Orbital contributions to the exchange-repulsion energy of atomic and molecular aggregates

Bachelorarbeit der Mathematisch-Naturwissenschaftlichen Fakultät der EBERHARD-KARLS UNIVERSITÄT TÜBINGEN im Fach Chemie
angefertigt im Sommersemester 2018
im Arbeitskreis Prof. Dr. Reinhold F. Fink

vorgelegt von
Gemma Miralles Adrover
Tübingen, Juni 2018
Contents

➢ Objective
➢ Energy decomposition analysis
➢ Exchange-repulsion energy
➢ N₂-He EDA
➢ N₂-He exchange-repulsion energy
➢ Cl₂-He exchange-repulsion energy
➢ N₂-He and Cl₂-He 2D
➢ PBI-PBI exchange repulsion energy
➢ Conclusions
➢ Bibliography
Objective

➢ In N₂-He, Cl₂-He and PBI-PBI:
   o Calculate $E_{exr}$ in horizontal and vertical displacements (HF).
   o Orbital contributions to $E_{exr}$.

➢ In N₂-He and Cl₂-He:
   o Calculate the $E_{int}$ contributions obtained from EDA.
   o Check the extend of $E_{exr}$ to the total $E_{int}$.
   o Use TZVP, cc-pVDZ, cc-pVTZ, and aug-cc-pVDZ.
Energy decomposition analysis

\[ \Delta E^{\text{int}} = \Delta E^{\text{elec}} + \Delta E^{\text{pol}} + \Delta E^{\text{disp}} + \Delta E^{\text{exr}} \]

interaction    electronic    polarization    dispersion    exchange-repulsion

**Hartree-Fock**

\[ \Delta E^{\text{HF}} = \Delta E^{\text{elec}} + \Delta E^{\text{pol}} + \Delta E^{\text{ex}} + \Delta E^{\text{rep}} + \Delta E^{\text{disp}} \]

(empirical)

**Kohn-Sham**

\[ \Delta E^{\text{KS}} = \Delta E^{\text{elec}} + \Delta E^{\text{pol}} + \Delta E^{\text{ex}} + \Delta E^{\text{rep}} + \Delta E^{\text{disp}} \]
Exchange-repulsion energy

- Pauli repulsion energy:
  \[ E''_{\text{Pauli}} = \sum_{a,b} E''_{\text{Pauli}}(a, b) \]
  
a: orbitals of monomer A.
b: orbitals of monomer B.

- Orbital contribution to the repulsion energy:
  \[ E''_{\text{Pauli}}(a, b) = 2 S_{ba} \left\{ [(\epsilon_a + \epsilon_b)S_{ab} - 2(a|\hat{F}_A + \hat{F}_B|b) + 2T_{ab}] + \right. \]
  \[ \sum_{a'}(a|\hat{V}_B|a')S_{a'b} + \sum_{b'}(b|\hat{V}_A|b')S_{b'a} - \sum_{aa'}(aa'|bb')S_{b'a} \right\} \]

\( \hat{V}_A \) and \( \hat{V}_B \): nuclear attraction operators comprising all nuclei at molecule A and B respectively.
\( \hat{F} \): kinetic energy operator.
\( S \): overlap matrix between the occupied orbitals in the two systems.
Exchange-repulsion energy

• Exchange energy:

\[ E_{\text{exc}}(a, b) = \left\langle \Psi_{a(1)} \Psi_{b(1)} \left\lvert \frac{1}{r_{12}} \right\rvert \Psi_{a(2)} \Psi_{b(2)} \right\rangle \]

• Exchange repulsion energy:

\[ E_{\text{exr}}(a, b) = E_{\text{exc}}(a, b) + E''_{\text{Pauli}}(a, b) \]
N$_2$-He and Cl$_2$-He

Description of the system

Figure 1: Left: initial position. Middle: final position when the He is on the x-axis. The final position when the He is on the y-axis is the same as the photo on the right but on the y-axis. Right: final position when the He is on the z-axis.
N$_2$-He EDA

Hartree-Fock calculation

**Figure 2:** B-LYP, aug-cc-pVDZ. EDA representation. He shifted on the z-axis.

**Figure 3:** Zoom of figure 2.
**N₂-He exchange-repulsion energy**

### Basis sets quality

![Figure 4: N₂-He, representation of basis sets behaviour when He is shifted on the x-axis.](image)
N$_2$-He exchange-repulsion energy

Orbitals studied

Figure 5: Seven molecular orbitals of N$_2$.

Figure 6: 1s He orbital.
Results

**Figure 7:** Representation of $E_{\text{exr}}(E_h)$ vs distance ($\text{Å}$). He is shifted along the x-axis.

**Figure 8:** Zoom of figure 7.

**Figure 9:** $1\pi_{ux}$ with the He 1s orbital when $x=4.0$ Å.
Cl$_2$-He exchange-repulsion energy

Basis sets quality

**Figure 10**: Cl$_2$-He, representation of basis sets behaviour when He is shifted on the x-axis.
Orbitals studied

Figure 11: Seven molecular orbitals of Cl$_2$. 
Cl$_2$-He exchange repulsion energy

Results

**Figure 12**: Representation of $E_{\text{exr}}$ ($E_{\text{nh}}$) vs distance (Å). He is shifted along the x-axis.

**Figure 13**: Zoom of figure 12.

**Figure 14**: $2\pi_{u_x}$ of Cl$_2$ with the He 1s orbital when x=4.2 Å
Description of the system

Illustration 1: Planar PBI studied in this work.

Figure 15: Left: Initial position. Middle: PBI2 shifted along the y-axis. Right: PBI2 shifted along the z-axis.
PBI exchange-repulsion energy

Orbitals studied

**Figure 16:** the PBI 16 π molecular orbitals studied.
PBI exchange-repulsion energy

Results (z-axis)

Figure 17: Left: representation of $E_{\text{exr}}$ ($E_h$) vs distance (Å) when PB2 is shifted along the z axis. Right: orbitals which contribute most to the $E_{\text{exert}}$ when PB2 is shifted along the z axis.

Figure 18: Orbitals overlaped when z=2.4 Å. Left: both HOMO. Right: both HOMO -4. Bottom: both HOMO -3.

Figure 19: Overlap of both HOMO -1 when z=4.4 Å.
Results (y-axis)

Figure 20: Left: representation of $E_{\text{exr}} (E_r)$ vs distance (Å) when PB2 is shifted along the y-axis. Right: orbitals which contribute most to the $E_{\text{xert}}$ when PB2 is shifted along the y-axis.

Figure 21: Orbitals overlapped when $y=2.4$ Å. Top left: both HOMO. Top right: both HOMO -3. Bottom left: both HOMO -1. Bottom right: both HOMO -2.

Figure 22: Orbitals overlapped when $y=4.8$ Å. Left: both HOMO -13. Right: both HOMO -11.
Conclusions

- EDA: $E_{\text{exr}}$ is the one that contributes most to $E_{\text{int}}$.

- In the $\text{N}_2$-He system:
  - X-axis $\rightarrow 1\pi_u x$.

- In the $\text{Cl}_2$-He system:
  - X-axis $\rightarrow 2\pi_u x$.

- TVZP $\rightarrow$ good compromise. (aug-cc-pVDZ).

- cc-pVDZ underestimates $E_{\text{exr}}$ by 20%.

- In the PBI1-PBI2 system:
  - $E_{\text{exr}}$ shows an oscillatory behaviour. (4-6 mE$_h$ and 10 mE$_h$).
  - Z-axis $\rightarrow$ HOMO, HOMO -1, -3 and -4.

Orbital contributions to the exchange-repulsion energy of atomic and molecular aggregates

Bachelorarbeit der Mathematisch-Naturwissenschaftlichen Fakultät der EBERHARD-KARLS UNIVERSITÄT TÜBINGEN im Fach Chemie
angefertigt im Sommersemester 2018
im Arbeitskreis Prof. Dr. Reinhold F. Fink

vorgelegt von
Gemma Miralles Adrover
Tübingen, Juni 2018