

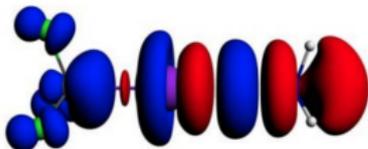
## Lesson 12: Bond Energy Analysis

# Chemical Bonding Analysis

- below are some of the bonding decomposition schemes
  - EDA-NOCV
  - NBO
  - SAPT
  - IQA(QTAIM based)
  - NCI
- partitioning of classical part and quantum mechanical part of interactions
- all include certain degree of arbitrariness
- in this session we will be looking into EDA-NOCV and IQA(QTAIM based)

# EDA-NOCV

- the energy decomposition analysis (**EDA**) or extended transition state (**ETS**) analysis
- powerful methods to dissect the interactions that constitute a chemical bond
- **fragments** should be clearly defined

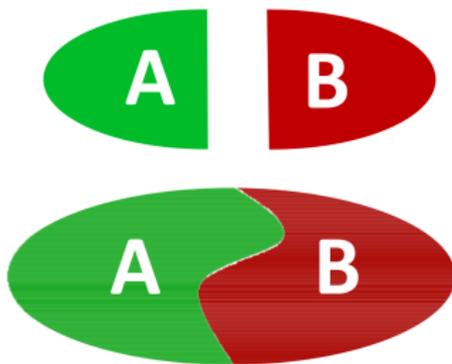


# EDA-NOCV

- the total bonding energy consists of the interaction energy  $\Delta E_{int}$  between the fragments and  $\Delta E_{strain}$

$$\Delta E_{bond} = \Delta E_{int} + \Delta E_{strain} \quad (1)$$

- the **strain or preparation energy** involved in deforming the fragments to the geometries in supra molecule



# Interaction Energy ( $\Delta E_{int}$ )

- the **interaction energy**  $\Delta E_{int}$  is further decomposed:

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} + \Delta E_{disp} \quad (2)$$

- the electrostatic attraction and pauli repulsion ( $\Delta V_{elstat} + \Delta E_{Pauli}$ ) conveniently summed together into a steric repulsion term
- the stabilizing orbital interactions ( $\Delta E_{oi}$ ) describe the orbital mixing and charge transfer between the fragments when they form the molecule
  - can be further decomposed into representations of the corresponding point group in the case of symmetric molecules.
  - the bonding interactions can be partitioned in the context of natural orbitals for chemical valence (**NOCV**).

- NOCV Natural Orbitals for Chemical Valence

$$\Psi_i = \sum_j C_{ij} \lambda_j \quad (3)$$

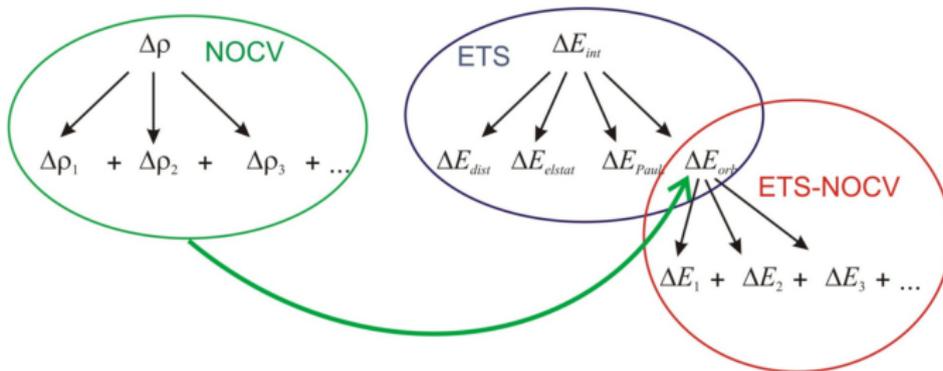
$$\Delta P C_i = v_i C_{ij} \quad (4)$$

- where  $\Delta P = P - P^0$ , matrix of charge and bond order in molecule  $P$ , and in promolecule  $P^0$

$$\Delta \rho(r) = \sum_{k=1}^{M/2} v_k [-\psi_{-k}^2(r) + \psi_k^2(r)] = \sum_{k=1}^{M/2} \Delta \rho_r(r) \quad (5)$$

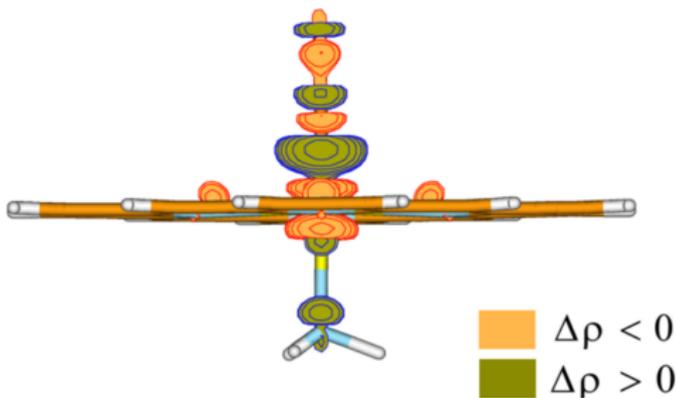
# ETS-NOCV

- ETS-NOCV representation of the deformation density



# ETS-NOCV, *application*

- deformation density,  $\Delta\rho = \rho_{mol} - \rho_A^O - \rho_B^O$



# Quantum Theory of Atoms in Molecules (QTAIM)

- works with electron density and its derivatives
- electron density is a 3-dimensional function in contrast to wavefunction which is  $4N$ -dimensional per  $N$ -electrons.
- an 'observable property'
- IQA in the context of QTAIM
  - lower dependence of results on basis set
  - electron delocalization Index (DI) is descriptor of covalency
  - can be performed employing overlapping (fuzzy atoms) or non-overlapping (QTAIM) molecular subspaces.
  - non-overlapping atoms permits defining "chemically meaningful fragments" and studying inter-fragment interactions
  - satisfy atomic virial theorem.

# IQA-QTAIM : Energy Decomposition Schemes

- self-interaction energy

$$E_{self}(\Omega) = T(\Omega_A) + V_{en}(\Omega_A) + V_{ee}(\Omega_A) \quad (6)$$

- interaction energy energy

$$\begin{aligned} E_{self}(\Omega_A, \Omega_B) &= V_{nn}(\Omega_A, \Omega_B) + V_{XCee}(\Omega_A, \Omega_B) + V_{coulombee}(\Omega_A, \Omega_B) \\ &\quad + V_{en}(\Omega_A, \Omega_B) + V_{ne}(\Omega_A, \Omega_B) \\ &= V_{el} + V_{xc} \end{aligned} \quad (7)$$

# IQA-QTAIM : Energy Decomposition Schemes

- IQA recovers the binding energy components in terms of physically meaningful terms:

$$E_{Bind} = V_{EL} + V_{XC} + E_{Pr} \quad (8)$$

- $V_{EL}$  and  $V_{XC}$  represent contribution of all classical and exchange-correlation energy components, respectively.
- the promotion energy,  $E_{Pr}$ , is the sum of all factors that change the energy of an atomic sub-space, including kinetic energy, electron-electron repulsion, and electron-nucleus attraction.
- in IQA analysis the kinetic energy has no interatomic component and nuclear-nuclear repulsion clearly has no atomic component.

# ACTIVITY

- in order to demonstrate **EDA and IQA bond analysis schemes**, we will be using at least three systems:
  1. H-H
  2. H<sub>2</sub>C=CH<sub>2</sub>
  3. NaF
- perform an optimization on Gaussian for this three molecules using:  
M06-2X with Def2TZVP basis sets
- use the geometries for IQA(QTAIM) and EDA(ETS-NOCV) bonding analysis in the manner of this fragments:  
H-/H, H<sub>2</sub>C=/CH<sub>2</sub>, and Na/F

# ACTIVITY 1: EDA (ETS-NOCV)

- USING ADF
- refer to the provided input files and script
- there are 3 sets of input files (2 for the separated fragments and 1 for molecule), unless its a bimolecular systems
- use M06-2X with tz2p basis sets
- don't impose symmetry
- complete manual/sample is found in this link:  
{<https://www.scm.com/doc/ADF/Examples/Examples.html>}
- watch out for the multiplicity of your fragments

# ACTIVITY 1: EDA (ETS-NOCV)

- USING ADF, *cont.*
  - final results of decomposition can be found in the 3rd (paired) output using keyword:  
**BONDING ENERGY**
  - the results presents **Electrostatic Energy, Kinetic Energy, Coulomb (Steric+OrbitInteraction), Exchange Correlation (XC)**
- you can also search for **NOCV Eigenvalues** in the output file
  - for the visualizations of the channels open the TAPE21  
**\$ adfview TAPE21**
  - go to **Add > Isosurface with phase > open NOCV Def. Dens.**
  - for Def. Dens. the direction of electronic polarization is from red to blue region

## ACTIVITY 2: IQA (QTAIM)

- using AIMALL
  - analogous to EDA(ETS-NOCV), there are 3 sets of jobs (2 separated fragments and 1 for molecule), unless it's a bimolecular systems
  - for the IQA, it consists of Gaussian single point calculation to generate the wavefunction
    - use **M06-2X with Def2TZVP basis sets**
  - then AIMALL will use the checkpoint files for IQA analysis
  - **refer to the provided input files and script**
  - watch out for the multiplicity of your fragments
  - the final output will provide **.sum** and **.sumviz** files
  - **.sumviz** files can be use for the GUI, AimStudio.

## ACTIVITY 2: IQA (QTAIM)

- using AIMALL, cont.
  - the binding energy is not explicitly stated in the output
  - rather the output only presents "Intraatomic Self Energy Components" and "Diatomic Interaction Energy Components"
  - these components has corresponding Kinetic (T), Classical ( $V_{Cl}$ ), Exchange Correlation ( $V_{xc}$ ) Energy parts
- to get the Bonding Energy from the AIMALL output, one must use this scheme:

$$E_{BE} = (E_{self}(fragment) - E_{self}(free))[A, B] + E_{int}(A, B)$$

- be sure to subtract only the T,  $V_{Cl}$  and  $V_{xc}$  parts on the self energy components separately first
- then add it with corresponding values on interaction energy

# QUESTIONS TO PONDER

- after calculating the energy components of the various systems using the two methods:
  - how close are the total **bonding energy** values relative to the experiment?  
(check online expt. values)
  - which component of the binding energy they differ? how large are the deviations of the differences
  - which method distributes the 'classical and quantum' parts more?
  - which one do you prefer, the method that allows orbital partitioning?  
or the method that allows atom-atom partitioning?

**END**