A Chemical Bond From the Natural Orbitals for Chemical Valence (NOCV) Perspective

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Bonding Analysis Workshop 2015, 05, 18-22, Marburg
Experimental visualization chemical bond?

Atomic Force Microscopy

“Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy”

Bonding Analysis Workshop 2015, 05, 18-22, Marburg
Experimental seeing the chemical reaction at quantum level?

REPORT
Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions
Dimas G. de Oteyza, Patrick Gorman, Yen-Chia Chen, Sebastian Wickenburg, Alexander Riss,
Duncan J. Mowbray, Grisha Etkin, Zahra Pedramrazi, Hsin-Zon Tsai, Angel Rubio, Michael F. Crommie,
and Felix R. Fischer
Science 21 June 2013: 1434-1437. Published online 30 May 2013

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Examples of theoretical quantities for visualization of chemical bond

Bader theory of Atoms-in-Molecules

- electron density divided in physical space, based on derivatives and critical points of electron density

R.F.W. Bader, "Theory of Atoms in Molecules"
http://www.chemistry.mcmaster.ca/faculty/bader/aim/
Quantum Theory of Atoms in Molecules (QTAIM) by Richard Bader

*start- electron (charge) density from wavefunction \( \psi \)
(N electrons, with positions \( x_1, x_2, \ldots, x_N \)):

\[
\rho(\vec{r}) = N \int \cdots \int |\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)|^2 \, ds_1 \, d\vec{x}_2 \ldots d\vec{x}_N
\]

\[
\rho(\vec{r} \to \infty) = 0
\]

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

charge density is delocalized over the whole molecule,

how then extract any information about bonding between selected atoms C-C or C-H?
*construct the Hessian matrix (second derivatives of density) and perform diagonalization to obtain various „critical points”.

Critical points of $\rho(r)$: maximum, minimum or saddle where the gradient of $\rho(r)$ vanish ($\nabla \rho(r_c) = 0$), where

$$\nabla \rho(r) = \frac{\partial \rho(r)}{\partial x} u_x + \frac{\partial \rho(r)}{\partial y} u_y + \frac{\partial \rho(r)}{\partial z} u_z$$

Hessian of $\rho$ at a critical point: $\Lambda(r_c) = \begin{pmatrix}
\frac{\partial^2 \rho}{\partial x^2} & \frac{\partial^2 \rho}{\partial x \partial y} & \frac{\partial^2 \rho}{\partial x \partial z} \\
\frac{\partial^2 \rho}{\partial y \partial x} & \frac{\partial^2 \rho}{\partial y^2} & \frac{\partial^2 \rho}{\partial y \partial z} \\
\frac{\partial^2 \rho}{\partial z \partial x} & \frac{\partial^2 \rho}{\partial z \partial y} & \frac{\partial^2 \rho}{\partial z^2}
\end{pmatrix}$

The Hessian matrix is real and symmetric

=> we can put it in a diagonal form:

$$\Lambda = \begin{pmatrix}
\frac{\partial^2 \rho}{\partial x^2} & 0 & 0 \\
0 & \frac{\partial^2 \rho}{\partial y^2} & 0 \\
0 & 0 & \frac{\partial^2 \rho}{\partial z^2}
\end{pmatrix}$$

$$\begin{pmatrix}
\lambda_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{pmatrix}$$

$$r = r_c$$

eigenvalues = curvatures of $\rho$
Quantum Theory of Atoms in Molecules (QTAIM) by Richard Bader, ethane($C_2H_6$), water($H_2O$), sodium chloride ($NaCl$), benzene($C_6H_6$) examples

- Ethane: $C C$ with $\lambda_{\text{BCP}} = -0.31 \text{a.u.}$ (covalent bond) and $0.2068 \text{a.u.}$, $0.2573 \text{a.u.}$
- Water: $H H$ with $\lambda_{\text{BCP}} = +0.16 \text{a.u.}$ (ionic bond)
- Sodium chloride: $Na Cl$ with $\lambda_{\text{BCP}} = 0.03 \text{a.u.}$

- Benzene ($C_6H_6$) with ring-critical point (RCP) (3,+1) and $0.2669 \text{a.u.}$

- Two eigenvalues positive (in plane axes) and one negative (perpendicular)

- $\pi$-electrons
Examples of theoretical quantities for visualization of chemical bond

**Differential density (deformation density)**

\[ \Delta \rho(r) = \rho_{mol.}(r) - \sum_{i=1}^{N_{at}} \rho_{at.}^i(r) \]

Positive values describe the point of density accumulation in the molecule (relative to isolated atoms). When the molecule is formed from atoms the density flows from the area of negative value towards the area with positive value.
Formation of chemical bond in $H_2$ – $\Delta \rho$ based picture

1. Start from promolecular state (atom/fragments)

\[ \rho_H = 1s^2 \]

\[ \rho_{H2} \]

\[ \Delta \rho = \rho_{H2} - 2\rho_H \]

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

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Experimental visualization of chemical bond vs calculated $\Delta \rho$

Tetramer of 8-hydroxyquinoline connected via hydrogen bonds

$\Delta \rho = \rho_{\text{molecule}} - \rho_1 - \rho_2 - \rho_3 - \rho_4$

Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy”
Formation of chemical bond in hem-CO; $\Delta \rho$ based picture

In the A/B resolution (fragment / ligand):

$$\Delta \rho = \Delta \rho_{AB}(r) - \rho_A(r) - \rho_B(r)$$
Formation of chemical bond in hem-CO; $\Delta \rho$ based picture

**Heme - CO**

Deformation density description

difficult to extract $\sigma$- or $\pi$-contributions of Fe-C bond

The Natural Orbitals for Chemical Valence (NOCV)

NOCV’s \( (\psi_i = \sum_i C_{ij} \lambda_i) \) diagonalize the deformation density matrix:

\[
\Delta P C_i = \nu_i C_i \quad ; \quad i = 1, M
\]

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 \( \Delta \rho \):

\[
\Delta \rho(r) = \sum_{k=1}^{M} \nu_k \psi_k^2(r)
\]

useful qualitative data by inspection of the sign of \( \Delta \rho \): negative (outflow), positive (inflow) of density

NOCV’s are in pairs:

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


The contours of the deformation density ($\Delta \rho$) and the contributions from the pairs of complementary orbitals for the heme/CO system

$$\Delta \rho(r) = \sum_{i=1}^{n} v_i \phi_i^2(r)$$

$\Delta \rho_1 = -0.74 * \phi_{-1}^2 + 0.74 * \phi_1^2$

$\Delta \rho = \Delta \rho_1 + \Delta \rho_2 + \Delta \rho_3$

$\Delta \rho_2 = -0.52 * \phi_{-2}^2 + 0.52 * \phi_2^2$

$\Delta \rho_3 = -0.52 * \phi_{-3}^2 + 0.52 * \phi_3^2$
A combination of ETS/EDA and NOCV - (ETS-NOCV)

ETS/EDA:  
\[-D_e = \Delta E_{\text{total}} = \Delta E_{\text{dist}} + \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}\]

\[\Delta E_{\text{orb}} = \sum_{\lambda} \sum_{\mu} \Delta P_{\lambda\mu}^\text{orb} F_{\lambda\mu}^\text{TS}\]

NOCV:  
\[\Delta \rho_{\text{orb}}^\text{orb}(r) = \sum_{k=1}^{N/2} v_k [ -\psi_k^2(r) + \psi_k^2(r) ] = \sum_{k=1}^{N/2} \Delta \rho_k(r)\]

ETS-NOCV:  
\[\Delta E_{\text{orb}} = \text{Tr}(\Delta P_{\text{orb}}^\text{orb} F_{\text{TS}}) = \text{Tr}(C^+ \Delta P_{\text{orb}}^\text{orb} C C^+ F_{\text{TS}} C) = \sum_{k=1}^{N/2} v_k [-F_{-k,-k}^\text{TS} + F_{k,k}^\text{TS}] = \sum_{k=1}^{N/2} \Delta E_{\text{orb}}^k\]

\[\Delta E_{\text{orb}}^k = \sum_{k=1}^{M/2} v_k [-F_{-k}^\text{TS} + F_{-k}^\text{TS}] = \sum_k \Delta E_{\text{orb}}^k\]

Energetic estimation of \(\Delta \rho_k\)

Dative bonds – systems with symmetry

\[(\text{CO})_5\text{Cr=CH}_2\]

\[\Delta E_{\pi \text{orb}} = -46.3\]

\[\Delta E_{\sigma \text{orb}} = -51.9\]

Donor/acceptor properties of ligands for Ni(NH$_3$)$_3$ X complexes:

\[\sigma: \text{CN}^- > \text{PH}_3 > \text{NH}_3 > \text{C}_2\text{H}_4 > \text{CS} > \text{CO} > \text{N}_2 > \text{NO}^+\]

\[\pi: \text{NO}^+ > \text{CS} > \text{CO} > \text{N}_2 > \text{C}_2\text{H}_4 > \text{PH}_3 > \text{CN}^- > \text{NH}_3\]

Experimental visualization of chemical bond vs calculated $\Delta \rho$

Tetramer of 8-hydroxyquinoline connected via hydrogen bonds

$\Delta \rho = \rho_{\text{molecule}} - \rho_1 - \rho_2 - \rho_3 - \rho_4$

“Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy”


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ETS-NOCV- tetra-8-hydroxyquinoline

$\Delta \rho_1$

$\Delta E_{orb}(1) = -12.2 \text{ kcal/mol}$

$\Delta \rho_2$

$\Delta E_{orb}(2) = -6.3 \text{ kcal/mol}$
ETS-NOCV- tetra-8-hydroxyquinoline

$\Delta E_{\text{orb}(3)} = -2.0$ kcal/mol

$\Delta E_{\text{orb}(4)} = -1.0$ kcal/mol
Dative Bond NH$_3$ $\rightarrow$ BH$_3$ - Calculations

- Define closed shell fragments, NH$_3$ and BH$_3$
- Run SP calculations to get the fragment MO’s
- Run SP ETS-NOCV calculations for whole molecule in the basis of previously calculated fragment MO’s

In order to perform EDA/ETS in NOCV resolution one must add the keywords:

**ETSNOCV**
**PRINT ETSLOWDIN**

and **NOSYM** must be used
Dative Bond $\text{NH}_3 \rightarrow \text{BH}_3$ - Calculations

\[ \Delta \rho_1 \]
\[ \Delta q_1 = 0.564 \]
\[ \Delta E_{orb}^1 (A - B) = -65.5 \text{kcal/mol} \]

\[ \Delta \rho_2 \]
\[ \Delta q_2 = 0.136 \]
\[ \Delta E_{orb}^2 (A - B) = -2.3 \text{kcal/mol} \]

\[ \Delta \rho_3 \]
\[ \Delta q_3 = 0.136 \]
\[ \Delta E_{orb}^3 (A - B) = -2.3 \text{kcal/mol} \]

\[ \Delta \rho_{\text{rest}} \]
\[ \Delta q_{\text{rest}} = 0.211 \]
\[ \Delta E_{orb}^{\text{rest}} (A - B) = -5.7 \text{kcal/mol} \]

Inter-Molecular-Hydrogen Bonds

**Adenine-Thymine**

<table>
<thead>
<tr>
<th>Energy Component</th>
<th>Value (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{\text{int}}$</td>
<td>-13.0</td>
</tr>
<tr>
<td>$\Delta E_{\text{orb}}$</td>
<td>-22.0</td>
</tr>
<tr>
<td>$\Delta E_{\text{Pauli}}$</td>
<td>38.7</td>
</tr>
<tr>
<td>$\Delta E_{\text{prep}}$</td>
<td>2.1</td>
</tr>
<tr>
<td>$\Delta E_{\text{elstat}}$</td>
<td>-31.9</td>
</tr>
<tr>
<td>$\Delta H_{\text{total}}$</td>
<td>-12.1 (experiment)</td>
</tr>
<tr>
<td>$\Delta E_{\text{total}}$</td>
<td>-13.2 (other theoretical results)</td>
</tr>
</tbody>
</table>

$\Delta E_{\text{orb}} = -22.0$

**N$\rightarrow$σ*(H-N)**

$\Delta E_{\sigma_1} = -12.6$ kcal/mol

H-N covalency!

**O$\rightarrow$σ*(H-N)**

$\Delta E_{\sigma_2} = -5.8$

Rafal Kurczab, Mariusz P. Mitoraj, Artur Michalak and Tom Ziegler

Hydrogen Bond A-T Calculations

- Define closed shell fragments, Adenine and Thymine
- Run SP calculations to get the fragment MO’s
- Run SP ETS-NOCV calculations for whole molecule in the basis of previously calculated fragment MO’s
Covalent bonds

**CH₃-CH₃**

$\Delta E_{\sigma}^{\text{orb}} = -173.4 \text{kcal/mol}$

$\Delta \rho_{\sigma}^{\text{orb}} = \Delta \rho_{\sigma,\alpha}^{\text{orb}} + \Delta \rho_{\sigma,\beta}^{\text{orb}}$

$\Delta E_{\pi x}^{\text{orb}} = -7.2 \text{kcal/mol}$

$\Delta \rho_{\pi x}^{\text{orb}}$

$\Delta E_{\pi y}^{\text{orb}} = -7.2 \text{kcal/mol}$

$\Delta \rho_{\pi y}^{\text{orb}}$

**CH₂=CH₂**

$\Delta E_{\sigma}^{\text{orb}} = -220.6 \text{kcal/mol}$

$\Delta \rho_{\sigma}^{\text{orb}}$

$\Delta E_{\pi 1}^{\text{orb}} = -67.8$

$\Delta \rho_{\pi 1}^{\text{orb}}$

**GeH₂=GeH₂**

$\Delta E_{\sigma}^{\text{orb}} = -75.2 \text{kcal/mol}$

$\Delta \rho_{\sigma}^{\text{orb}}$

$\Delta E_{\pi 1}^{\text{orb}} = -37.0$

$\Delta \rho_{\pi 1}^{\text{orb}}$

**H₃CC≡CCH₃**

$\Delta E_{\sigma}^{\text{orb}} = -209.7 \text{kcal/mol}$

$\Delta \rho_{\sigma}^{\text{orb}}$

$\Delta E_{\pi 1}^{\text{orb}} = -88.8$

$\Delta \rho_{\pi 1}^{\text{orb}}$

$\Delta E_{\pi 2}^{\text{orb}} = -88.8$

$\Delta \rho_{\pi 2}^{\text{orb}}$
Quadruple bond; $\text{Re}_2\text{Cl}_8^{2-}$

- $\sigma [-84.3 \text{ kcal/mol}]$
- $\pi_1 [-65.5 \text{ kcal/mol}]$
- $\pi_2 [-65.5 \text{ kcal/mol}]$
- $\delta [-1.3 \text{ kcal/mol}]$
Ethane Built from two methyl radicals

1. Define CH₃ regions (uneven number of electrons);
2. Run SP RESTRICTED ! Calculations for CH₃ fragments to get the fragment MO’s; (1/2α + 1/2β electrons for SOMO of CH₃)
3. Use **fragoccupations** keyword in order to keep the right occupations for each CH₃
   fragoccupations
   f₁ A 5 // 4
   subend
   f₂ A 4 // 5
   subend
   End
4. Run SP ETS-NOCV calculations for whole molecule in the basis of previously calculated fragment MO’s -alpha-and beta-NOCV’s
Agostic intramolecular RH---Metal interaction

Ni-diimine cationic Brookhart model catalyst

Mariusz P. Mitoraj, Artur Michalak and Tom Ziegler „On the Nature of the Agostic Bond between Metal Centers and β-Hydrogen Atoms in Alkyl Complexes. An Analysis Based on the Extended Transition State Method and the Natural Orbitals for Chemical Valence Scheme (ETS-NOCV)”

Organometallics, 2009, 28 (13), pp 3727
Role of Agostic Interaction in Hydride Transfer – Release of Ethene Molecule

-75.8 kcal/mol
ETS-NOCV in a description chemical reactions

Diels – Alder cycloaddition: ethene + 1,3-butadiene

Δρ₁ trajectory

Dehydrogenation of Ammonia Borane by Ru-complex
Mechanism obtained from DFT/CPMD calculations

Organometallics, 2013, 32, 4103-4113
Ammonia Borane binding to the Ru-catalyst

AB binds to NCMe of the catalyst by BH-HC and BH-π interactions
Halogen Bonding CF$_3$I---NH$_3$ from ETS-NOCV perspective

\[\Delta E_{\text{total}} = -7.4 \text{kcal/mol}\]
\[\Delta E_{\text{orb}} = -9.2\]
\[\Delta E_{\text{elstat}} = -15.2\]
\[\Delta E_{\text{Pauli}} = 18.3\]

Charge outflow, increase positive charge

ETSNOCV(red-outflow,blue-inflow) -8.3 kcal/mol

N-I covalency

charge accumulation, increase s-character
(pointed out by prof. Grabowski)

Domination of the electrostatic factor is due to the presence of σ-hole on iodine atom:

$$\Delta E_{\text{total}} = -7.4 \text{kcal/mol}$$
$$\Delta E_{\text{orb}} = -9.2$$
$$\Delta E_{\text{elstat}} = -15.2$$
$$\Delta E_{\text{Pauli}} = 18.3$$

ETS-NOCV perspective, $\sigma$-hole

Electrostatic potential picture

ETS-NOCV picture

$\sigma$-hole

$\sigma$(C-F) bond

Hands-on-session agenda

**Exercise 1.** Getting started with the simple bond formed between ammonia and borane – typical *donor–acceptor* bond $\text{H}_3\text{N} \rightarrow \text{BH}_3$.

**Exercise 2.** Why ammonia (with one lone electron pair) can form the bond with iodine (containing three lone pairs)? ($\text{H}_3\text{N} \cdots \text{ICF}_3$)

**Exercise 4.** Analysis of carbon–carbon bond in ethane $\text{H}_3\text{C} \uparrow + \downarrow \text{CH}_3$.

**Exercise 5.** Analysis of $\text{C} = \text{C}$ bond in ethene $\text{H}_2\text{C} \uparrow \uparrow + \downarrow \downarrow \text{CH}_2$

**Exercise 6.** Analysis of quadruple bond between Re atoms in $[\text{Cl}_4\text{ReReCl}_4]^{2-}$ ($\text{Cl}_4\text{Re} \uparrow \uparrow \uparrow \uparrow + \downarrow \downarrow \downarrow \downarrow \text{Re Cl}_4$) (Cotton Re complex).

**Exercise 7.** Analysis of weak homopolar dihydrogen interaction $\text{CH} \cdots \text{HC}$ formed between closed shell two dodecahedran hydrocarbon units:
**Exercise 8.** Interaction between four monomers of tetra-hydroxoquinoline bonded via O\(^{-}\)HO hydrogen bonds. All necessary input files (quin1.in, quin2.in, quin3.in, quin4.in and Quin-tetramer-NOCV.in) are in the directory /home/baw/baw-workshop/mitoraj/Exercise8. Compare the most important NOCV-deformation density channels to the experimental picture of bonding emerging from the tunneling microscope:

(Science, 2013, 342, 611-614)
Thank You very much for Your Attention!