Extracting chemical information from \textit{ab initio} calculations

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Outline

• Atom in a molecule
  • Hilbert Space vs 3D-space analysis
• Effective atomic density matrices: a formalism
• Chemical concepts from wavefunction analysis
  • Population analysis
  • Bond Orders
  • One and two-center energy components
    • The (difficult) DFT case
  • Effective atomic orbitals
• Applications
What is a molecule?

A system of electrons and nuclei (Physicist)

**Physical Information:**
Hamiltonian, Wavefunction,
Hermitian operators associated to observables and their expectation values

A system of bonded (interacting) atoms (Chemist)

**Chemical Information:**
Bonding interactions, steric repulsion, electron distribution
Functional groups $\rightarrow$ **Transferability** $\rightarrow$ **Predictions**

It is interesting to interpret the results of quantum chemical calculations in classical chemical terms

**DATA COMPRESION**
Hilbert-space vs 3D-space analysis

Decomposing different (molecular) quantities in terms of atomic (and diatomic) contributions.

Expectation values of operators
One or two-electron functions

Within the LCAO-MO approach

\[
\left\{\chi_{\mu}(\vec{r})\right\}\quad\text{Atomic centered one-electron basis} \\
\left\{\chi_{\mu}(\vec{r})\right\}_{\mu \in A}\quad\text{Atomic Hilbert subspace}
\]

\[
\varphi_{i}^{MO}(\vec{r}) = \sum_{\mu} c_{\mu i} \chi_{\mu}^{AO}(\vec{r}) \equiv \sum_{A} \sum_{\mu \in A} c_{\mu i} \chi_{\mu}^{AO}(\vec{r})
\]
Hilbert-space analysis

Expressions in the atomic orbital basis. For the 1-RDM

\[ \rho(\vec{r}) = \sum_{\mu} \sum_{\nu} D_{\mu\nu} \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) \]

\[ N = \int \rho(\vec{r}) d\vec{r} = \sum_{\mu} \sum_{\nu} D_{\mu\nu} \int \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) d\vec{r} = \sum_{\mu} \sum_{\nu} D_{\mu\nu} S_{\nu\mu} = \sum_{\mu} (DS)_{\mu\mu} \]

Classic example: Mulliken Population analysis

\[ N = \sum_A \sum_{\mu \in A} (DS)_{\mu\mu} = \sum_A N_A \quad \text{Gross atomic population} \]

\[ N = \sum_A \sum_B \sum_{\nu \in B} \sum_{\mu \in A} D_{\mu\nu} S_{\nu\mu} = \sum_A N_{AA} + \sum_A \sum_{B \neq A} N_{AB} \]

Net atomic population \quad \text{Overlap population}
3D-space partitioning: disjoint domains

Bader’s Topological atom

\[ \nabla \rho(\vec{r}_s) \cdot n(\vec{r}_s) = 0 \]

Zero-flux surface condition

Atoms defined in space by their atomic basin \( \Omega_A \)

Voronoi cells

The position of the interatomic planes can be adjusted according to empirical relative atomic radii.
3D space partitioning : Fuzzy atoms

For each atom $A$ and every point of the 3D space a weight function is introduced in order to measure to what extent the point belongs/contributes to the respective atom. The weight function for an atom $A$ should fulfil

$$w_A(\vec{r}) > 0 \quad \sum_A w_A(\vec{r}) = 1$$

Disjoint domains are a particular case where

$$w_A(\vec{r}) = 1 \quad \forall \vec{r} \in \Omega_A$$
3D space partitioning: Fuzzy atoms

**Hirshfeld atoms**

\[ w_A(\vec{r}) = \frac{\rho_A^{(0)}(\vec{r})}{\sum_B \rho_B^{(0)}(\vec{r})} \]

\[ \rho^{(0)}(\vec{r}) = \sum_B \rho_B^{(0)}(\vec{r}) \]

Promolecular density

**Iterative Hirshfeld**

\[ \int \rho_A^{(0)}(\vec{r}) d\vec{r} = N_A \]

Promolecular density integrates to the population of the fragment

**Becke atoms**

Fuzzy Voronoi cells

Stiffness from analytical polynomial

Size of the atom can be adjusted according to the position of the bcp of the density (Becke-$\rho$)
3D space analysis

For the 1-RDM

\[ N = \int \rho(\vec{r}) d\vec{r} = \int \left( \sum_A w_A(\vec{r}) \right) \rho(\vec{r}) d\vec{r} = \]

\[ = \sum_A \int w_A(\vec{r}) \rho(\vec{r}) d\vec{r} = \sum_A \int \rho_A(\vec{r}) d\vec{r} = \sum_A N_A \]

Atomic population

\[ \int f(\vec{r}) d\vec{r} \equiv \int w_A(\vec{r}) f(\vec{r}) d\vec{r} \]

Involve numerical integrations over the atomic basins

Computational efficiency is an issue: Fuzzy atoms
A formalism: effective atomic and diatomic RDM
For closed-shell single-determinant case

\[
\rho(\vec{r}, \vec{r}') = 2 \sum_i \phi_i^*(\vec{r}') \phi_i(\vec{r}) = \sum_\mu \sum_\nu D_{\mu\nu} \chi_\nu^*(\vec{r}') \chi_\mu(\vec{r})
\]

\[
\sum_A \rho^A(\vec{r}, \vec{r}') = \sum_{A,B} \rho^{AB}(\vec{r}, \vec{r}') = \rho(\vec{r}, \vec{r}')
\]

### Hilbert-space analysis

\[
\rho^A(\vec{r}, \vec{r}') = \sum_{\mu \in A} \sum_\nu D_{\mu\nu} \chi_\nu^*(\vec{r}') \chi_\mu(\vec{r})
\]

\[
\rho^{AB}(\vec{r}, \vec{r}') = \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu\nu} \chi_\nu^*(\vec{r}') \chi_\mu(\vec{r})
\]

### 3D-space analysis

\[
\rho^A(\vec{r}, \vec{r}') = w^A(\vec{r}) \rho(\vec{r}, \vec{r}')
\]

\[
\rho^{AB}(\vec{r}, \vec{r}') = w^A(\vec{r}) w^B(\vec{r}) \rho(\vec{r}, \vec{r}')
\]

POPULATION ANALYSIS

\[ \int \rho(\vec{r})d\vec{r} = N \]

\[ \int \rho^A(\vec{r})d\vec{r} = \sum_{\mu \in A} \sum_{\nu} D_{\mu \nu} \int \chi^*_\nu(\vec{r}) \chi_\mu(\vec{r})d\vec{r} = \sum_{\mu \in A} \sum_{\nu} D_{\mu \nu} S_{\nu \mu} = N_A \]

\[ \int \rho^{AB}(\vec{r})d\vec{r} = \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu \nu} S_{\nu \mu} = N_{AB} \]

\[ \int \rho_A(\vec{r})d\vec{r} = \int w_A(\vec{r}) \rho(\vec{r})d\vec{r} = N_A \]

\[ \int \rho_{AB}(\vec{r})d\vec{r} = \int w_A(\vec{r})w_B(\vec{r}) \rho(\vec{r})d\vec{r} = N_{AB} \]
BOND ORDERS

\[ \int \int \rho_x(\vec{r}, \vec{r}') d\vec{r} d\vec{r}' = N \]
\[ \rho_x(\vec{r}, \vec{r}') = \frac{1}{2} \rho(\vec{r}, \vec{r}') \rho(\vec{r}', \vec{r}) \]

\[ B_{AB} = \int \int \rho_x^{AB}(\vec{r}, \vec{r}') d\vec{r}' d\vec{r} = \int \int \rho^A(\vec{r}, \vec{r}') \rho^B(\vec{r}', \vec{r}) d\vec{r}' d\vec{r} \]

\[ B_{AB} = \sum_{\mu \in A} \sum_{\nu \in \sigma \in B} \sum_{\lambda} \sum \sum D_{\mu \nu} D_{\sigma \lambda} \int \int \chi^*_v(\vec{r}) \chi^*_\mu(\vec{r}') \chi^*_\lambda(\vec{r}') \chi^*_\sigma(\vec{r}) d\vec{r} d\vec{r}' = \]

\[ = \sum_{\mu \in A} \sum_{\nu \in \sigma \in B} \sum_{\lambda} \sum D_{\mu \nu} D_{\sigma \lambda} S_{\nu \sigma} S_{\lambda \mu} = \sum_{\mu \in A} \sum_{\sigma \in B} [DS]_{\mu \sigma} [DS]_{\sigma \mu} \]
BOND ORDERS

\[ \int \int \rho_x(\vec{r}, \vec{r}') d\vec{r} d\vec{r}' = N \]

\[ \rho_x(\vec{r}, \vec{r}') = \frac{1}{2} \rho(\vec{r}, \vec{r}') \rho(\vec{r}', \vec{r}) \]

\[ B_{AB} = \int \int \rho_x^{AB} (\vec{r}, \vec{r}') d\vec{r}' d\vec{r} = \int \int \rho^A (\vec{r}, \vec{r}') \rho^B (\vec{r}', \vec{r}) d\vec{r}' d\vec{r} \]

\[ B_{AB} = 4 \sum_i \sum_j \int \int w_A(\vec{r}) \varphi_i^*(\vec{r}) \varphi_i(\vec{r}') w_B(\vec{r}) \varphi_j^*(\vec{r}') \varphi_j(\vec{r}) d\vec{r} d\vec{r}' = \]

\[ = 4 \sum_i \sum_j S_{ij}^A S_{ji}^B \]

\[ S_{ij}^A = \int w_A(\vec{r}) \varphi_i^*(\vec{r}) \varphi_j(\vec{r}) d\vec{r} \equiv \int_{\Omega_A} \varphi_i^*(\vec{r}) \varphi_j(\vec{r}) d\vec{r} \]
MULTICENTER BOND INDICES

A three-center bond index can be obtained by decomposing the integral of a product of off-diagonal one-electron density matrices:

\[
\rho_x(\vec{r}, \vec{r}', \vec{r}'') = \rho(\vec{r}, \vec{r}') \rho(\vec{r}', \vec{r}'') \rho(\vec{r}'', \vec{r})
\]

\[
\rho_{x}^{ABC}(\vec{r}, \vec{r}', \vec{r}'') = \rho^A(\vec{r}, \vec{r}') \rho^B(\vec{r}', \vec{r}'') \rho^C(\vec{r}'', \vec{r})
\]

\[
I_{ABC} = \iiint \rho_{x}^{ABC}(\vec{r}, \vec{r}', \vec{r}'') \, d\vec{r} \, d\vec{r}' \, d\vec{r}'' = \sum_{\mu \in A} \sum_{\sigma \in B} \sum_{\lambda \in C} [DS]_{\mu \sigma} [DS]_{\sigma \lambda} [DS]_{\lambda \mu}
\]

\[
I_{ABC} = \iiint \rho_{x}^{ABC}(\vec{r}, \vec{r}', \vec{r}'') \, d\vec{r} \, d\vec{r}' \, d\vec{r}'' = 8 \sum_{i} \sum_{j} \sum_{k} S_{ij}^A S_{jk}^B S_{ki}^C
\]
Molecular Energy Decomposition

\[ E = \int \hat{h}(\vec{r}) \rho(\vec{r}, \vec{r}') |_{r=r'} \, d\vec{r} + \frac{1}{2} \int \int \frac{\rho^{(2)}(\vec{r}_1, \vec{r}_2)}{\mid \vec{r}_1 - \vec{r}_2 \mid} \, d\vec{r}_1 d\vec{r}_2 \]

Natural energetic counterpart of population and bond order analysis

\[ E = \sum_A E_A + \sum_A \sum_{B > A} E_{AB} \]

\[ \Delta E = \sum_A \left( E_A - E_A^0 \right) + \sum_A \sum_{B > A} E_{AB} \]
MOLECULAR ENERGY DECOMPOSITION

Exact decomposition of the Hartree-Fock energy  I. Mayer, CPL 382 265 (2003)

\[ E_A = \sum_{\mu, \nu \in A} D_{\mu \nu} <\nu| -\frac{1}{2} \nabla^2 |\mu> + \sum_{\mu \in A, \nu} D_{\mu \nu} <\nu| \frac{Z_A}{|\vec{r} - \vec{R}_A|} |\mu> + \]

\[ + \frac{1}{2} \sum_{\mu, \rho \in A} \sum_{\sigma, \nu} D_{\mu \nu} D_{\sigma \rho} [\mu \sigma | \nu \rho] - \frac{1}{4} \sum_{\mu, \rho \in A} \sum_{\sigma, \nu} D_{\mu \nu} D_{\sigma \rho} [\mu \sigma | \rho \nu] \]

\[ E_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu \nu} <\nu| -\frac{1}{2} \nabla^2 |\mu> + \sum_{\mu \in A, \nu} D_{\mu \nu} <\nu| \frac{Z_B}{|\vec{r} - \vec{R}_B|} |\mu> + \]

\[ + \sum_{\mu \in B, \nu} D_{\mu \nu} <\nu| \frac{Z_A}{|\vec{r} - \vec{R}_A|} |\mu> + \sum_{\mu \in A} \sum_{\rho \in B} \sum_{\sigma, \nu} D_{\mu \rho} D_{\sigma \nu} [\mu \sigma | \nu \rho] - \]

\[ - \frac{1}{2} \sum_{\mu \in A} \sum_{\rho \in B} \sum_{\sigma, \nu} D_{\mu \rho} D_{\sigma \nu} [\mu \sigma | \rho \nu] + \frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} \]
MOLECULAR ENERGY DECOMPOSITION

\[ V_A^{en} = \int \frac{Z_A}{|\vec{r} - \vec{R}_A|} \rho^A(\vec{r}) d\vec{r} \]

\[ V_A^{ee} = \frac{1}{2} \iiint \frac{\rho^A(\vec{r}_1) \rho^A(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 - \frac{1}{4} \iiint \frac{\rho^A(\vec{r}_1, \vec{r}_2) \rho^A(\vec{r}_2, \vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \]

\[ V_{AB}^{en} = \int \frac{Z_A}{|\vec{r} - \vec{R}_A|} \rho^B(\vec{r}) d\vec{r} + \int \frac{Z_B}{|\vec{r} - \vec{R}_B|} \rho^A(\vec{r}) d\vec{r} \]

\[ V_{AB}^{ee} = \iiint \frac{\rho^A(\vec{r}_1) \rho^B(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 - \frac{1}{2} \iiint \frac{\rho^A(\vec{r}_1, \vec{r}_2) \rho^B(\vec{r}_2, \vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \]

Vyboishchikov et al JCP 122, 24410 (2005)
MOLECULAR ENERGY DECOMPOSITION

\[ T_A = -\frac{1}{2} \int \nabla^2 \rho^{AA}(\vec{r}, \vec{r}') \mid_{r'=r} \, d\vec{r} \]
\[ T_{AB} = -\frac{1}{2} \int \nabla^2 \rho^{AB}(\vec{r}, \vec{r}') \mid_{r'=r} \, d\vec{r} \]

Alternatively

\[ T = -\frac{1}{2} \int \nabla^2 \sum_A \rho^A(\vec{r}, \vec{r}') \mid_{r'=r} \, d\vec{r} = \sum_A \sum_{\mu} \sum_{\nu} D_{\mu\nu} <\nu \mid \nabla^2 \mid \mu> = \sum_A T_A' \]

One and two-center energies are on the chemical scale (provided that diatomic kinetic energy terms are considered) but show counterintuitive behaviour for non equilibrium structures.
Computationally inexpensive.

Extension to post-HF methods (MP2,CID)

- Large negative interatomic contributions for bonded atoms that compensate for positive atomic promotion energies
- Small values for non-bonding interactions: either attractive or repulsive
- Potentially basis set dependent

<table>
<thead>
<tr>
<th>Molecule/bond</th>
<th>RHF kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₆</td>
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</tr>
<tr>
<td>C–C</td>
<td>-120.49</td>
</tr>
<tr>
<td>C–H</td>
<td>-108.20</td>
</tr>
<tr>
<td>C···H</td>
<td>4.38</td>
</tr>
<tr>
<td>H···H&lt;sub&gt;gem&lt;/sub&gt;</td>
<td>8.54</td>
</tr>
<tr>
<td>H···H&lt;sub&gt;vic gauch&lt;/sub&gt;</td>
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</tr>
<tr>
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<tr>
<td>CH–CH&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-326.65</td>
</tr>
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</table>
MOLECULAR ENERGY DECOMPOSITION: 3D-space

\[
E^{HF} = 2 \sum_{i=1}^{N/2} < \phi_i | \hat{h} | \phi_i > + \sum_{i,j=1}^{N/2} 2[\phi_i \phi_j | \phi_i \phi_j] - [\phi_i \phi_j | \phi_j \phi_i]
\]

\[
E^{HF}_A = 2 \sum_{i=1}^{N/2} < \phi_i | -\frac{1}{2} \nabla^2 - \frac{Z_A}{R_A} | \phi_i >_A + \sum_{i,j=1}^{N/2} 2[\phi_i \phi_j | \phi_i \phi_j]_{A,A} - [\phi_i \phi_j | \phi_j \phi_i]_{A,A}
\]

\[
E^{HF}_{AB} = -2 \sum_{i=1}^{N/2} \left( < \phi_i | \frac{Z_B}{R_B} | \phi_i >_A + < \phi_i | \frac{Z_A}{R_A} | \phi_i >_B \right) + \\
+ 2 \sum_{i,j=1}^{N/2} \left( 2[\phi_i \phi_j | \phi_i \phi_j]_{A,B} - [\phi_i \phi_j | \phi_j \phi_i]_{A,B} \right) + \frac{Z_A Z_B}{R_{AB}}
\]

AIM Salvador, Duran, Mayer, JCP 115 1153 (2001)

Fuzzy atoms Salvador, Mayer, JCP 120 5046 (2004)
MOLECULAR ENERGY DECOMPOSITION

Improved (!?) scheme for fuzzy atoms

\[ T = -\frac{1}{2} \sum_{i} \int \phi_{i}^{*}(\vec{r}) \nabla^{2} \phi_{i}(\vec{r}) d\vec{r} = \]

\[ = -\frac{1}{2} \sum_{A} \sum_{B} \sum_{i} \int w^{A}(\vec{r}) w^{B}(\vec{r}) \phi_{i}^{*}(\vec{r}) \nabla^{2} \phi_{i}(\vec{r}) d\vec{r} = \sum_{A} \sum_{B} T_{AB} \]

Connection with Hilbert-space expressions

Only possible for overlapping atomic definitions
Energy partitioning for Atoms in Molecules theory

Expensive 6D numerical integrations. Exchange part is bottleneck

\[
\left[ \varphi_i \varphi_j | \varphi_k \varphi_l \right]_{A,B} = \int_{\Omega_A} d\nu_1 \int_{\Omega_B} d\nu_2 \varphi_i^* \left( \vec{r}_1 \right) \varphi_j^* \left( \vec{r}_2 \right) \frac{1}{r_{12}} \varphi_k \left( \vec{r}_1 \right) \varphi_l \left( \vec{r}_2 \right)
\]

About 40,000 points per atomic domain were needed to get reasonable accuracy with PROAIM.

One and two-center energy (a.u.) components for H\textsubscript{2}, N\textsubscript{2}, BH and HF molecules using the 6-31G(d,p) basis set.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \varepsilon_a )</th>
<th>( \varepsilon_{ab} )</th>
<th>Total Energy</th>
<th>Bader's Energy</th>
<th>Exact Energy</th>
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<td>-1.13065</td>
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<td>-100.0128</td>
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### Energy partitioning for Fuzzy Atoms (Becke’s Atoms)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>$E_A$ [a.u.]</th>
<th>$\Delta E_A$ [kcal/mol]</th>
<th>Atomic Pair</th>
<th>$E_{AB}$ [a.u.]</th>
<th>$E_{AB}$ [kcal/mol]</th>
<th>$\Delta$ [kcal/mol]</th>
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<tbody>
<tr>
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<td>H,H</td>
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Energy partitioning for Fuzzy Atoms (Becke’s Atoms)

<table>
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<tr>
<th>Molecule</th>
<th>Atom</th>
<th>$E_A$ [a.u.]</th>
<th>$\Delta E_A$ [kcal/mol]</th>
<th>Atomic</th>
<th>$E_{AB}$ [a.u.]</th>
<th>$E_{AB}$ [kcal/mol]</th>
<th>$\Delta$ [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_6$</td>
<td>C</td>
<td>-37.5973</td>
<td>50.1</td>
<td>C,C</td>
<td>-0.1777</td>
<td>-111.5</td>
<td>0.4</td>
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<tr>
<td></td>
<td>H</td>
<td>-0.4722</td>
<td>16.3</td>
<td>C,H</td>
<td>-0.1575</td>
<td>-98.8</td>
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<tr>
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<td>C</td>
<td>-37.6182</td>
<td>37.0</td>
<td>C,C</td>
<td>-0.2243</td>
<td>-140.8</td>
<td>-1.6</td>
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<tr>
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<td>14.8</td>
<td>C,H</td>
<td>-0.1580</td>
<td>-99.1</td>
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<td>21.5</td>
<td>C,C</td>
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<td>-0.4759</td>
<td>14.0</td>
<td>C,H</td>
<td>-0.1549</td>
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<td>C</td>
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<td>39.74</td>
<td>C,C</td>
<td>-0.1796</td>
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<td>C,H</td>
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<td>-96.9</td>
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<tr>
<td>$C_{60}$</td>
<td>C</td>
<td>-37.5775</td>
<td>62.5</td>
<td>C,C(6,6)</td>
<td>-0.1723</td>
<td>-108.1</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C,C(5,6)</td>
<td>-0.1557</td>
<td>-97.7</td>
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</tr>
</tbody>
</table>
Practical Implementation

- Programs ([http://occam.chemres.hu/programs](http://occam.chemres.hu/programs)) use Gaussian’s FChk file as input.

- Becke’s multicenter numerical integration.

- Weight factors defined by Becke with atomic radii from Koga et al. Many fuzzy atom definition are possible (Hirshfeld, Hirshfeld-I,...).

- Typical settings: 30x110 points/atom grid for the one-electron integrations.

- 6D double numerical integration are be very expensive and main source of error. A good accuracy can be achieved with a modest grid of ca 5800 points/atom by rotating the grid set. A grid of ca 3000 points is sufficient for the one electron part.
Molecular energy decomposition schemes

The DFT case
Hartree-Fock vs DFT exchange energy

For a closed-shell single-determinant wavefunction

\[ E_{x}^{HF} = -\frac{1}{4} \int \int \frac{\rho(\vec{r}, \vec{r}')}{||\vec{r} - \vec{r}'||} \rho(\vec{r}', \vec{r}) \, d\vec{r} d\vec{r}' \]

\[ E_{x} = \int \eta_{x}[\rho(\vec{r})] \, d\vec{r} = \int \varepsilon_{x}[\rho(\vec{r})] \rho(\vec{r}) \, d\vec{r} \]

\[ \eta_{x}[\rho(\vec{r})] \]
Exchange energy density

\[ \varepsilon_{x}[\rho(\vec{r})] \]
Exchange energy density per electron (EEDE)
How do the HF and DFT-based exchange energy density and exchange energy density per electron compare?

Hartree-Fock exchange energy density

\[ \eta_x^{HF} (\vec{r}) \equiv \eta_x^{HF} [\rho(\vec{r}, \vec{r}')] = -\frac{1}{4} \int \frac{\rho(\vec{r}, \vec{r}')\rho(\vec{r}', \vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' \]

Hartree-Fock exchange energy density per electron

\[ \varepsilon_x^{HF} (\vec{r}) \equiv \varepsilon_x^{HF} [\rho(\vec{r}, \vec{r}')] = -\frac{1}{4 \rho(\vec{r})} \int \frac{\rho(\vec{r}, \vec{r}')\rho(\vec{r}', \vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' \]

\[ \varepsilon_x^{HF} (\vec{r}) = -\sum_i^{occ} \sum_j^{occ} \frac{\varphi_i^*(\vec{r})\varphi_i (\vec{r})}{\rho(\vec{r})} \int \frac{\varphi_i^*(\vec{r}')\varphi_j (\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \]
Exchange energy density for H$_2$
Exchange energy density per electron for H\textsubscript{2}
Exchange energy density per electron for $N_2$
• Qualitative differences on the EEDE values for H atoms are attributed to the absence of core electrons for the hydrogen.

• For heavy atoms the shape of both density functions is similar deeper values at the atomic positions for the DFT approximations.

We should be able to extract similar chemical picture in the DFT case (except possibly for core-less atoms such as H).
Diatomic HF exchange energy components

\[
E_{x,AB}^{HF} = -\frac{1}{2} \int \int \frac{\rho_A(\vec{r}, \vec{r}') \rho_B(\vec{r}', \vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'
\]

\[
E_{x,AB}^{HF} = \int \epsilon_{x, A}^{HF}(\vec{r}) \rho_B(\vec{r}) d\vec{r} + \int \epsilon_{x, B}^{HF}(\vec{r}) \rho_A(\vec{r}) d\vec{r}
\]

\[
\epsilon_{x, A}^{HF} [\rho (\vec{r}, \vec{r}'); \omega_A (\vec{r}')] = -\frac{1}{4 \rho(\vec{r})} \int \frac{\rho(\vec{r}, \vec{r}') \rho_A(\vec{r}', \vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}'
\]

\[
\epsilon_x^{HF} [\rho (\vec{r}, \vec{r}')] = \epsilon_x^{HF} \left[ \sum_A \rho_A(\vec{r}, \vec{r}') \right] = \sum_A \epsilon_x^{HF} [\rho_A (\vec{r}, \vec{r}')] = \sum_A \epsilon_{x, A}^{HF} (\vec{r})
\]

This is not the case for DFT approximations of the exchange energy
Diatomic DFT exchange energy components

Hilbert-space decomposition

Vyboishchikov et al JCP 122, 24410 (2005)

\[ E_{xc,AB} = \int \varepsilon_{xc,A}(\vec{r}) \rho_B(\vec{r}) \, d\vec{r} + \int \varepsilon_{xc,B}(\vec{r}) \rho_A(\vec{r}) \, d\vec{r} \]

\[ w(\vec{r}) \varepsilon_{xc}(\vec{r}) \approx \sum_{\mu} \xi_{\mu} \chi_{\mu}(\vec{r}) \]

\[ w(\vec{r}) \equiv \rho^{1/2}(\vec{r}) \]

\[ \varepsilon_{xc,A}(\vec{r}) \approx \sum_{\mu \in A} \frac{\xi_{\mu} \chi_{\mu}(\vec{r})}{w(\vec{r})} \]

Diagram: Graph showing the exchange-correlation energy as a function of distance.
Diatomic DFT exchange energy components

\[ \varepsilon_{x,A}(\vec{r}) = w_A(\vec{r}) \varepsilon_x [\rho(\vec{r})] \]

\[ E_{x,AB} = 2 \int w_A(\vec{r}) \varepsilon_x [\rho(\vec{r})] w_B(\vec{r}) \rho(\vec{r}) \, d\vec{r} = 2 \int w_A(\vec{r}) w_B(\vec{r}) \eta_x [\rho(\vec{r})] \, d\vec{r} \]

\[ E_x = \int \left( \sum_A w_A(\vec{r}) \right) \left( \sum_B w_B(\vec{r}) \right) \eta_x [\rho(\vec{r})] \, d\vec{r} = \sum_A \sum_B \int w_A(\vec{r}) w_B(\vec{r}) \eta_x [\rho(\vec{r})] \, d\vec{r} \]

Results are neither conceptually nor numerically satisfactory

No diatomic exchange for non-overlapping domains (AIM)
Exchange energy density per electron for CO

- R (a.u.)

- C
- O

HF Exch
B88
Two-center exchange energy density for CO

HF Exch

B88
Bond Order Density (BOD)

\[ \beta_{AB}(\mathbf{r}) = \frac{1}{2} \int \left( \rho_A(\mathbf{r}, \mathbf{r}') \rho_B(\mathbf{r}', \mathbf{r}) + \rho_B(\mathbf{r}, \mathbf{r}') \rho_A(\mathbf{r}', \mathbf{r}) \right) d\mathbf{r}' \]

\[ \downarrow \]

\[ \beta_{AB}(\mathbf{r}) = 2 \sum_{i}^{\text{occ}} \sum_{j}^{\text{occ}} \left( W_A(\mathbf{r}) S_{ij}^B + W_B(\mathbf{r}) S_{ij}^A \right) \varphi_i^* (\mathbf{r}) \varphi_j (\mathbf{r}) \]

The name “bond order density” has been proposed because this function integrates to the bond order index between the pairs of atoms A and B.

Actually, it represents the part of the total electron density that is used by the bonding interaction between atoms A and B through the exchange of their electrons.
Bond order density profile
The electron density actually involved in the bond is not solely localized in the interatomic region but is partially concentrated also in the regions close to the nuclei.

This observation is in full agreement with the character of the exchange interaction and stresses again the differences between bond orders and overlap populations.

It also accounts for the delocalization indices between non-bonded atoms (PDI)

\[
\rho(\bar{r}) \equiv \sum_A \sum_{B > A} \beta_{AB}(\bar{r}) = \sum_A \beta_{AA}(\bar{r}) + \frac{1}{2} \sum_A \sum_{B \neq A} \beta_{AB}(\bar{r})
\]
The BOD *does not vanish* when non-overlapping atomic domains are used.
Diatomic DFT exchange energy components (II)

\[ E_{x,AB} = \int \eta_x \left[ \beta_{AB}(\vec{r}) \right] d\vec{r} \]

The decomposition is not exact but one can regroup as a correction to the atomic contributions the effects due to the nonlinearity of the functional.

\[ E_{x,A} = \int w^A(\vec{r}) \eta_x \left[ \rho(\vec{r}) \right] d\vec{r} - \frac{1}{2} \sum_{B \neq A} E_{x,AB} \]

Alternatively (Cioslowski)

\[ E_{x,AB} = \int \eta_x \left[ \rho(\vec{r}) \right] d\vec{r} - \int \left[ \rho(\vec{r}) - \beta_{AB}(\vec{r}) \right] d\vec{r} \]
Diatomic exchange energy density profile
LDA vs Hartree-Fock diatomic exchange energy
(BLYP/6-31G**)
Becke88 vs Hartree-Fock diatomic exchange energy

\[ y = 1.124x + 0.052 \]

\[ R^2 = 0.993 \]
Becke88 vs Hartree-Fock atomic exchange (H atoms)
Effective atomic orbitals for fuzzy atoms
Effective atomic orbitals for fuzzy atoms

Salvador, Mayer, JCP 130 234106 (2009)

\[
\rho^{AA}(\vec{r}) = w^2_A(\vec{r}) \rho(\vec{r}) \quad \text{Net atomic population of atom/fragment A}
\]

\[
\rho^{AA}(\vec{r}) = \sum_i \nu_i^A \varphi_i^{A*}(\vec{r}) \varphi_i^A(\vec{r}) \quad \text{Natural atomic hybrids}
\]

\[
\varphi_i^A(\vec{r}) = N_i^A w_A(\vec{r}) \varphi_i(\vec{r}) \quad \text{Truncated renormalized canonic MO, but}
\]

\[
< \varphi_i^A(\vec{r}) | \varphi_j^A(\vec{r}) > \neq 0
\]
Effective atomic orbitals for fuzzy atoms

\[ Q_{ij} = \int \phi_i^*(\vec{r})w_A^2(\vec{r})\phi_j(\vec{r})d\vec{r} \quad \rightarrow \quad QU = U\Lambda \]

\[ \Lambda = \text{diag}\{\lambda_1, \lambda_2, \ldots\} \quad 0 \leq \lambda_i \leq 1 \]

\[ \phi_{i}^{loc}(\vec{r}) = \sum_{j} U_{ji}\phi_{i}(\vec{r}) \quad \text{Localized atomic orbitals} \]

\[ \phi_i^A(\vec{r}) = \frac{1}{\sqrt[\lambda_i]} w_A(\vec{r})\phi_{i}^{loc}(\vec{r}) \quad \text{Atomic hybrids} \quad \nu_i^A = 2\lambda_i \]

There seem to be as many effective orbitals that have considerable occupation numbers as orbitals in the classical minimal basis (except hypervalent compounds...
Alanine HF/cc-pVTZ

Iterative Hirshfeld

- N
- H
- C
- O
For single-determinant case and for disjoint domains (AIM) the localized atomic orbitals are identical to those originating from the DAFH before isopycnic transformation.

Truncated atomic hybrids for O atom on Ala
Applications: The rotational barrier of ethane
Hyperconjugation vs steric repulsion debate

Interactions/delocalizations between electrons of vicinal C-H bonds mainly through the C-C bond.

In an MO picture this corresponds to favorable two-electron two-orbital interactions between occupied C-H orbital of one methyl group and virtual antibonding C-H orbital of the other.

Antisymmetrization of a wave function originally formed by strictly localized descriptions of two methyl groups brought up to the final ethane geometry.
Hyperconjugation vs steric repulsion debate

Clearly, the two effects (and possibly some other ones) coexist in ethane so in order to quantify the magnitude of one of them one must be able to **switch off** the other in the model calculation.

Valence bond-theory $\rightarrow$ Steric repulsion

MO fragment models $\rightarrow$ Steric repulsion

Reference state $\rightarrow$ Hyperconjugation

**Energy Decomposition**

$$\Delta E_{\text{tot}} = \sum_A \Delta E_A + \sum_A \sum_{B \neq A} \Delta E_{AB}$$

- $\Delta E_{\text{tot}}$
- $\Delta E_C$
- $\Delta E_C$
- $\Delta E_{CH}$
- $\Delta E_{HH'}$
STO-6G

Pure sp³
STO-6G

Unrelaxed HF

Δ$E_{\text{tot}}$

Δ$E_C$

Δ$E_H$

Δ$E_{CC}$

Δ$E_{CH}$

Δ$E_{HH'}$
STO-6G

Relaxed HF

\[ \Delta E_{\text{tot}}, \Delta E_C, \Delta E_H, \Delta E_{CC}, \Delta E_{CH}, \Delta E_{HH} \]
The hyperconjugation/delocalization effects give rise to energy components (namely the enhancement of the C-C bond and the weakening of the C-H bonding energy) which are larger than the steric repulsion between the two methyl groups; that is the case even if simple SLMO's are used, due to nonorthogonality effects which mimic delocalization.

The relatively large terms originating from hyperconjugation cancel almost completely.

In that sense one may claim, that the simple picture of attributing the barrier to the repulsion between the hydrogen atoms is indeed legitimate.