

# Introduction to Computational Quantum Chemistry

Energy Decomposition Analysis

# Energy Decomposition Analysis

## Deformation density

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

Positive values describe the point of density accumulation in the molecule. When the molecule is formed from atoms the density flows from the area of negative value towards the area of positive value.

# Formation of chemical bond in H<sub>2</sub> – $\Delta\rho$ based picture

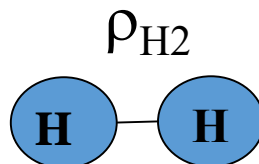
1. Start from promolecular state (atom/fragments)



$$\rho_H = 1s^2$$

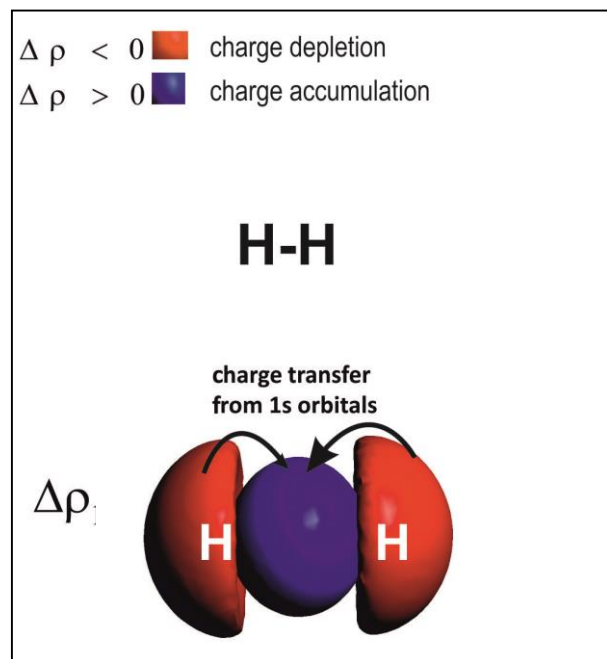


$$\rho_H = 1s^2$$



$$\Delta\rho = \rho_{H_2} - 2\rho_H$$

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

# Extended Transition State Method

Ziegler-Rauk : Bond formation in three steps

1. A system A—B is cut into 2 (or more) fragments along an interesting bond: A—B  $\rightarrow$  A and B. The fragments are then overlapped from infinite distance to final position, i.e. form a superposition of  $\rho_A + \rho_B$ . The electrostatic attraction between the fragments is calculated quasi-classically ( $\Delta E_{\text{elstat}}$ ).
2. The wavefunctions are allowed to overlap. The resulting wavefunction has to be antisymmetrized which increases the energy ( $\Delta E_{\text{Pauli}}$ ).
3. The orbitals of the fragments are allowed to relax and electrons get redistributed to achieve the electronic state of the complete system. This lowers the energy again. This step involves mixing of orbitals. ( $\Delta E = \Delta E_{\text{orb}}$ )

# Energy components

- Decomposition of binding energy into different contributions.
- $\Delta E_{\text{int}}$ : Total intrinsic interaction energy between two (or more) fragments.
- $\Delta E_{\text{elstat}}$ : Attractive, quasi-classical electrostatic interaction between the electrons and the nuclei.
- $\Delta E_{\text{Pauli}}$ : Repulsive energy between electrons of the same spin. Comes from the antisymmetrization of the wavefunction.
- $\Delta E_{\text{orb}}$ : Comes from the relaxation of the fragment orbitals (mixing). Most interesting contribution to  $\Delta E_{\text{int}}$  for a chemist.

$\Delta E_{\text{orb}}$  can be decomposed into different contributions ( $\sigma$ ,  $\pi$ , ...) via ETS-NOCV

# The Natural Orbitals for Chemical Valence (NOCV)

**NOCV's 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:**

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

In short: The NOCV observes the electron flow when overlapping the fragments to come the final electron distribution.

Each NOCV has a eigenvalue  $v$  assigned to it which shows how many electron are being moved into or out of the NOCV.

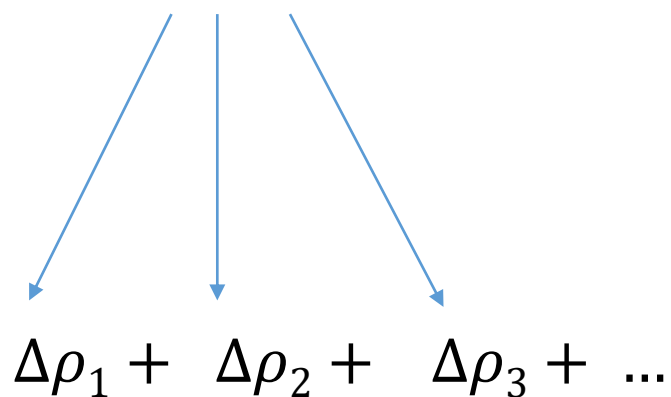
The NOCVs are paired according to their eigenvalues and are then called NOCV pairs. NOCV pairs can be superimposed and are then called deformation densities. These are used to assign contributions of the orbital term to certain orbital interactions of the fragments in a compact way.

In the deformation densities, the electrons flow from red  $\rightarrow$  blue

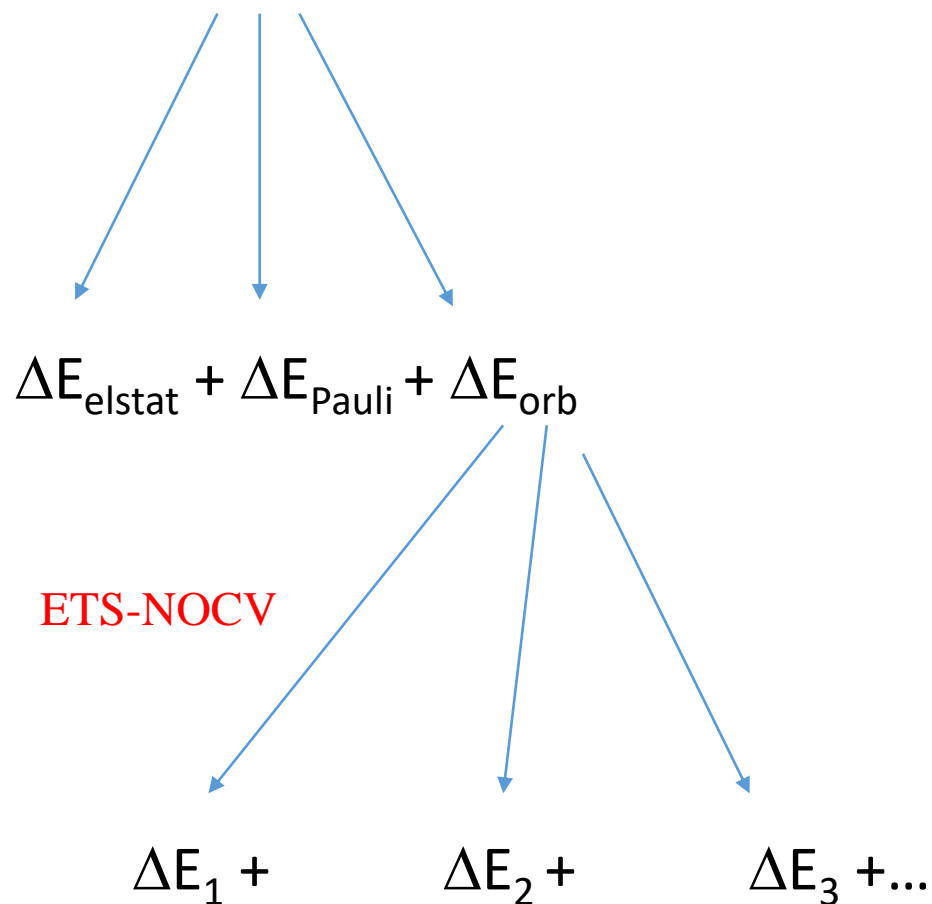
# A combination of ETS and NOCV - (ETS-NOCV)

**ETS:**  $-D_e = \Delta E_{\text{total}} = \Delta E_{\text{prep}} + \Delta E_{\text{int}}$

$\Delta\rho$  NOCV



$\Delta E_{\text{int}}$  ETS



# Amsterdam Density Functional

- Very fast code
- Uses **Slater-type** basis functions
- Functionalities:
  - Optimizations
  - Response properties (NMR, EPR, UV-VIS, IR, Mössbauer..)
  - NOCV
  - EDA
  - COSMO model of solvation
  - ZORA scalar and spin-orbit relativistic approach**



# Running ADF jobs

- Input: keywords in blocks
- `adf {-n nproc} < input.adf > output.out`
- `nmr {-n nproc} < input_nmr.adf > output_nmr.out`
- INFINITY takes care of the number of CPUs
- Tape files: binaries containing the orbitals
- <http://www.scm.com/Doc/Doc2014/ADF/ADFUsersGuide/page262.html#keyscheme%20SAVE>

## Advantages

- Many quantum-chemical tools implemented
- Relativistic effects included via ZORA Easy and intuitive syntax
- Good powerful GUI (ADFView)

## Disadvantages

- Slow geometry optimization
- Sometimes cryptic error messages
- Sometimes serious convergence problems

# Task

- Perform EDA with ETS-NOCV for  $\text{NH}_3\text{-BH}_3$
- Use the prepared input files distributed in IS.
- Three input files
  - For fragment one  $\text{NH}_3$
  - For fragment two  $\text{BH}_3$
  - For the system  $\text{NH}_3\text{-BH}_3$
  - Run adf for fragment 2. Rename the TAPE21 file to TAPE21 t21.frag2
  - Run adf for fragment 1. Rename the TAPE21 file to TAPE21 t21.frag1
  - Run adf for the system

# Relativistic calculation

# Why relativistic quantum chemistry

$$\hat{H}^{nrel} = \sum_{i=1} \frac{\hat{p}_i^2}{2m} + \sum_i V_{Ni} + V_{e_e} + V_{n_{uc}}$$

$\frac{\hat{p}_i^2}{2m}$  is the non relativistic kinetic energy operator

- In heavy elements the inner shell electrons move with a speed comparable with speed of light.
- So the core electrons of heavy atoms show sizable relativistic effect.
- For accurate predictions of various properties of chemical system containing heavy elements.

$$m_{rel} = \frac{m_o}{\sqrt{1 - \frac{v^2}{c^2}}}$$

- Properties like NMR are very sensitive to this

# The Dirac equation

Quantum mechanics

Relativity



The Dirac equation

$$\hat{H}^{DCB} = \hat{P} + \left[ \sum_{i=1}^N (c\alpha_i \hat{p}_i + \beta_i c^2) + VNi + Ve_e + \sum_{j>i=1}^N \hat{H}_{ij}^B + Vn_{uc} \right] \hat{P}^+$$

Here,  $\alpha$  and  $\beta$  are 4 X 4 matrices is written in terms of the well known Pauli spin-matrices  $\sigma_s$ .

Breit interaction are relativistic corrections to  $V_{ee}$

$P^+$  is the projection operator

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

The main difference here is kinetic energy operator . Its takes into account the relativistic increase of electron mass due to high velocities, it includes the electron's rest mass energy, it incorporates the electron spin also causes the spin orbit coupling.

# Two-component relativistic methods

- High computational cost of four-component relativistic calculations has motivated the development of computationally less demanding two-component Hamiltonians.
- Two-component relativistic Hamiltonians (involving only positive-energy orbitals) : pseudopotential and all-electron methods

# ZORA: accurate and efficient relativistic DFT

The zeroth order regular approximation (ZORA) to the Dirac equation accurately and efficiently treats relativistic effects in chemistry. ZORA can be applied with spin-orbit coupling or as scalar correction only.

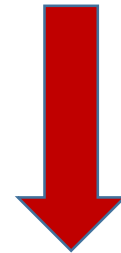
- Spin Orbit Coupling can be included self-consistently
- All electron relativistic basis sets for all elements
- Available for most spectroscopic properties
- Include relativistic effects on structure and reactivity



# From Dirac to ZORA equation

Four-component Dirac Hamiltonian

$$\begin{bmatrix} V & c(\sigma \cdot p) \\ c(\sigma \cdot p) & V - 2c^2 \end{bmatrix} \cdot \begin{pmatrix} \phi \\ \chi \end{pmatrix} = E \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$



Unitary transformation

Two-component zeroth order regular approximation

$$H^{zora} \phi_{zora} = E z_{ora} \phi_{zora}$$

$$H^{zora} = V + p \frac{c^2}{2c^2 - V} p + \frac{c^2}{(2c^2 - V)^2} \sigma \cdot (\nabla V \times p)$$

# NMR calculations

- Calculate the NMR properties of hydrogen in HI and HCl
- Use the prepared input files distributed in IS
- Write the molecular geometry in same format as .xyz (Å)
- Bond lengths:
  - HCl(scalar): 1.276930
  - HI(scalar) : 1.606797
  - HCl(SO): 1.276467
  - HI(SO): 1.609681
- For relativity use **ZORA Scalar** and **ZORA Spin-Orbit** Approximations
- Compare the Experimental, Nonrelativistic, ECP, and Two component approach
- Chemical shielding for benzene 1H nuclei:

# ReSpect

There are two parts of ReSpect calculation

- SCF module- Calculation of unperturbed ground state MO Coefficient.
- MAG module- Calculation of the magnetic properties .
- Each part requires a specific input file (.inp and .M)

List of properties

EPR

- G-tensor
- Hyperfine coupling tensor

NMR

- NMR shielding tensor
- Nuclear spin-rotation coupling tensor
- Indirect nuclear spin-spin coupling tensor

Functional:

PBE, BP86, PBE0 etc(hybrid only for epr)

Solvent: PCM model

- Calculate the NMR chemical shielding of H in HI using ReSpect
- Use the prepared input files distributed in IS.
- Three input file required.
  - Initial guess, guess.inp
  - Run using the command  
**respect --np=4 --inp=guess**
  - Restart the calculation at 4 component level from the initial guess  
**respect --np=4 --inp=4c --restart=guess**
  - Calculate the NMR parameters using .M file.  
**respect --np=4 --inp=4c --M=CS**