# Exercise 1. Energy decomposition analysis and MO interaction diagrams

## Reading material

The following two papers (see blackboard) will provide you with the background necessary to understand donor-acceptor interactions:

C. Fonseca Guerra, F. M. Bickelhaupt, J. G. Snijders, E. J. Baerends. *Chem. Eur. J.* **1999**, *5*, 3581.
C. Fonseca Guerra, T. van der Wijst, F. M. Bickelhaupt. *Chem. Eur. J.* **2006**, *12*, 3032-3042.

## Introduction

In this exercise, you will study the donor-acceptor interactions between $NH_3$ and $BH_3$:
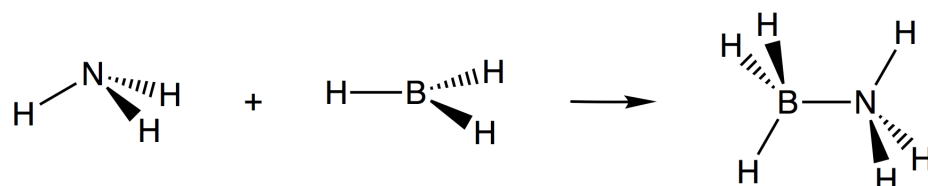


The analysis will be carried out within the framework of Kohn-Sham molecular orbital (KS-MO) theory, in combination with a quantitative energy decomposition analysis (EDA). The main objective is 1) to achieve a detailed understanding of the bonding mechanism and 2) to tune the donor-acceptor interactions in similar complexes.

You can familiarize yourself with fragment calculations by completing the following tutorial: https://www.scm.com/doc.2017/Tutorials/ADF/ADF_Fragment_Analysis.html. Note that this tutorial is done by using the graphical user interface (GUI), while the computations in this course will be done on the Bazis computer cluster (see additional document on blackboard). Nevertheless, the tutorial is relevant because it demonstrates how the results can be vizualized.

## Step 1. Optimize structures, compute Δ*E* and analyze the HOMO & LUMO

Optimize the structures ($NH_3$, $BH_3$ and $H_3N-BH_3$) at the BP86 / TZ2P level of theory (see Appendix for input file). Open the .out files with ADFoutput or Vim and write down the absolute energies (these can be found at the end of the output files). What is the physical meaning of the energy in ADF? Use the absolute energies to compute the bond energy Δ*E*.

Open the optimized $NH_3$ and $BH_3$ molecules in ADFview, and visualize their HOMO (Properties → HOMO) and LUMO (Properties → LUMO). Rationalize which donor-acceptor interactions will be possible.

## Technical Notes

The bond energy $\Delta E$ of the complex $H_3B-NH_3$ is defined as:

$$\Delta E = E_{complex} - E_{BH_3} - E_{NH_3} \tag{1}$$

where $E_{complex}$ is the energy of the optimized complex and $E_{BH_3}$ and $E_{NH_3}$ are the energies of the optimized reactants $BH_3$ and $NH_3$, respectively. The overall bond energy $\Delta E$ is made up of two major components:

$$\Delta E = \Delta E_{prep} + \Delta E_{int} \tag{2}$$

In this formula, the preparation energy $\Delta E_{prep}$ is the amount of energy required to deform the separate fragments $BH_3$ and $NH_3$ from their equilibrium structure to the geometry that they acquire in the complex. The interaction energy $\Delta E_{int}$ corresponds to the actual energy change when the prepared fragments (that is in the geometry of the complex) are combined to form the complex.

The interaction energy in the donor-acceptor systems can be examined in the framework of the Kohn-Sham MO model using a quantitative energy decomposition analysis (EDA), which divides the interaction energy into the electrostatic interaction $\Delta V_{elstat}$, Pauli repulsion $\Delta E_{Pauli}$, and attractive orbital interactions $\Delta E_{oi}$:

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} \tag{3}$$

The term $\Delta V_{elstat}$ corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared (i.e. deformed) fragments and is usually attractive. The Pauli repulsion $\Delta E_{Pauli}$ comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The orbital interaction $\Delta E_{oi}$ accounts for charge transfer (i.e., donor–acceptor interactions between occupied orbitals on $NH_3$ with unoccupied orbitals of $BH_3$, including the HOMO-LUMO interactions) and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment).
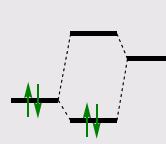
An extensive discussion of the physical meaning of all the terms in the energy decomposition is given in F.M. Bickelhaupt and E.J. Baerends, *Kohn-Sham Density Functional Theory: Predicting and Understanding Chemistry*, In: Rev. Comput. Chem.; Lipkowitz, K. B. and Boyd, D. B., Eds.; Wiley-VCH: New York, 2000, Vol. 15, 1-86.
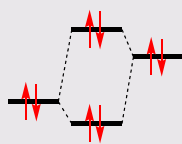


$\Delta V_{elstat}$          $\Delta E_{Pauli}$          $\Delta E_{oi}$

## Step 2. Fragment analysis on the optimized complex $H_3N-BH_3$

Analyze the chemical interaction between $NH_3$ and $BH_3$ by performing an energy decomposition analysis (EDA) on the optimized complex. In order to do so, you first need to do a single point computation on the two reactants in the geometry they have in the optimized, interacting system (see Appendix for input file). This will result in two .t21 files; one for $NH_3$ and one for $BH_3$. Next, you do the actual fragment analysis (see Appendix for input file) in which you compute the interaction between the two deformed reactants. Write down the individual energy terms $\Delta V_{elstat}$, $\Delta E_{Pauli}$ and $\Delta E_{oi}$, which can be found in the .out file under Properties $\rightarrow$ Bonding Energy Decomposition.

*Technical notes*

The molecular coordinates in the single point computations should be identical to the coordinates in the fragment analysis input file.

Make sure that the two .t21 files of the single point computation are in the same directory as the actual fragment analysis. If you prefer to store them in a different folder, you should adjust the fragment analysis input file accordingly.

## Step 3. Analyzing the covalent component

Open the MO diagram of the complex with ADFlevels, and analyze which fragment orbitals participate in HOMO-LUMO interactions. Is this in line with what you predicted in Step 1? Analyze the gross populations by placing your mouse on the associated energy levels, and write down their energy difference (HOMO-LUMO gap). Analyze their mutual overlap in ADFoutput (Properties $\rightarrow$ SFO populations).

*Technical notes*
*The MO diagram contains the donor-acceptor interactions but also the Pauli repulsion.*

*To verify whether the SFO's form a bonding or antibonding combination, you should consider the product of the MO coefficients and also their overlap. The MO coefficients are given in the section "SFO MO coefficients"; the overlap matrix is given in the section "SFO populations".*

## Step 4. Tuning the donor-acceptor interactions

The next step will be to tune the donor-acceptor interactions. Repeat step 1, 2 and 3 for the following cases, where X is F, Cl, Br and $R_1$, $R_2$, $R_3$ can be H or $CH_3$:
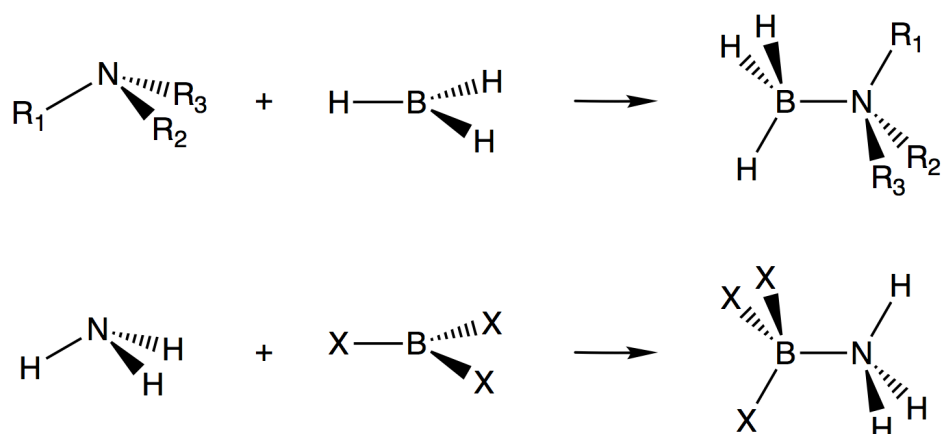
How does the bond energy $\Delta E$ change upon substitution of the hydrogen atoms? Rationalize the results by using the energy decomposition analysis scheme, HOMO-LUMO gaps and HOMO-LUMO overlap.

## Step 5 (optional). Verify trends with other systems

If there is still time left: think of additional systems that can be used to verify your trends. Can you come up with a system that has even stronger orbital interactions than the ones studied so far?

# Appendix. Input files

## GEOMETRY OPTIMIZATION

```bash
#!/bin/bash
export SCM_TMPDIR=/local/datastore0/$USER/$SLURM_JOBID
srun mkdir -p $SCM_TMPDIR
chmod 700 $SCM_TMPDIR
cd $SCM_TMPDIR
export TC_SUBMISSION_DIR=$SLURM_SUBMIT_DIR

$ADFBIN/adf <<eor>$SLURM_SUBMIT_DIR/$SLURM_JOB_NAME.out

XC
  GGA BP86
END

BASIS
  TYPE TZ2P
  CORE none
END

SCF
  iterations 250
END

Geometry
  Iterations 300
  Optim Cartesian
  Convergence E=1e-4 grad=1e-4
End
```

*Remove this part to run a single point calculation*

```
SYMMETRY nosym
CHARGE 0
```

`nosym` *can be changed to symmetry point groups like* `C(3V)`.

```
ZLMFIT
  Quality normal
END

BECKEGRID
  Quality good
End

ATOMS
END
```

*Add molecular coordinates here*

```
ENDINPUT
eor

cp TAPE21 $SLURM_SUBMIT_DIR/$SLURM_JOB_NAME.t21
```

## FRAGMENT ANALYSIS

```bash
#!/bin/bash
export SCM_TMPDIR=/local/datastore0/$USER/$SLURM_JOBID
srun mkdir -p $SCM_TMPDIR
chmod 700 $SCM_TMPDIR
cd $SCM_TMPDIR
export TC_SUBMISSION_DIR=$SLURM_SUBMIT_DIR

$ADFBIN/adf <<eor>$SLURM_SUBMIT_DIR/$SLURM_JOB_NAME.out

XC
  GGA BP86
END

BASIS
  TYPE TZ2P
  CORE none
END

FRAGMENTS
NH3 $SLURM_SUBMIT_DIR/NH3.t21
BH3 $SLURM_SUBMIT_DIR/BH3.t21
END

SCF
  iterations 250
END

EPRINT
  SFO Eig Ovl
END

ZLMFIT
  Quality normal
END

BECKEGRID
  Quality good
End

SYMMETRY nosym
CHARGE 0

ATOMS
    Atom1  x y z  f=NH3
    Atom2  x y z  f=BH3
END

ENDINPUT
eor

cp TAPE21 $SLURM_SUBMIT_DIR/$SLURM_JOB_NAME.t21
```

*This part specifies which .t21 file belongs to which fragment.*

*Add molecular coordinates here and specify to which fragment ($NH_3$ or $BH_3$) they belong.*