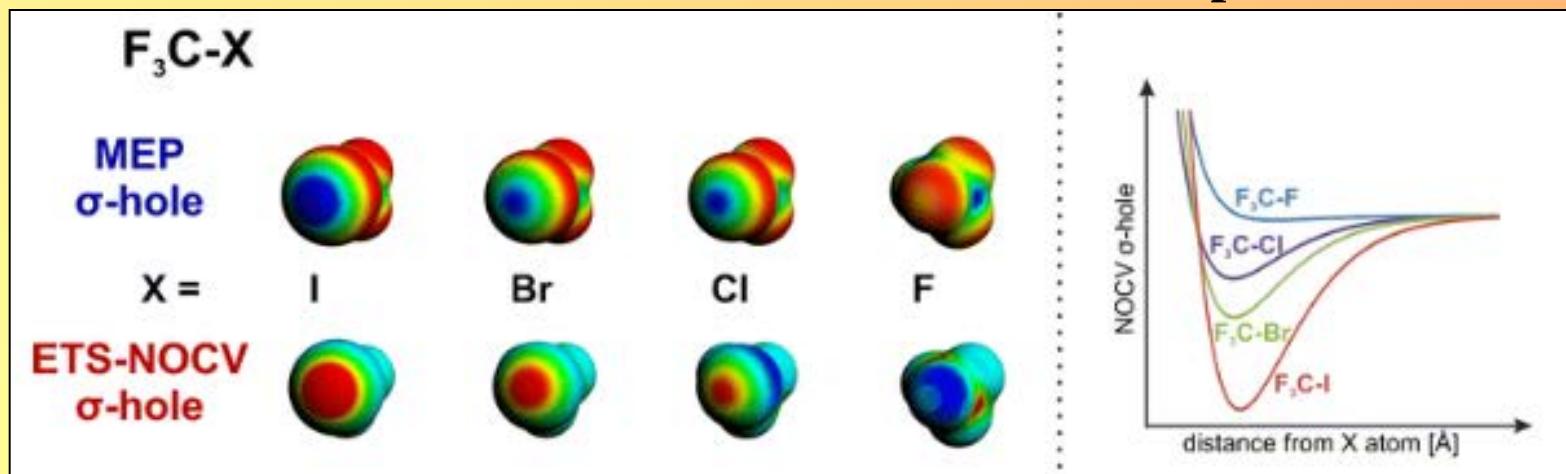
ETS-NOCV perspective, σ -hole



Electrostatic potential
picture



ETS-NOCV picture



Hands-on-session agenda

Exercise1. Getting started with the simple bond formed between ammonia and borane – typical donor–acceptor bond $\text{H}_3\text{N} \rightarrow \text{BH}_3$.

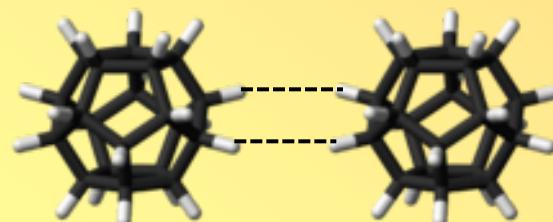
Exercise2. Why ammonia (with one lone electron pair) can form the bond with iodine (containing three lone pairs)? $(\text{H}_3\text{N} \cdots \text{ICl}_3)$

Exercise4. Analysis of carbon–carbon bond in ethane $\text{H}_3\text{C} \uparrow + \downarrow \text{CH}_3$.

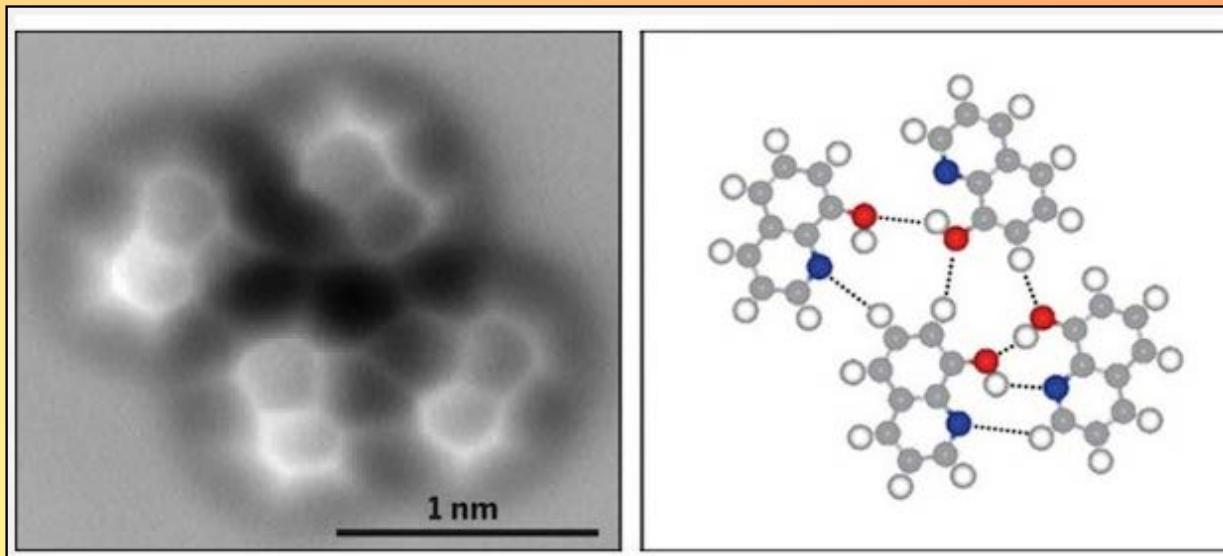
Exercise 5. Analysis of C=C bond in ethene $\text{H}_2\text{C} \uparrow \uparrow + \downarrow \downarrow \text{CH}_2$

Exercise 6. Analysis of quadruple bond between Re atoms in $[\text{Cl}_4\text{ReReCl}_4]^{2-}$ ($\text{Cl}_4\text{Re} \uparrow \uparrow \uparrow \uparrow + \downarrow \downarrow \downarrow \downarrow \text{Re Cl}_4$) (Cotton Re complex).

Exercise7. Analysis of weak homopolar dihydrogen interaction $\text{CH} \cdots \text{HC}$ formed between closed shell two dodecahedran hydrocarbon units:

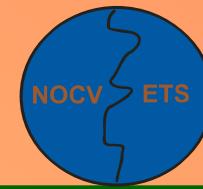
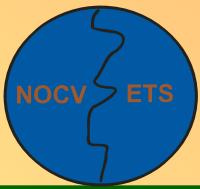


Exercise8. Interaction between four monomers of tetra-hydroxyquinoline bonded via O \cdots HO hydrogen bonds. All necessary input files (quin1.in, quin2.in, quin3.in, quin4.in and Quin-tetramer-NOCV.in) are in the directory /home/baw/baw-workshop/mitoraj/Exercise8. Compare the most important NOCV-deformation 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} | $\Delta E_{\text{dispersion}}$ |
|---|-------------------------|-------------------------|----------------------------|---------------------------|--------------------------------|
| $\text{H}_3\text{N} \rightarrow \text{BH}_3$ | | | | | |
| $\text{H}_3\text{N} \cdots \text{ICF}_3$ | | | | | |
| $\text{F}_3\text{C} \uparrow + \downarrow \text{I}$ | | | | | |
| $\text{H}_3\text{C} \uparrow + \downarrow \text{CH}_3$ | | | | | |
| $\text{H}_2\text{C} \uparrow \uparrow + \downarrow \downarrow \text{CH}_2$ | | | | | |
| $\text{LRe} \uparrow \uparrow \uparrow \uparrow + \downarrow \downarrow \downarrow \downarrow \text{ReL}$ | | | | | |
| dimer-dodekahedran | | | | | |



Thank You very much for
Your Attention!

