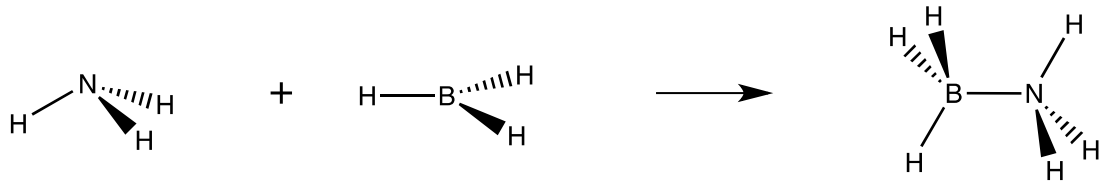
Hands-On Energy Decomposition Analysis (EDA)

Energy decomposition analysis and MO interaction diagrams.

1. Fragments

In this exercise we want to understand the donor-acceptor interactions between NH_3 and BH_3:

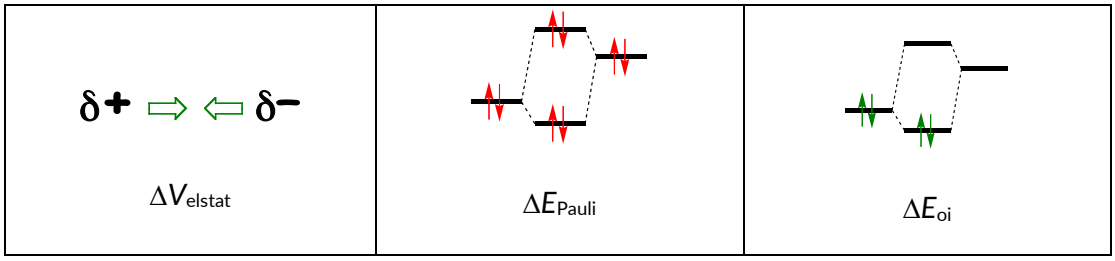


Before starting to analyze the interaction you have to get acquainted to the fragments. **Optimize the structures of NH_3 and BH_3 at the BP/TZ2P level of theory and analyze the HOMO and LUMO of the two molecules.** Use ADFview to view the orbitals of the HOMO and LUMO of both molecules. Rationalize which donor-acceptor interactions will be possible and write down the total energy of NH_3 and BH_3.

2. Donor-acceptor interactions in the complex.

The next step is to analyze the chemical interaction between the two fragments. For that purpose, you **optimize $H_3B{\bullet}{\bullet}{\bullet}NH_3$ at the BP/TZ2P level of theory** (core None; relativistic correction None; numerical quality Normal) **and perform the EDA calculation based on the relaxed structure**.

The MO diagram can be visualized with ADFlevels. This MO diagram shows the interactions between fragment orbitals as the donor-acceptor interactions or the Pauli repulsion. The former one can be the interaction between e.g. the lone pair of the nitrogen (HOMO of the NH_3 fragment) and the LUMO in the BH_3 fragment, while the latter one is the repulsive interaction between occupied orbitals of NH_3 and BH_3.



With the MO-diagram and the SFO gross populations, you will be able to analyze an orbital of the complex in terms of the fragment orbitals. Of which fragment orbitals is the HOMO-1 (5A1) of the complex composed? (Put your mouse on the energy level in adflevels)

$$\Delta E_{bond} = E_{complex} - (E_{BH3} + E_{NH3}) \qquad (1)$$

$$\Delta E_{bond} = \Delta E_{prep} + \Delta E_{int} \qquad (2)$$

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} \qquad (3)$$

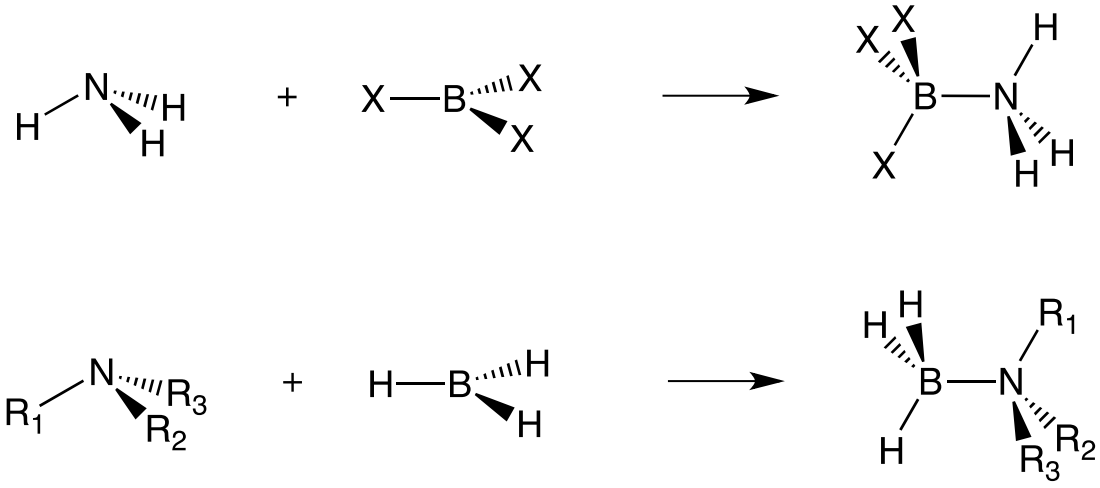
Calculate the bond energy of equation (1) and get the terms of equation (3) from the output. Take care that the "Total Bonding Energy" in the output (ADFoutput → Properties → Bonding Energy Decomposition) is the energy of the system with respect to fragments, i.e. it is the ΔE_{int} in equation (2) or (3). By default, the fragments are the

spherical spin-restricted neutral atoms, if other larger fragments (e.g. NH_3 , BH_3 , etc.) are not defined.

3. Tuning the Donor-acceptor interactions in the complex

The next step will be to tune the donor-acceptor interactions. **Perform for the following cases the energy decomposition analysis as in equation 2 and 3.**

The X will change from F, Cl, Br and R_1, R_2 and R_3 can be H or CH_3.



The following Tables have to be used for understanding the tuning.

Table 1 Energy decompositions (in kcal/mol) for BX_3NH_3

X	ΔE_{bond}	ΔE_{prep}	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}	A1 LUMO of BX_3 (in eV)
F							
Cl							
Br							

Table 2 Energy decompositions (in kcal/mol) for $BH_3NH_{(3-n)}CH_3)_n$

	ΔE_{bond}	ΔE_{prep}	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}	A1 HOMO of $NH_{(3-n)}(CH_3)_n$ (in eV)
$R_1=CH_3$							
$R_1=R_2=CH_3$							
$R_1=R_2=R_3=CH_3$							

Try to use the energy decomposition analysis and the level of the orbitals to rationalize your results. As you already have had the MO diagram of $H_3B{\bullet\bullet\bullet}NH_3$.

Hands-On Periodic Energy Decomposition Analysis (pEDA)

In this exercise we want to understand the donor-acceptor interactions between CO and the MgO(001) surface. Here, a variety of variables have to be taken into account.

The MgO(001) surface: (for example)

- Number of layers
- Size of super cell
- Number of k points for the sampling of the reciprocal space

The CO molecule: (for example)

- The coverage, which shall be defined as ratio between number of CO molecules and number of Mg surface atoms per unit cell

For sake of simplicity one shall simulate a surface with only 2 layers. To get an idea what one can learn with the pEDA, the adsorption shall be studied for different coverages: 0.5, 0.25 and 0.125. These can be represented by the adsorption of a single CO molecule on a (sqrt(2) x sqrt(2)), a (2 x 2) and a (2sqrt(2) x 2sqrt(2)) supercell. Experimental studies show that the interaction/absorption energy is coverage dependent – a lower coverage leads to a stronger bond between surface and adsorbate. Another approximation is the negligence of surface reconstruction and the assumption of orthogonal absorption of CO w. r. t. the surface on top of a Mg position ($d_{Mg\text{-}C}$ = 261 pm).

Theoretical Level: PBE/TZP(small frozen core), numerical quality Basic, Kspace Grid Quality [Gammaonly|Basic|Normal|Good|VeryGood]

Tasks:

1. Converge the number of k points used to describe the reciprocal space for each surface (provided by organizers) separately. Start with 'Gammaonly' and proceed ('basic', 'normal', 'good', 'verygood') until convergence is reached. (deviation below 1% or 1 kJ/mol)

(sqrt(2) x sqrt(2))	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}
Gamma-only				
Basic				
Normal				
Good				
VeryGood				

(2 x 2)	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}
Gamma-only				
Basic				
Normal				
Good				
VeryGood				

(2sqrt(2) x 2sqrt(2))	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}
Gamma-only				
Basic				
Normal				
Good				
VeryGood				

2. Try to rationalize the findings by looking for trends.

Super cell	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}
(sqrt(2) x sqrt(2))				
(2 x 2)				
(2sqrt(2) x 2sqrt(2))				