New tools for chemical bonding analysis

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All these slides and other material will be uploaded at:
http://iQC.udg.edu/~eduard/master.html

There, you will also find notes of this course.

Many files output and other data in beta.udg.edu:
/users/eduard/master
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- Wavefunction: \( \Psi(1, 2, \ldots, N) \)
- Atomic orbitals: \( \phi_\mu(\mathbf{1}) \)
- Molecular orbitals: \( \phi_i(\mathbf{1}) \)
- Vectors are indicated in bold or using an superscripted arrow, e.g., \( \mathbf{n} = \vec{n} = (n_x, n_y, n_z) \). Exception: \( \nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \)
"The theory behind chemistry, which atoms combine with which at which rate and so forth, is in principle theoretical chemistry deeply, is physics."

[Audience laughs]

"It is not a joke, it is a direct chemists would admit. That’s exactly their point of view, that atoms in deepest level is physics, except that the atoms have some many particles that is very hard to calculate what is going to happen so they have to use a lot of empirical rules to help them...

Richard Feynmann
Lecture on Quantum ElectroDynamics
Auckland (1979)
The simplest (antisymmetric) wavefunction is the Slater determinant:

\[
\psi_K(1, 2, \ldots, n) = \frac{1}{\sqrt{N}} \left| \begin{array}{cccc}
\phi_{k_1}(1) & \phi_{k_1}(2) & \cdots & \phi_{k_1}(n) \\
\phi_{k_2}(1) & \phi_{k_2}(2) & \cdots & \phi_{k_2}(n) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_{k_N}(1) & \phi_{k_N}(2) & \cdots & \phi_{k_N}(n)
\end{array} \right|
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The HF and KS-DFT wavefunction are single-determinant wavefunctions.

The exact wavefunction can be obtained from a linear combination of Slater determinants,

$$\psi(1, 2, \ldots, n) = \sum_{K=1}^{N} c_K \psi_K(1, 2, \ldots, n) \quad \text{with} \quad \sum_{K=1}^{N} |c_K|^2 = 1$$
**The Born Interpretation**

**Born:** the probability of finding one electron at $d_1$ ($dr_1$ with $\sigma_1$) is

$$P(1)d_1 = \int d_2 \int d_3 \ldots \int d_n |\Psi(1, 2, \ldots, N)|^2 d_1$$
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\rho(1) = N \cdot P(1)
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regardless the position of the other $N-1$ electrons.

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$$\rho(1) = N \cdot P(1)$$

that integrated over $\Omega$ it gives the average number of electrons in $\Omega$.

$$N_\Omega \equiv \langle \Psi | \hat{N} | \psi \rangle_\Omega = \langle \Psi | \sum_i a_i^\dagger a_i | \psi \rangle_\Omega = N \cdot P(\Omega) = \int_\Omega \rho(1)d_1$$
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This is the basis of electron population analysis.
The electron density is the central quantity in DFT and QTAIM.
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$$\rho(\mathbf{1}) = \sum_i^N \phi_i^*(\mathbf{1})\phi_i(\mathbf{1}) = \sum_i^N |\phi_i(\mathbf{1})|^2$$
The first-order reduced density matrix (1-RDM) reads:

$$\rho_1(1; 1') = N \int d_2 d_3 \ldots \int d_n \Psi^*(1, 2, \ldots, N) \Psi(1', 2, \ldots, N)$$
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It does not have any probabilistic interpretation but it can be also written in terms of molecular orbitals:

\[ \rho_1(1;1') = \sum_{i}^{N} \phi_i^*(1)\phi_i(1') \]
The Pair Density

Born’s interpretation can be further extended to include electron pairs,

$$P(1, 2)d_1d_2 = \int d_3 \ldots \int d_n |\psi(1, 2, \ldots, N)|^2 d_1d_2$$

$P(1, 2)$ is the probability of finding two electrons, one at $1$ and the other at $2$, regardless of the position of the other $N - 2$ electrons.
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By an analogous procedure we can obtain $n$-densities ($n > 2$).
The pair density can be easily written in terms of the 1-RDM for single-determinant methods

\[
\rho_2(1, 2) = \begin{vmatrix} \rho(1) & \rho_1(1; 2) \\ \rho_1(2; 1) & \rho(2) \end{vmatrix}
\]

which can be expanded in terms of molecular orbitals

\[
\rho_2(1, 2) = \sum_i \sum_j \phi_i^*(1) \phi_j^*(2) \left[ \phi_i(1) \phi_j(2) - \phi_j(1) \phi_i(2) \right]
\]
The expected number of electron pairs in the region $A$ is obtained from the pair density:

$$N_{AA} = \int_A \int_A \rho_2(1, 2) \, d_1 \, d_2 + N_A$$
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The expected number of electron pairs with one electron at $A$ and another at $B$ reads:

$$N_{AB} = \int_A \int_B \rho_2(1, 2) \, d_1 \, d_2 + N_{A \cap B}$$
The variance of $N_A$

$$\sigma^2 [N_A] = N_{AA} - N_A \cdot N_A = \int_A \int_A \rho_2(1, 2) d_1 d_2 - N_A(N_A - 1)$$
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\]

The uncertainty is minimal when the electron pairs in \(A\) are maximal, \(i.e.,\) when the electrons are independent.
The covariance of electrons populations gives the measure of how much the number of electrons in A and B change together.

\[ \text{cov} (N_A, N_B) = N_{AB} - N_A \cdot N_B \]

\[ \sigma^2 [N_A] = \text{cov} (N_A, N_A) \]

\[ r_{N_A N_B} = \frac{\text{cov} (N_A, N_A)}{\sigma[N_A] \sigma[N_B]} \]
The Covariance Bounds

Non-overlapping regions

$- \min (N_A, N_B) \leq \text{cov} (N_A, N_B) \leq 0$
The Covariance Bounds

Non-overlapping regions

$$- \min (N_A, N_B) \leq \text{cov} (N_A, N_B) \leq 0$$

Overlapping regions

$$- \min (N_{A \setminus C}, N_{B \setminus C}) \leq \text{cov} (N_A, N_B) \leq N_C$$
The Covariance Bounds

Non-overlapping regions

\[ -\min(N_A, N_B) \leq \text{cov}(N_A, N_B) \leq 0 \]

Overlapping regions

\[ -\min(N_A \setminus C, N_B \setminus C) \leq \text{cov}(N_A, N_B) \leq N_C \]

The \( \text{cov}(N_A, N_B) \) gives a measure of the number of electron pairs shared between \( A \) and \( B \).
All the electrons in a molecule are either localized in an atom or delocalized with other atoms.

The delocalization index (DI):

\[ \delta_{AB} = -\text{cov}(N_A, N_B) \]

The localization index (LI):

\[ \lambda_A = N_A - \sigma^2[N_A] \]

---


We can decompose all the electrons in a molecule.

\[ N = \sum_A N_A \]

\[ N_A = \lambda_A + \delta_A \]

\[ \delta_A = \frac{1}{2} \sum_{X \neq A} \delta_{AX} \]

Fradera, Austen, Bader *JPCA* 103, 304 (1999)
From Born’s interpretation we obtain average values that can be easily used to calculate other statistics such as the covariance and higher-order moments (cumulants).

**Chemical Insight**

The key to obtain chemical insight is the Born interpretation of the \( n \)-densities, which provides a framework for counting electrons, electrons pairs, etc.

Population analysis, delocalization indices, electron localization function and indicator (ELF and ELI), etc. are based on probabilities, expected values and other statistics derived from the Born’s interpretation of the wavefunction.
The atom: the origin

- Two opposite views of the world: Greeks vs. Hebrews.
- The least expected city: Abdera (ca. 460 BC).
- The atomists: philosophers that study the existence, looking for the primordial substance.
- Three people: Leucippus, Democritus and Epicurus.
- Two principles: the void and the full.
- Atomic *passive* corpuscles: incompressible, compact, hard, indestructible, full and homogeneous.
- Atoms are animated by an ethernal constant motion.
- Atoms have shape, order and position.
- The soul was made of atoms.
Epicurus adds the weight as a property of atoms.

Two giants opposed the atomistic view: Aristotle and Plato (geometric shapes).

*Clinamen* introduced by Lucretius to defend Epicurus' atom.

When atoms move straight down through the void by their own weight, they deflect a bit in space at a quite uncertain time and in uncertain places, just enough that you could say that their motion has changed. But if they were not in the habit of swerving, they would all fall straight down through the depths of the void, like drops of rain, and no collision would occur, nor would any blow be produced among the atoms. In that case, nature would never have produced anything.

*Clinamen* adds free will ("the atom’s soul" —Augustine of Hippo)
Observe what happens when sunbeams are admitted into a building and shed light on its shadowy places. You will see a multitude of tiny particles mingling in a multitude of ways... their dancing is an actual indication of underlying movements of matter that are hidden from our sight... It originates with the atoms which move of themselves (i.e., spontaneously). Then those small compound bodies that are least removed from the impetus of the atoms are set in motion by the impact of their invisible blows and in turn cannon against slightly larger bodies. So the movement mounts up from the atoms and gradually emerges to the level of our senses, so that those bodies are in motion that we see in sunbeams, moved by blows that remain invisible.

On the Nature of Things (Lucretius, 60 BC).
In 1807 Dalton provided the modern atomic theory (father of chemistry).

In 1891 Stoney coined the term *electron*.

In 1913 Bohr formulated his atomic model including orbits and quanta.

In 1924 Pauli provided the forth quantum number: the spin.

The advent of quantum mechanics brought the concept of wavefunction.
The chemical bond is one of the most fundamental concepts in chemistry.

The Lewis model describes the electronic structure of a molecule in terms of electron pairs (2c-2e bonds).

These electron pairs can be classified as lone pairs (electrons which are localized in one atom), bonding pairs (electrons that are shared between two atoms), core electrons.

However, this intuitive picture of electron distribution does not take into account the quantum nature of electrons.
Non-standard Chemical Bonds

- Multicenter Bonding: $B_2H_6$
- Hypervalence: $SF_6$
- Metal-Metal Bonding: $Fe_2(CO)_9$
- Ultrashort Cr-Cr Bond
- Charged-Shifted Bond: $F_2$
- Controversial Bond Orders: $C_2$
- Tetracoordinated Planar Carbon: $C_3H_4$
- Pentacoordinated Carbon: $CaI_2Be_2^-$
- Hexacoordinated Carbon: $C_6(CH_3)_6^{2+}$
- Agostic Bonds
- Halogen Bonding: $CF_3...O(CH_3)_2$
- All-metal Aromatic Clusters
- Metalloporphyrins
- Expanded Porphyrins
- Boron Wheel: $B_{19}^-$
- Molecular Electrides: TCNQLi$_2$
Need to characterize an atom inside a molecule → atomic partition.
From an atomic partition we can define atomic properties.
There is not a unique atomic partition, there have been many suggestions.
Two main groups:
   (i) Hilbert-space based.
   (ii) Real space partitioning.
• Schrödinger Eq. solved by a finite basis set → atomic orbitals.
• This partition uses the assignment of orbitals to atomic centers.
• Mulliken was the first to use it to compute populations.

We use the definition of MOs in terms of AOs:

$$\phi_{i}^{A}(1) = \sum_{\mu \in A} c_{\mu i} \phi_{\mu}(1)$$

This assignment provides a partition of the MO:

$$\phi_{i}^{MO}(1) = \sum_{A} \phi_{i}^{A}(1) = \sum_{A} \sum_{\mu \in A} c_{\mu i} \phi_{\mu}(1)$$

Mulliken, *JCP* 23, 1833 (1955)
The Hilbert-space partition

- Advantage: low cost (it is analytical!)
- Drawback: basis set dependence, not clear assignment (diffuse, polarization functions).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Basis set</th>
<th>Mulliken</th>
<th>QTAIM</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>DZ</td>
<td>-0.982</td>
<td>-0.329</td>
</tr>
<tr>
<td></td>
<td>DZP</td>
<td>0.047</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>TZ2P+</td>
<td>0.607</td>
<td>0.047</td>
</tr>
<tr>
<td>H</td>
<td>DZ</td>
<td>0.246</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td>DZP</td>
<td>-0.012</td>
<td>-0.009</td>
</tr>
<tr>
<td></td>
<td>TZ2P+</td>
<td>-0.152</td>
<td>-0.011</td>
</tr>
</tbody>
</table>

Table: Bader and Mulliken atomic charges for methane calculated using three different basis sets (DZ: double zeta, DZP: double zeta with polarization and TZ2P+: triple zeta with double polarization and diffuse functions).
Quantum Theory of Atoms-in-Molecules

- Due to Richard F.W. Bader (1931-2012), McMaster University (Ontario).
- It consists on the topological analysis of the electron density.
- The density defines the distribution of electrons, and electrons determine the chemistry.
- Behind the electron density hides the concepts of atoms, bonds, chemical structure and structural stability.

Bader RFW, ACR 18, 9-15 (1985)
The atom that has the electron distribution makes the same contribution to the total energy of the system.

Quantum subsystems are open systems defined in real space, their boundaries being determined by a particular property of the electronic charge density.

QTAIM defines the atom through a partitioning of the real space as determined by the topological analysis of a molecular charge distribution.

Bader RFW, Beddall PM, JCP 56, 3320-3329 (1972)
The density is a continuous function.

Defined at every point in the space.

The critical points fulfill $\nabla \rho(r_c) = 0$.

The three curvatures $(x,y,z)$ define the nature of the CP.

$$H[\rho(r)] = \begin{pmatrix} \frac{\partial^2 \rho(r)}{\partial x^2} & \frac{\partial^2 \rho(r)}{\partial x \partial y} & \frac{\partial^2 \rho(r)}{\partial x \partial z} \\ \frac{\partial^2 \rho(r)}{\partial y \partial x} & \frac{\partial^2 \rho(r)}{\partial y^2} & \frac{\partial^2 \rho(r)}{\partial y \partial z} \\ \frac{\partial^2 \rho(r)}{\partial z \partial x} & \frac{\partial^2 \rho(r)}{\partial z \partial y} & \frac{\partial^2 \rho(r)}{\partial z^2} \end{pmatrix} \rightarrow \begin{pmatrix} \frac{\partial^2 \rho(r)}{\partial x_1^2} & 0 & 0 \\ 0 & \frac{\partial^2 \rho(r)}{\partial y_1^2} & 0 \\ 0 & 0 & \frac{\partial^2 \rho(r)}{\partial z_1^2} \end{pmatrix}$$
Critical points of a 3D function

There are four types of critical points (CP):

\[ H[\rho(r)] \rightarrow \begin{pmatrix} \frac{\partial^2 \rho(r)}{\partial x_1^2} & 0 & 0 \\ 0 & \frac{\partial^2 \rho(r)}{\partial y_1^2} & 0 \\ 0 & 0 & \frac{\partial^2 \rho(r)}{\partial z_1^2} \end{pmatrix} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \]

(3,-3): Attractors (ACP) all the curvatures at \( r_c \) are negative.

(3,-1): Bond CP (BCP) 2 curvatures are negative and 1 positive.

(3,+1): Ring CP (RCP) 1 curvatures are negative and 2 positive.

(3,+3): Cage CP (CCP) 3 curvatures are positive.

Poncairé-Hopf relationship:

\[ n_{ACP} - n_{BCP} + n_{RCP} - n_{CCP} = 1 \]
An atom: a density maximum surrounded by a zero-flux gradient surface.

\[ \nabla \rho(r) \cdot n(r) = 0 \quad \forall r \in S(r) \] (1)

- Gradient lines (red) perpendicular density isocontour lines (black).
- Blue line is the **bond path**: connects to nuclei and passes through the BCP.
The presence of a bond path [...] provides a universal indicator of bonding between the atoms so linked.

Bader RFW, JPCA 102, 7314-7223 (1998)
Topological analysis of water
Topological analysis of water
Topological analysis of water
Topological analysis of water
Topological analysis of water
AIM2000. Molecular graphs and isocontour plots

Molecular representation  Isocountour plot  with gradient lines

Biegler-König and Schönbohm, JCC 23 1489 (2002)
Input example to obtain wfn file with Gaussian

#HF/6-31G*  out=wfn

comment

0 1
H 0.0 0.0 0.0
H 0.0 0.0 1.0

H2.wfn

H2.wfn contains the molecular orbitals to construct the wavefunction of H2 at the HF/6-31G(d) level.
Maxima other than the nuclei (NNA) are not frequent and often due to wavefunction artifacts.

For instance, acetylene at the HF/6-31G*.

There is, however, some exceptions: Li$_2$ and electrides.
The Laplacian of the electron density accounts for electron localization.

\[ \nabla^2 \rho(r) = \frac{\partial^2 \rho(r)}{\partial x^2} + \frac{\partial^2 \rho(r)}{\partial y^2} + \frac{\partial^2 \rho(r)}{\partial z^2} \]

- \( \nabla^2 \rho(r) < 0 \) electron accumulation → localization.
- \( \nabla^2 \rho(r) > 0 \) electron depletion → delocalization.
Real-Space partitions: Voronoi Cells

- Atoms defined as Voronoi polyhedra.
- Polyhedra constructed by assigning the point to the nearest atom.
- Provides non-overlapping partition of the real space.
- Only uses the molecular geometry: atom types are not explicitly considered.
Real-Space partitions: Hirshfeld Partition

- Atoms defined from weight functions.
  
  \[
  w_A(r) = \frac{\rho_A^0(r)}{\sum_B \rho_B^0(r)} \quad \sum_A w_A(r) = 1 \quad \forall r
  \]

- \(\rho_A^0\) is the density of the isolated atom (promolecular density)
- The promolecule formed by superposing the densities of the isolated atoms. \(\sum_B \rho_B^0(r)\).
- Overlapping atomic partition.
- Drawback: The electronic state of the isolated atom can change the result.
Real-Space partitions: Becke Partition

- Uses Becke’s 1988 multicenter integration technique.

\[ w_A(r) = \frac{f_A(r)}{\sum_B f_B(r)} \quad \sum_A w_A(r) = 1 \quad \forall r \]

- \( f_A(r) \) are obtained from empirical atomic radii.
- Overlapping atomic partition.
- **Becke-rho**: uses the BCP as dynamic atomic radii.

---

Summary: Atoms in a molecule (AIM)

1. **Mulliken**: Hilbert space partitioning.\(^a\)
   * AIM → set of orbitals. Overlapping Atoms (OA)
   * Cheap, exact (analytic). **Issue**: Basis set dependence (BSD).

2. **QTAIM**: 3D-space, based on the density.\(^b\)
   * AIM → an attractor surrounded by zero flux surface or by infinity.
   * Non-OA. No BSD. **Issue**: Expensive (Not w AIMall)

3. **Fuzzy**: 3D-space, based on Becke Multicenter scheme.\(^c\)
   * AIM → a sum weights through the space.
   * Uses weight functions. No BSD. Cheap. **Issue**: Bond-orders.

4. **Becke-rho**: 3D-space, mixed Bader-Becke scheme.\(^d\)
   * AIM → boundaries determined by BCPs.
   * Gives QTAIM-like results at fuzzy expense.

---

Population analysis

Assuming $M$ number of basis functions an MO can be expanded:

$$\phi_i(1) \equiv \phi_i^{\text{MO}}(1) = \sum_{\mu} c_{\mu i} \phi_{\mu}^{\text{AO}}(1)$$

$$|\phi_i(1)|^2 = \sum_{\mu \nu} c_{\mu i} c_{\nu i} \phi_{\mu}^{\text{*}}(1) \phi_{\nu}(1)$$

and

$$N = \int \rho(1) d_1 = \sum_{i} n_i \int |\phi_i(1)|^2 d_1 = \sum_{i} \sum_{\mu \nu} c_{\mu i} c_{\nu i} n_i \int \phi_{\mu}^{\text{*}}(1) \phi_{\nu}(1) d_1$$

$$= \sum_{\mu \nu} \left( \sum_{i} c_{\mu i} c_{\nu i} n_i \right) \int \phi_{\mu}^{\text{*}}(1) \phi_{\nu}(1) d_1 = \sum_{\mu \nu} P_{\mu \nu} S_{\mu \nu} = \text{Tr} (P \cdot S)$$

where $P$ and $S$ are the density matrix (in AO) and the overlap matrix, respectively.
Population analysis: Mulliken

By taking the functions of each atom separately

\[ N = \int \rho(1) d_1 = \sum_{A} \sum_{\mu \in A} \sum_{\nu} P_{\mu \nu} S_{\mu \nu} = \text{Tr} (P \cdot S) \]

we can define the Mulliken electron population and gross charge of \( A \):

\[ N_A = \sum_{\mu \in A} \sum_{\nu} P_{\mu \nu} S_{\mu \nu} \]

\[ Q_A = Z_A - N_A \]

where \( Z_A \) is atomic number of \( A \).

Gaussian keyword for electron population analysis: \texttt{pop=full}.
Gaussian keyword for Löwin pop. and Mayer BO: \texttt{iop(6/80)=1}.
Population analysis: real space

In the real space we need to perform a **numerical integration** over the atomic domain of A:

\[
N_A = \int_A \rho(\mathbf{1}) d\mathbf{1} = \sum_i n_i \int_A |\phi_i(\mathbf{1})|^2 d\mathbf{1}
\]

\[
Q_A = Z_A - N_A
\]

where we need the diagonal part of the **atomic overlap matrix** (AOM):

\[
S_{ij}(A) = \int_A \phi_i^*(\mathbf{1}) \phi_j(\mathbf{1}) d\mathbf{1}
\]

- These analysis are done with the appropriate software
- One should check the accuracy of the integration performed.
- The computational cost can be beyond our possibilities.
The Exchange Correlation Function

A popular function in DFT is the exchange-correlation density (XCD),

\[ \rho_{xc}(1, 2) = \rho(1)\rho(2) - \rho_2(1, 2) \int \int \rho_{xc}(1, 2) \, d1 \, d2 = N \]

For single-determinant wavefunctions,

\[ \rho_{xc}(1, 2) = \rho(1)\rho(2) - \rho_2(1, 2) = \rho_1(1; 2)\rho_1(2; 1) = |\rho_1(1; 2)|^2 \geq 0 \]

We can easily prove that

\[ N_{\Omega_1\Omega_2} \leq N_{\Omega_1} N_{\Omega_2} + N_{\Omega_1\cap\Omega_2} \]

so that the maximum number of pairs between two regions is obtained by direct multiplication of its electron averages (plus the population of the intersection of the two regions). The maximum value is only achieved when the electrons are independent.

The XCD gives rise to the Electron Sharing Indices (ESI).

The delocalization index (DI):

\[ \delta(A, B) = \int_A \int_B d1 d2 \rho_{xc}(1, 2) \]

The localization index (LI):

\[ \lambda(A) = \int_A \int_A d1 d2 \rho_{xc}(1, 2) \]

Fulton *JPC* 97, 7516 (1993); Ángyán, Mayer, Loos, *JPC* 98, 5244 (1994)
Fradera, Austen, Bader *JPCA* 103, 304 (1999)
Multicenter Bonding

Accounts for electron-sharing between \( n \) centers (atoms). It is related to the \( n \)-order central moment of the electron population.

\[
D(A_1, \cdots, A_n) \sim \left\langle (\hat{N} - \overline{N})^n \right\rangle_{A_1, \cdots, A_n}
\]

---

Bochicchio, Ponec, Torre, Lain, *TCA* 105, 292 (2001)
nc-ESI: What is it good for?

Characterization of Multicenter Bonding

Identification of Agostic Bonds

Organic/Inorganic Aromaticity

Delocalization: Hyperconjugation/conjugation

Multicenter Indices

1,3-butadiene

1-butene

1-butine
Agostic Bonds

$\delta$(Ti-H-C) = 0.084

$\delta$(Cu-H-C) = 0.008

$\delta$(Co-H-N) = -0.033

d(Ti-H) = 2.29Å
d(Cu-H) = 2.45Å
d(Co-H) = 2.67Å

<table>
<thead>
<tr>
<th>Interaction</th>
<th>3-center ESI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agostic Bond (3c-2e)</td>
<td>3c-ESI &gt; 0</td>
</tr>
<tr>
<td>Anagostic Interaction</td>
<td>3c-ESI = 0</td>
</tr>
<tr>
<td>Hydrogen Bond (3c-4e)</td>
<td>3c-ESI &lt; 0</td>
</tr>
</tbody>
</table>

Feixas, Matito, Maseras, Poater, Solà, *in preparation*
### Conjugation and Hyperconjugation effects

<table>
<thead>
<tr>
<th>Conjugation</th>
<th>butane</th>
<th>1,3-butadiene</th>
<th>1,3-butadiyne</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Butane" /></td>
<td><img src="image2.png" alt="1,3-Butadiene" /></td>
<td><img src="image3.png" alt="1,3-Butadiyne" /></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4c-DI</th>
<th>B3LYP</th>
<th>CCSD</th>
<th>B3LYP</th>
<th>CCSD</th>
<th>B3LYP</th>
<th>CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta(C_1-C_2-C_3-C_4)$</td>
<td>-0.0045</td>
<td>-0.0034</td>
<td>-0.0798</td>
<td>-0.0452</td>
<td>-0.1678</td>
<td>-0.0929</td>
</tr>
<tr>
<td>$\delta_n(C_1-C_2-C_3-C_4)$</td>
<td>-0.0775</td>
<td>-0.1675</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Hyperconjugation

<table>
<thead>
<tr>
<th>Hyperconjugation</th>
<th>butane</th>
<th>1-butene</th>
<th>1-butine</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4.png" alt="Butane" /></td>
<td><img src="image5.png" alt="1-Butene" /></td>
<td><img src="image6.png" alt="1-Butine" /></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4c-DI</th>
<th>B3LYP</th>
<th>CCSD</th>
<th>B3LYP</th>
<th>CCSD</th>
<th>B3LYP</th>
<th>CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta(C_1-C_2-C_3-C_4)$</td>
<td>-0.0045</td>
<td>-0.0034</td>
<td>-0.0133</td>
<td>-0.0085</td>
<td>-0.0182</td>
<td>-0.0114</td>
</tr>
<tr>
<td>$\delta(C_1-C_2-C_3-H_3)$</td>
<td>-0.0005</td>
<td>-0.0003</td>
<td>-0.0013</td>
<td>-0.0009</td>
<td>-0.0191</td>
<td>-0.0121</td>
</tr>
<tr>
<td>$\delta(C_1-C_2-C_3-H_6)$</td>
<td>-0.0005</td>
<td>-0.0003</td>
<td>-0.0142</td>
<td>-0.0092</td>
<td>-0.0191</td>
<td>-0.0121</td>
</tr>
</tbody>
</table>
Aromaticity

Let \( \mathcal{A} = \{ A_1, A_2, \ldots, A_n \} \) represent a ring.

\[
I_{\text{ring}}(\mathcal{A}) = \sum_{i_1, i_2, \ldots, i_n} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \cdots S_{i_n i_1}(A_n)
\]

\[
MCI(\mathcal{A}) = \sum_{\mathcal{P}(\mathcal{A})} I_{\text{ring}}(\mathcal{A})
\]

The \( n^{th} \) root of these quantities correlates with the TREPE.

\[
\begin{align*}
C_6H_6 & \quad MCI = 0.071 \\
 & \quad MCI_\sigma = 0.000 \\
 & \quad MCI_\pi = 0.071 \\
Al_4^{2-} & \quad MCI = 0.356 \\
 & \quad MCI_\sigma = 0.169 \\
 & \quad MCI_\pi = 0.187
\end{align*}
\]

\[ \delta(A, B) = -2 \int_A \int_B d1 d2 \gamma(1, 2) = \text{Cov} (N(A), N(B)) \]

\[ \delta(A, B, C) = 2 \int_A \int_B \int_C d1 d2 d3 \gamma(1, 2, 3) \]

\[ \delta(A_1, A_2, \ldots, A_n) = \frac{(-2)^{n-1}}{(n-1)!} \int_{A_1} \int_{A_2} \cdots \int_{A_n} d1 d2 \cdots d_n \gamma(1, 2, \ldots, n) \]

Functions that upon integration give the above ESIs:

\[ \gamma(1, 2) = \rho_{xc}(1, 2) = \rho(1, 2) - \rho(1)\rho(2) \]
\[ \gamma(1, 2, 3) = \rho(1, 2, 3) - \rho(1)\rho(2)\rho(3) - \hat{P}_{1,2,3} (\rho_{xc}(1, 2)\rho(3)) \]
\[ \gamma(1, 2, \ldots, n) = \langle (\hat{\rho}_1 - \bar{\rho}_1)(\hat{\rho}_2 - \bar{\rho}_2) \cdots (\hat{\rho}_n - \bar{\rho}_n) \rangle \]

they depend on the \textit{n-order density} (\textit{n-density}).

Martín Pendás, Francisco, Blanco \textit{JCP} 127 144103 (2007)
Computational Details

Obtain the wavefunction

molecule.wfn (fchk)

Atomic partition

molecule*.int

DMn

many determinants

MCI

Gaussian, GAMESS, ADF, ...

APOST-3D, AIMall

PROAIM, ...

ESI-3D

ESI-3D: http://ematito.webs.com
OXIDATION STATE
DEFINITIONS:

- **IUPAC** (2018, formal): OS of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds.
- **IUPAC** (old, formal): Charge of TM after removing the L and the electrons sharing with it.
- **Physical** or **Spectroscopic**: Charge of TM that comes from $d^n$ and can be measured spectroscopically (e.g. Mössbauer).

---

Jørgensen, In *Oxidation Numbers and Oxidation States*; Springer; Heidelberg, 1969
**Oxidation state**

- **IUPAC (formal):** Charge of TM after removing the L and the electrons sharing with it.

- **Physical or Spectroscopic:** Charge of TM that comes from $d^n$ and can be measured spectroscopically (e.g. Mössbauer).

---

**Useful references:**

---

**SPECTROSCOPIC**

- Fe(III): [Ar]3d⁵

**FORMAL**

- Fe(IV): [Ar]3d⁴
There are many methods to calculate the OS:

- **Bond Valence Sum** (BVS) method. Empirical method based on M-L distances \( (R_i) \) and reference values \( (R_0, b=0.37\,\text{Å}) \).

  \[
  V = \sum_i \left( \frac{R_i - R_0}{b} \right)
  \]

- From atomic population analysis.
- **Spin densities** → atomic configuration → OS
- **Localization** methods (e.g. LOBA or EOS).

---

http://www.ccp14.ac.uk/solution/bond_valence/index.html
Ligand Field Theory. $O_h$ complexes

(a) Metal cation, $M^{n+}$

E

$\Delta_0$

$d_{x^2-y^2}$ $d_{z^2}$ $d_{xy}$ $d_{xz}$ $d_{yz}$

$\Delta_0$

$E_g$

Electrostatic attractions (+/-) considered

(b) $e_g$ orbitals go up in energy by $\frac{3}{5}\Delta_0$

t$_{2g}$ orbitals go down in energy by $\frac{2}{5}\Delta_0$
To evaluate the performance of OS methods the following test set of $O_h$ complexes is used:

<table>
<thead>
<tr>
<th></th>
<th>$V^{II}$</th>
<th>$Mn^{II}$</th>
<th>$Mn^{III}$</th>
<th>$Fe^{II}$</th>
<th>$Fe^{III}$</th>
<th>$Ni^{II}$</th>
<th>$Zn^{II}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$[ZnCl_6]^4-$</td>
<td>$[Zn(H_2O)_6]^{2+}$</td>
<td>$[Zn(CN)_6]^4-$</td>
<td>$[Zn(CO)_6]^{2+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Mulliken charges | TFVC charges
---|---
| Cl$^-$ | H$_2$O$^{HS}$ | H$_2$O$^{LS}$ | CN$^-$ | CO | Cl$^-$ | H$_2$O$^{HS}$ | H$_2$O$^{LS}$ | CN$^-$ | CO |
V$^{II}$ | 0.98 | 1.12 | 0.05 | 0.64 | 1.60 | 1.76 | - | 1.60 | 1.64 |
Mn$^{II}$ | 1.10 | 1.24 | 1.18 | 0.10 | 0.64 | 1.36 | 1.64 | 1.70 | 1.53 | 1.53 |
Mn$^{III}$ | 0.93 | 1.58 | 1.52 | 0.35 | 0.80 | 1.46 | 2.05 | 2.09 | 1.58 | 1.67 |
Fe$^{II}$ | 0.86 | 1.22 | 1.15 | 0.01 | 0.51 | 1.27 | 1.63 | 1.77 | 1.46 | 1.44 |
Fe$^{III}$ | 0.99 | 1.64 | 1.48 | 0.24 | 0.66 | 1.44 | 2.06 | 1.98 | 1.49 | 1.58 |
Ni$^{II}$ | 0.99 | 1.08 | -0.19 | 0.31 | 1.27 | - | 1.59 | 1.24 | 1.30 |
Zn$^{II}$ | 1.02 | 1.06 | -0.03 | 0.52 | 1.25 | - | 1.45 | 1.15 | 1.19 |

Mulliken population fails in all cases. TFVC gets more than 50% wrong.
The spin population suggests the atomic configuration of the TM. From it we can deduce the OS. It only makes sense for open-shell calculations.

<table>
<thead>
<tr>
<th></th>
<th>Cl⁻</th>
<th>H₂O&lt;sup&gt;HS&lt;/sup&gt;</th>
<th>H₂O&lt;sup&gt;LS&lt;/sup&gt;</th>
<th>CN⁻</th>
<th>CO</th>
<th>Cl⁻</th>
<th>H₂O&lt;sup&gt;HS&lt;/sup&gt;</th>
<th>H₂O&lt;sup&gt;LS&lt;/sup&gt;</th>
<th>CN⁻</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>V&lt;sup&gt;III&lt;/sup&gt;</td>
<td>3.06</td>
<td>2.99</td>
<td>2.84</td>
<td>2.79</td>
<td>2.90</td>
<td>2.71</td>
<td>-</td>
<td>2.52</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>Mn&lt;sup&gt;II&lt;/sup&gt;</td>
<td>4.96</td>
<td>4.88</td>
<td>1.01</td>
<td>1.09</td>
<td>1.06</td>
<td>4.86</td>
<td>4.66</td>
<td>0.95</td>
<td>1.01</td>
<td>0.98</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;III&lt;/sup&gt;</td>
<td>4.25</td>
<td>3.85</td>
<td>1.97</td>
<td>2.11</td>
<td>2.16</td>
<td>4.07</td>
<td>3.65</td>
<td>1.84</td>
<td>1.96</td>
<td>2.00</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;II&lt;/sup&gt;</td>
<td>3.86</td>
<td>3.86</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>3.72</td>
<td>3.71</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;III&lt;/sup&gt;</td>
<td>4.27</td>
<td>4.43</td>
<td>0.89</td>
<td>1.08</td>
<td>1.11</td>
<td>4.17</td>
<td>4.28</td>
<td>0.86</td>
<td>1.01</td>
<td>1.03</td>
</tr>
<tr>
<td>Ni&lt;sup&gt;II&lt;/sup&gt;</td>
<td>1.87</td>
<td>1.84</td>
<td>1.69</td>
<td>1.66</td>
<td>1.84</td>
<td>-</td>
<td>1.77</td>
<td>1.66</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>Zn&lt;sup&gt;II&lt;/sup&gt;</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Effective Oxidation State

\[ \phi_i^A(1) = w_A(1) \phi_i^{MO}(1) \]
\[ Q_{ij}^A = \int \phi_i^A(1) \phi_j^A(1) \, d_1 \]
\[ TrQ^A = N_A \]
\[ Q^A L^A = L^A \Lambda^A \]
\[ EOS_A = I_A - Z_A \]

\( w_A \) (atomic weights) define the atom, \( L \) contains the effective AOs (EF-FAOs) and \( \Lambda \) the occupancies. \( N_A \) is the net atomic population. One or zero electrons are assigned to each orbital according to its occupation. As a result, an integer number of electrons (\( I_A \)) is assigned to each atom.

EOS reproduce the correct OS for all the complexes in the test set.

---

Charges and spin population can be obtained from Gaussian (Mulliken) or real-space partitioning program (QTAIM, Becke-rho, etc.)

EOS can be obtained from APOST-3D program. We need to repeat the steps in the slide Computational Details: Fuzzy and Becke-rho. Only one difference: edit yourfile.inp and add the keyword UEFFAO.

Recommendations:

- Define a fragment for each ligand. Add they keyword DOFRAG and define the fragments under the label ## FRAGMENTS ### using the same method than in ESI-3D manual.
- The best working DFT functionals: UB3LYP and M062X.
AROMATICITY
Aromaticity Timeline

1825
Benzene

1938 Aromatic Transition States

Metalloaromaticity 1945

Möbius Aromaticity 1964
Aromaticity Timeline

1825
Benzene

1978
Three-dimensional Aromaticity

σ-Aromaticity

1979

1985
Fullerenes

1991
Nanotubes
Aromaticity Timeline

1825

Benzene

2001
All-metal Aromaticity

d-orbital Aromaticity

2005

2007
δ-Aromaticity

2008

ϕ-Aromaticity
Unhopefully, **aromaticity remains an ill- defined concept**. Unlike other similar quantities like *bond ionicity* or *bond order* aromaticity refers to not one, but several properties not necessarily mutually related.

However, in practice, **organic chemists still use this concept** to elucidate phenomena such as chemical stability/reactivity, bond length equalization/alternation, among others.

Saying that aromaticity is a multidimensional phenomena (an accepted fact), sometimes hinders the understanding of where certain aromaticity indices are failing. Two important goals in aromaticity are the study of the **domain of application of each aromaticity index**, as well as the **definition of universal low-cost aromaticity measure**.
Aromaticity descriptors

- **Energetic**: Isodesmotic reactions
- **Magnetic**: Ring currents, NICS and Λ
- **Geometrical**: HOMA
- **Electronic**: FLU, PDI, Multicenter
The harmonic oscillator model of aromaticity (HOMA).

- Only relies on geometrical data.
- Easy to compute:

\[
\text{HOMA} = 1 - 257.7 \frac{1}{n} \sum_{i}^{n} (R_{\text{opt}} - R_i)^2
\]

\[
= 1 - 257.7 \frac{1}{n} \left( (R_{\text{opt}} - \bar{R})^2 + \sum_{i}^{n} (R_i - \bar{R})^2 \right)
\]

\[
= 1 - (\text{EN} + \text{GEO})
\]

- \(R_{\text{opt}}\) available: C-C, C-N, C-O, C-P, C-S, N-N, N-O

---

HOMA can be computed with ESI-3D using the keyword $\text{GEOMETRY}$
A magnetic field directed perpendicular to the plane of an aromatic system induces a ring current in the delocalized electrons of the ring.

It influences the chemical shifts of $^{13}C$ and $^1H$ in molecules.

**NICS**: Nuclear Independent Chemical Shift. Calculates the (minus) absolute magnetic shielding at the center of the ring. The more negative, the more aromatic.

**Λ**: Diamagnetic Susceptibility Exaltation. The difference between the measured magnetic susceptibility and the calculated from group additivity tables.
NICS $\Lambda$ are easy to calculate.
They are both ring-size dependent.
NICS is computationally expensive.
Ring currents are better but complicated to calculate and expensive.
NICS is by far the most popular aromaticity index.
How to compute NICS

In Gaussian include keyword NMR and Bq in the points of interest.

#HF/6-31G* NMR

NICS automatic generation

0 1
C 0.00000000 1.38617405 0.00000000
...
Bq 0.00000000 0.00000000 -1.00000000
Aromaticity descriptors

Currents

Magnetic

Structural, electronic

Magnetic field generated by a benzene ring π-system current
We are concerned with the calculation of the local aromaticity of a given molecule which possesses at least one ring structure. Let us suppose such ring structure consists of $n$ atoms, represented by the following string $A = \{A_1, A_2, \ldots, A_n\}$, whose elements are ordered according to the connectivity of the atoms in the ring. For such system we can calculate the following electronic aromaticity indices:

1. FLU
2. PDI
3. $I_{\text{ring}}$
4. MCI

All these *electronic* aromaticity indices will be compared afterwards with the well-known NICS and HOMA descriptors.
The FLU index.

\[
\text{FLU}(A) = \frac{1}{n} \sum_{i=1}^{n} \left[ \left( \frac{V(A_i)}{V(A_{i-1})} \right)^{\alpha} \left( \frac{\delta(A_i, A_{i-1}) - \delta_{\text{ref}}(A_i, A_{i-1})}{\delta_{\text{ref}}(A_i, A_{i-1})} \right) \right]^2
\]

where \( A_0 \equiv A_n \) and \( V(A) \) is the atomic valence that for a closed-shell system reads as follows, and \( \alpha \) is a simple function to ensure the first term in the Eq. is always greater or equal to 1,

\[
V(A) = \sum_{B \neq A} \delta(A, B) \quad \alpha = \begin{cases} 
1 & V(A_{i-1}) \leq V(A_i) \\
-1 & V(A_i) < V(A_{i-1})
\end{cases}
\]

\( \delta(A, B), \delta_{\text{ref}}(A, B) \) are quantities that account for the electron sharing of \( A \) and \( B \); the latter is taken from an aromatic molecule which has the pattern of bonding \( A - B \).

\[1\] Matito, Duran, Solà \textit{JCP} 122, 014109 (2005); Bird \textit{Tetrahedron} 41, 1409 (1985)
Based on the works of Fulton and Bader, which showed that benzene has larger
para-related atoms electron sharing than meta-related one, the index uses the
para-related atoms electron sharing as a measure of aromaticity for
six-membered rings: \(^1\)

\[ PDI(A) = \frac{\delta(A_1, A_4) + \delta(A_2, A_5) + \delta(A_3, A_6)}{3} \]

\(^1\)Poater, Fradera, Duran, Solà *CEJ* 9, 400 (2003)
Aromaticity and Multicenter Indices

Let \( \mathcal{A} = \{A_1, A_2, \ldots, A_n\} \) represent a ring.

\[
I_{\text{ring}}(\mathcal{A}) = \sum_{i_1, i_2, \ldots, i_n} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \ldots S_{i_n i_1}(A_n)
\]

\[
MCI(\mathcal{A}) = \sum_{\mathcal{P}(\mathcal{A})} I_{\text{ring}}(\mathcal{A})
\]

The \( n^{th} \) root of these quantities correlates with the TREPE.

\[\begin{align*}
C_6H_6 & \quad \text{MCI} = 0.071 \\
& \quad \text{MCI}_\sigma = 0.000 \\
& \quad \text{MCI}_\pi = 0.071
\end{align*}\]

\[\begin{align*}
\text{Al}_4^{2-} & \quad \text{MCI} = 0.356 \\
& \quad \text{MCI}_\sigma = 0.169 \\
& \quad \text{MCI}_\pi = 0.187
\end{align*}\]

TREPE for annulenes. The normalized $I_{\text{ring}}$ index.

$$E_{\text{TRPE}} = 1.188 \, I_{\text{NG}} \, (\text{HMO}) - 0.004$$

$R^2 = 0.990$

TREPE for annulenes. The normalized MCI index.

FLU and HOMA are not valid for reactivity (references!).

Testing Aromaticity: Inorganic molecules

Feixas, Jiménez-Halla, Matito, Poater, Solà, JCTC 6, 118 (2010)

NICS(0) is not a reliable measure of aromaticity