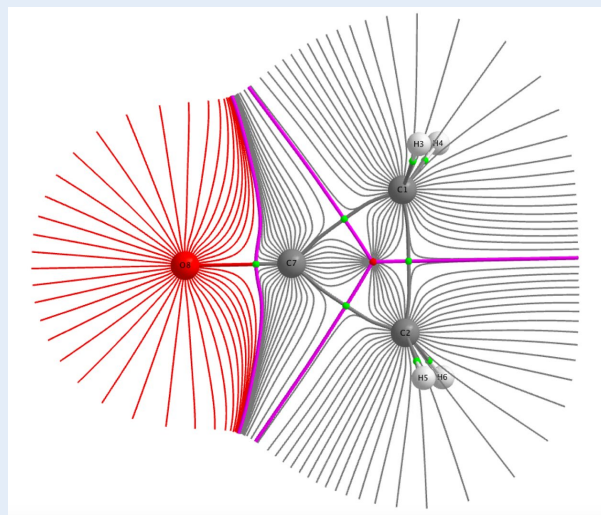




Modern2023
4-7 Sep 2023 Paris (France)



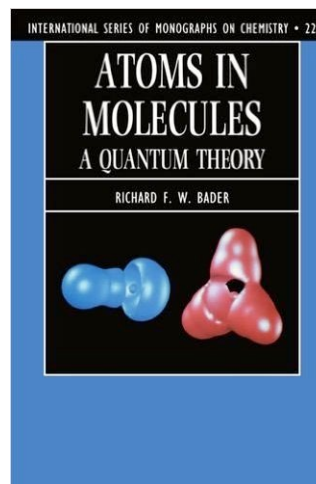
Electron Density Analysis: Quantum Theory of Atoms in Molecules (QTAIM)



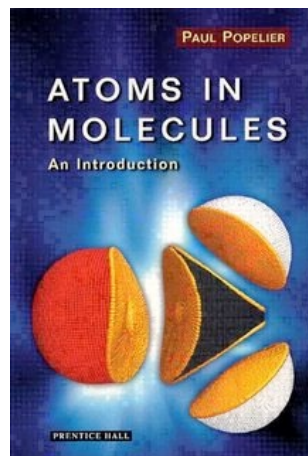
Richard Bader (1931-2012) and some textbooks



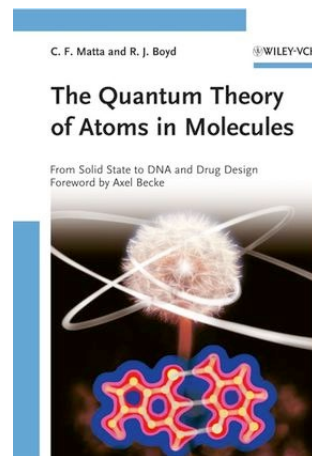
(1931-2012)



(1994)



(1999)



(2007)

Outline

1. The QTAIM partition
2. Local critical point properties
3. Integrated atomic properties
4. Energy decompositions
5. QTAIM in practice

Outline

1. The QTAIM partition
2. Local critical point properties
3. Integrated atomic properties
4. Energy decompositions
5. QTAIM in practice

1.1. The electron density

- ✓ From the *polyelectronic* wavefunction with $\vec{x} = (\vec{r}, s)$:

$$\rho(\vec{r}_1) = N \int |\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d^4x_2 \dots d^4x_N$$

- ✓ Physical interpretation:

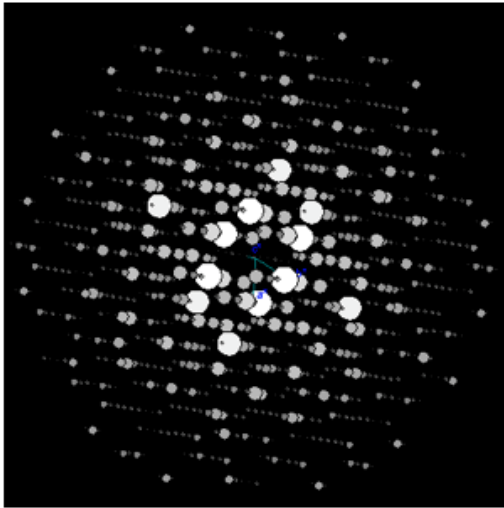
Mean number of electrons per volume unit (e⁻.Bohr⁻³)

- ✓ For a wavefunction built on *monoelectronic* orbitals φ_i (HF, KS):

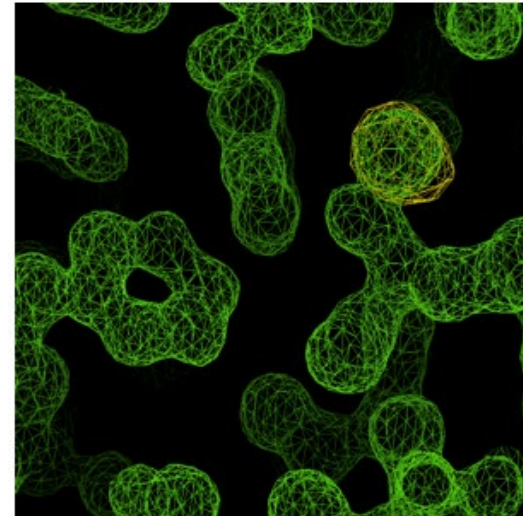
$$\rho(\vec{r}_1) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2$$

1.1. The electron density

- ✓ From *X-ray diffraction* experiments:



Diffraction pattern
(reciprocal space)



Electron density
(real space)

- ✓ From the measured *structure factor*, one can deduce the electron density:

$$\rho(\vec{r}) = \frac{1}{V} \sum_{\vec{H}} F(\vec{H}) e^{-2\pi i \vec{H} \cdot \vec{r}}$$

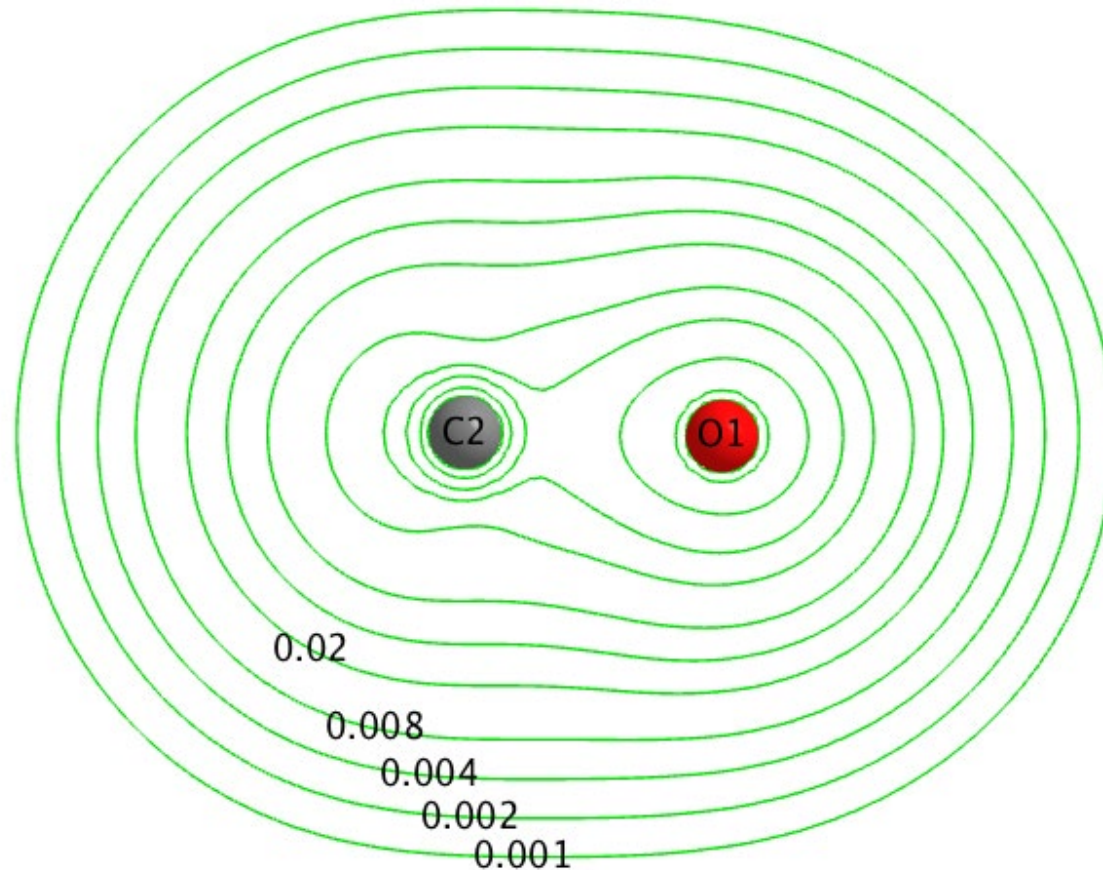
1.1. The electron density

- ✓ Advantages of the electron density:
 - a quantum *observable* that is experimentally *measurable*
 - is *universal* since it can be derived from any computational protocol (semi-empirical, DFT, (post)-HF)
 - although only a 3D function, it contains **all** information needed to determine any physical property of a stationary ground state (1964)



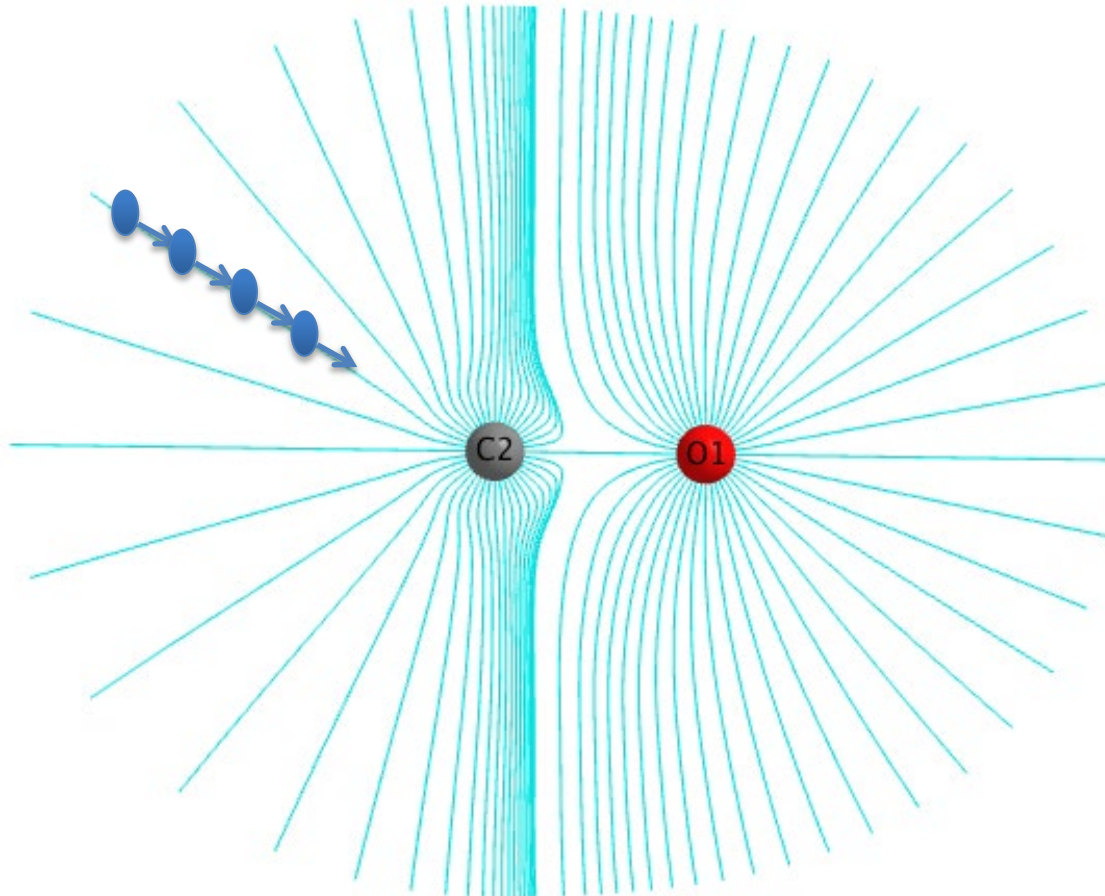
1.2. The topology of the electron density

- ✓ *Isodensity* surfaces projected on a plane (a.u.):



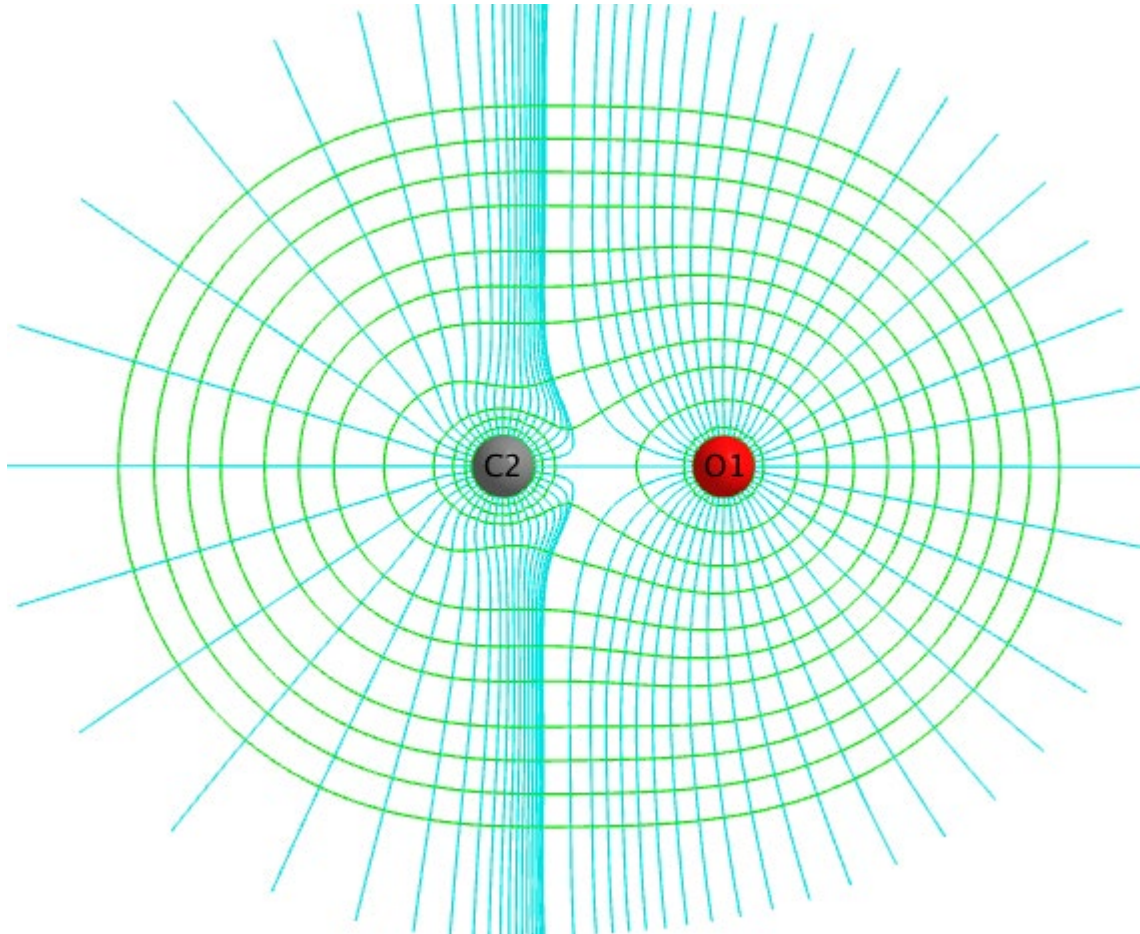
1.2. The topology of the electron density

- ✓ Field lines of $\vec{\nabla}\rho$: they are called *gradient paths*



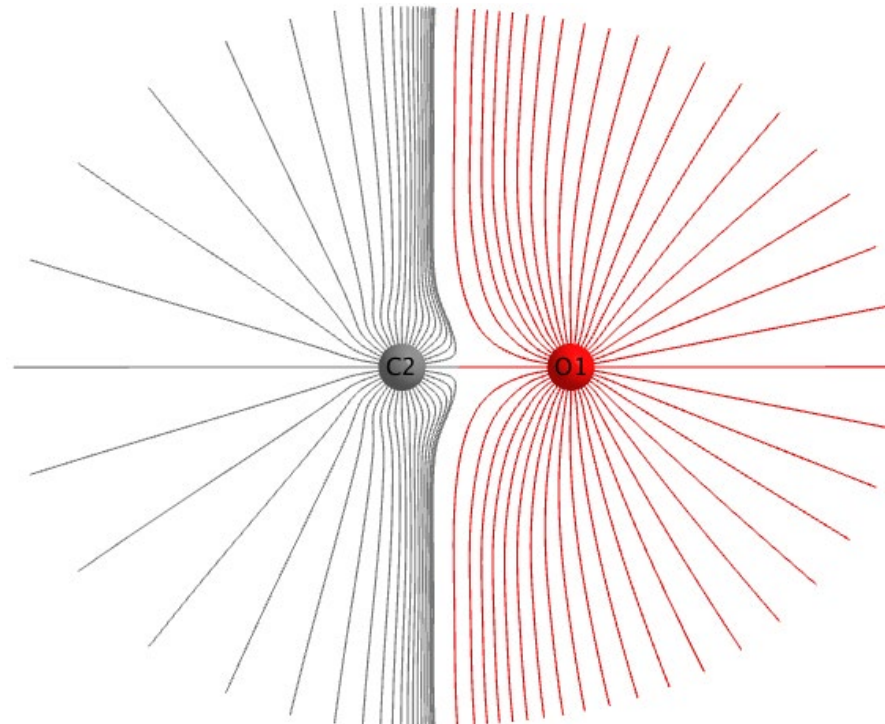
1.2. The topology of the electron density

- ✓ Gradient paths are orthogonal to isodensity surfaces



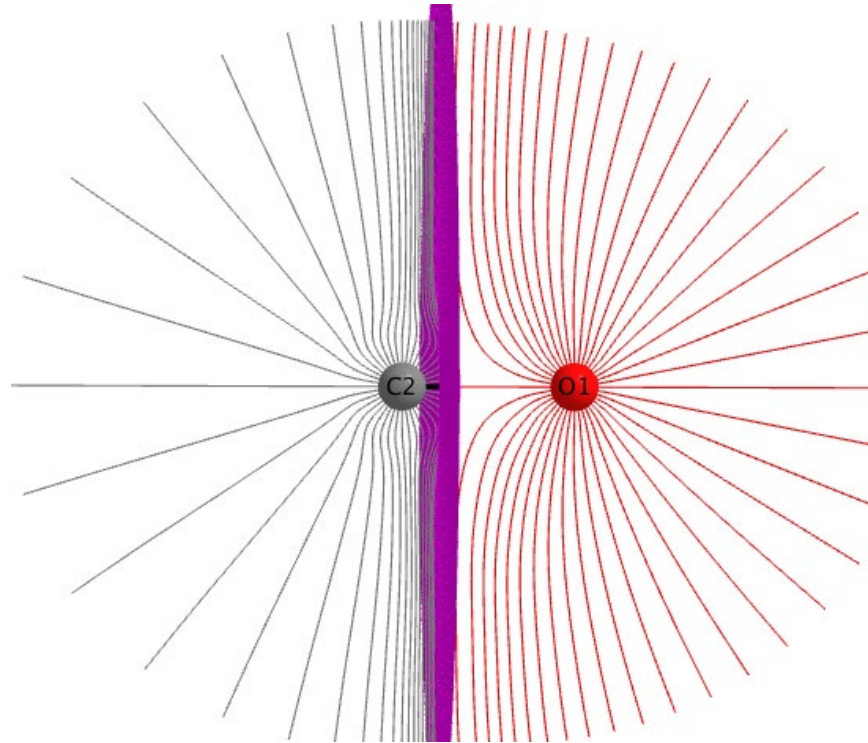
1.2. The topology of the electron density

- ✓ Observe that all gradient lines end up at a nucleus that are *attractors* (maximal density values, $(3,-3)$ critical points)
- ✓ Define the *atomic basin* at the *bundle* of gradient paths ending at the same nucleus



1.2. The topology of the electron density

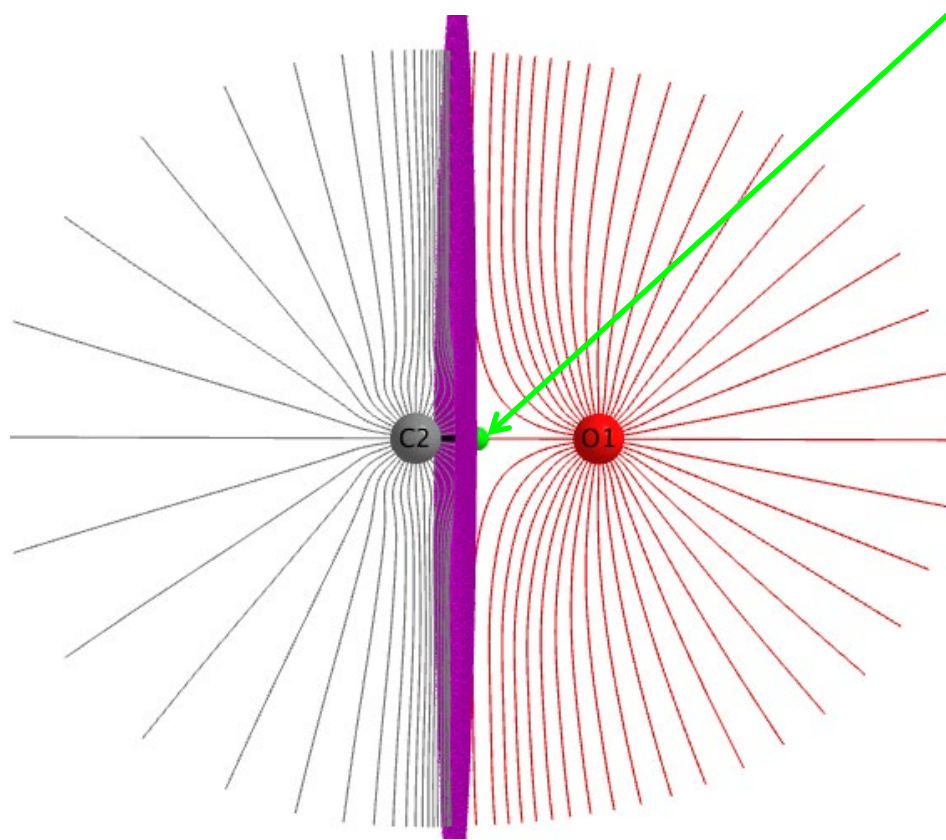
- ✓ These basins are not overlapping and are separated by the so-called *interatomic surface* (IAS) - (name of the separatrix in QTAIM)



- ✓ IAS fulfills the *zero-flux* condition: $\forall \vec{r} \in IAS \quad \vec{\nabla} \rho(\vec{r}) \cdot \vec{n}(\vec{r}) = 0$
- ✓ Basins are of *infinite* volume, but atoms are finite using density cutoffs

1.2. The topology of the electron density

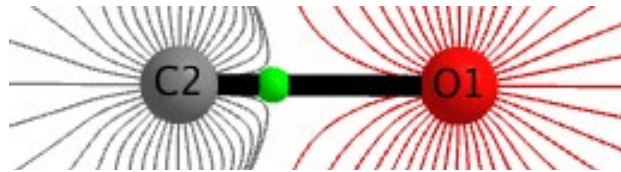
- ✓ One particular point on this IAS: a $(3,-1)$ CP where $\vec{\nabla}\rho = \vec{0}$



- ✓ At a PES equilibrium geometry, it is called a *bond critical point* (BCP)

1.2. The topology of the electron density

- ✓ A particular line: the *atomic interaction line* (AIL)



- ✓ At an equilibrium geometry, it is called the *bond path* between A and B
- ✓ R. Bader defined an *atom-in-molecule* as the union of the atomic *basin* (a volume in real space) and its *attractor*
- ✓ Unambiguous exhaustive partition on real space that can be also performed on experimental electron densities
- ✓ According to Bader, two atoms are bonded if and only if there exists a bond path between them

1.3. Reduced density matrices

- ✓ In the following sections, we will need some spin-less RDMs:

$$\rho_1(\vec{r}_1; \vec{r}'_1) = N \int \psi^*(\vec{r}'_1, \vec{r}_2, \dots, \vec{r}_N) \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) d^3 r_2 \dots d^3 r_N$$

$$\rho_2(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2) = \frac{N(N-1)}{2} \int \psi^*(\vec{r}'_1, \vec{r}'_2, \vec{r}_3, \dots, \vec{r}_N) \psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N) d^3 r_3 \dots d^3 r_N$$

- ✓ The electron-electron repulsion energy simply reads:

$$E_{ee}[\rho_2] = \int \frac{\rho_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2)}{\|\vec{r}_1 - \vec{r}_2\|} d^3 r_1 d^3 r_2$$

- ✓ The electronic kinetic is simply:

$$T_e[\rho_1] = -\frac{1}{2} \int_{R^3} \nabla_{\vec{r}_1}^2 \rho_1(\vec{r}_1; \vec{r}'_1) \Big|_{\vec{r}_1 = \vec{r}'_1} d^3 r_1$$

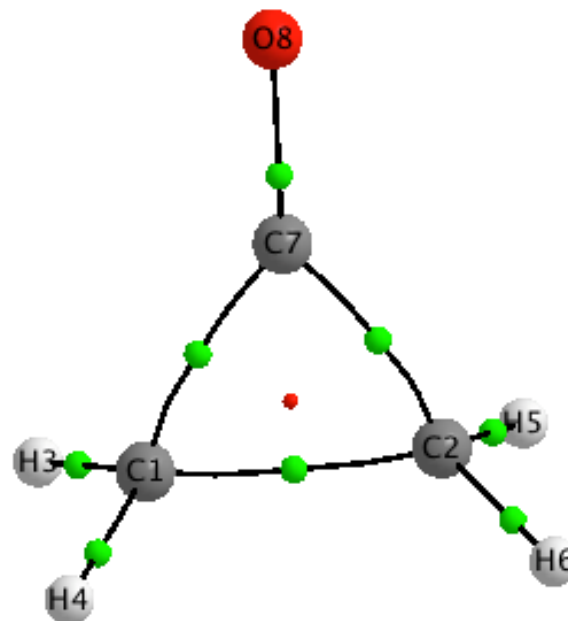
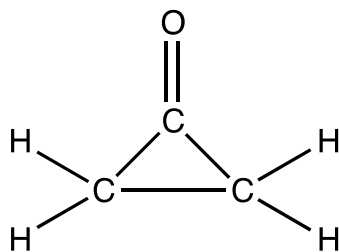
- ✓ Natural orbitals (NO) diagonalize the 1-RDM: $\rho_1(\vec{r}_1; \vec{r}'_1) = \sum_{i=1}^{+\infty} n_i^{NO} \varphi_i^{NO}(\vec{r}_1) \varphi_i^{NO}(\vec{r}'_1)$

Outline

1. The QTAIM partition
2. Local critical point properties
3. Integrated atomic properties
4. Energy decompositions
5. QTAIM in practice

2.1. Critical points typology

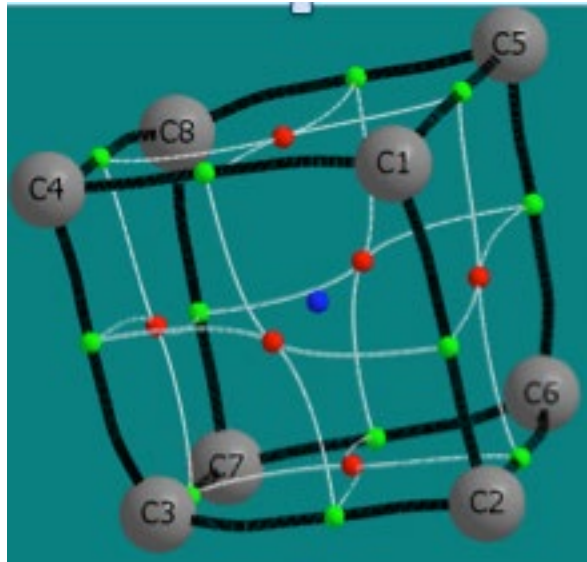
✓ Example: cyclopropanone



- ✓ **BCP**, (3,1) CP : density is minimal along the BP, maximal in orthogonal plane
- RCP**, (3,+1) CP, density is minimal in the plane, maximal orthogonally

2.1. Critical points typology

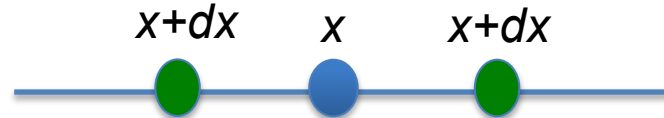
- ✓ Another example: cubane (C₈)



- ✓ **CCP**, (3,+3) CP: local minimum for the electron density
- ✓ By determining this topology, we have access to the *molecular graph*

2.2. Basic BCP properties

- ✓ BCP electron density to define *bond order*: $BO = \exp[A\rho_{BCP} + B]$
- ✓ Nature of the bond: one dimensional case:



$$\Delta\rho_{mean}(x) = \rho(x) - \underbrace{\frac{\rho(x+dx) + \rho(x-dx)}{2}}_{\rho_{average\ around\ x}}$$

$$= \rho(x) - \frac{\rho(x) + dx\rho'(x) + \frac{dx^2}{2}\rho''(x) + \rho(x) - dx\rho'(x) + \frac{dx^2}{2}\rho''(x)}{2} + O(dx^3)$$

$$= -dx^2\rho''(x) + O(dx^3)$$

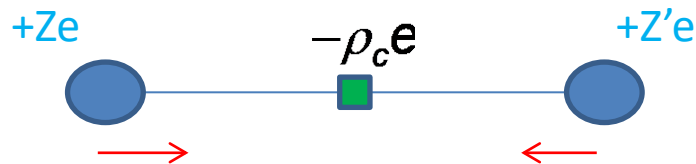
- ✓ Electron concentration at point x if $\Delta\rho_{mean}(x) > 0 \Leftrightarrow \rho''(x) < 0$
- ✓ Electron depletion at point x if $\Delta\rho_{mean}(x) < 0 \Leftrightarrow \rho''(x) > 0$

2.2. Basic BCP properties

✓ Generalizing in 3D:

- electron *concentration* at a BCP if the density *laplacian* value is *negative*
- electron *depletion* at a BCP if the density *laplacian* value is *positive*

✓ Covalent bonds: electron density is moved towards the bonding region



✓ Ionic bonds: electron density in the bonding region is *depleted* so that one atom can get excess electrons, creating a charge separation and an electrostatic attraction between a cation and an anion

2.3. More BCP properties

✓ One can define *local* energetic properties at a bond critical point \vec{r}_c :

- Lagrangian kinetic energy density (in a.u.):

$$G(\vec{r}_c) = \frac{1}{2} \sum_{i=1}^{+\infty} n_i^{NO} \left\| \nabla \varphi_i^{NO}(\vec{r}_c) \right\|^2$$

- virial potential energy density:

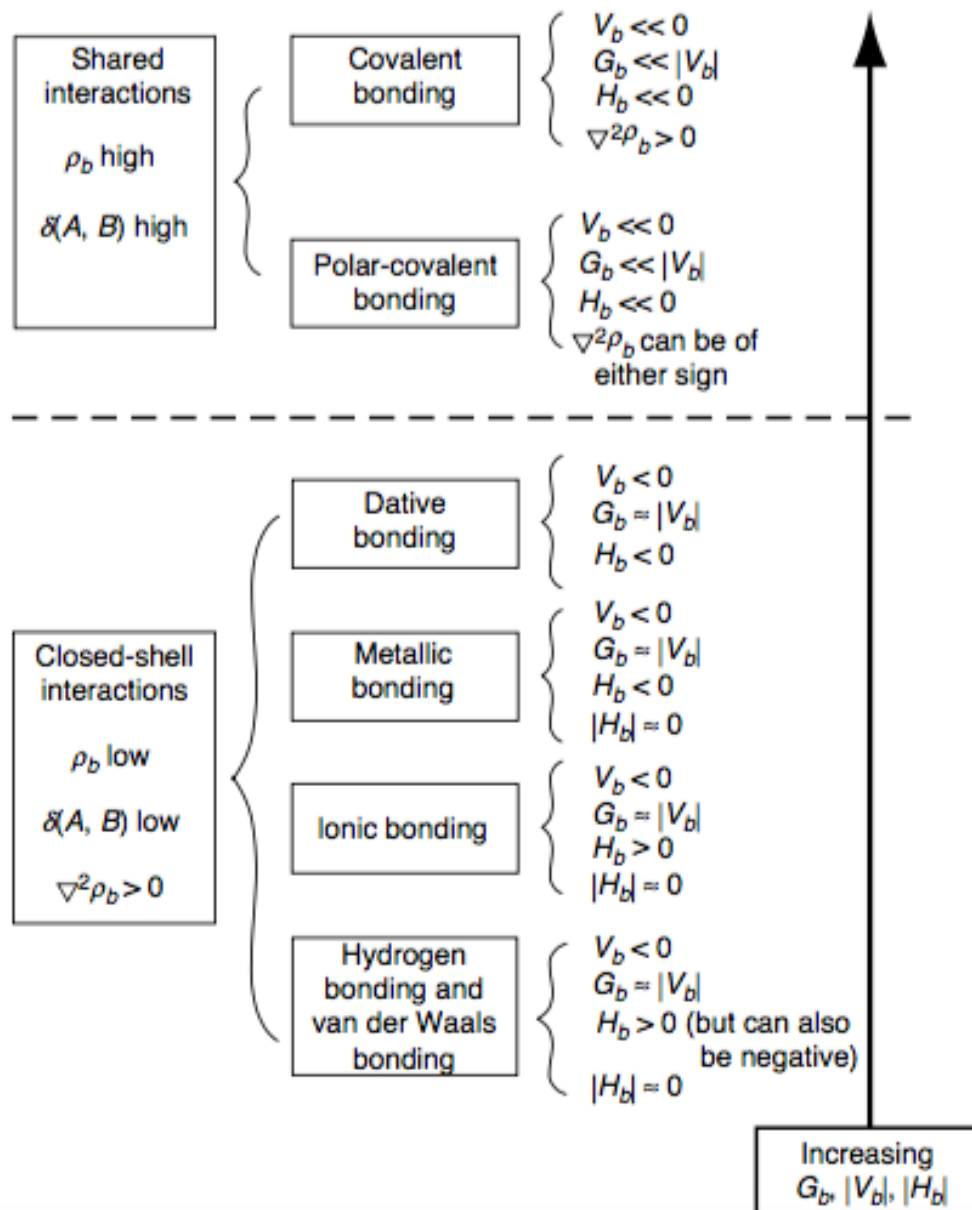
$$V(\vec{r}_c) = \frac{1}{4} \nabla^2 \rho(\vec{r}_c) - 2G(\vec{r}_c)$$

- Hamiltonian energy density:

$$H(\vec{r}_c) = G(\vec{r}_c) + V(\vec{r}_c)$$

✓ and many other descriptors (ellipticity...)

2.4. Using BCP properties to classify bonds

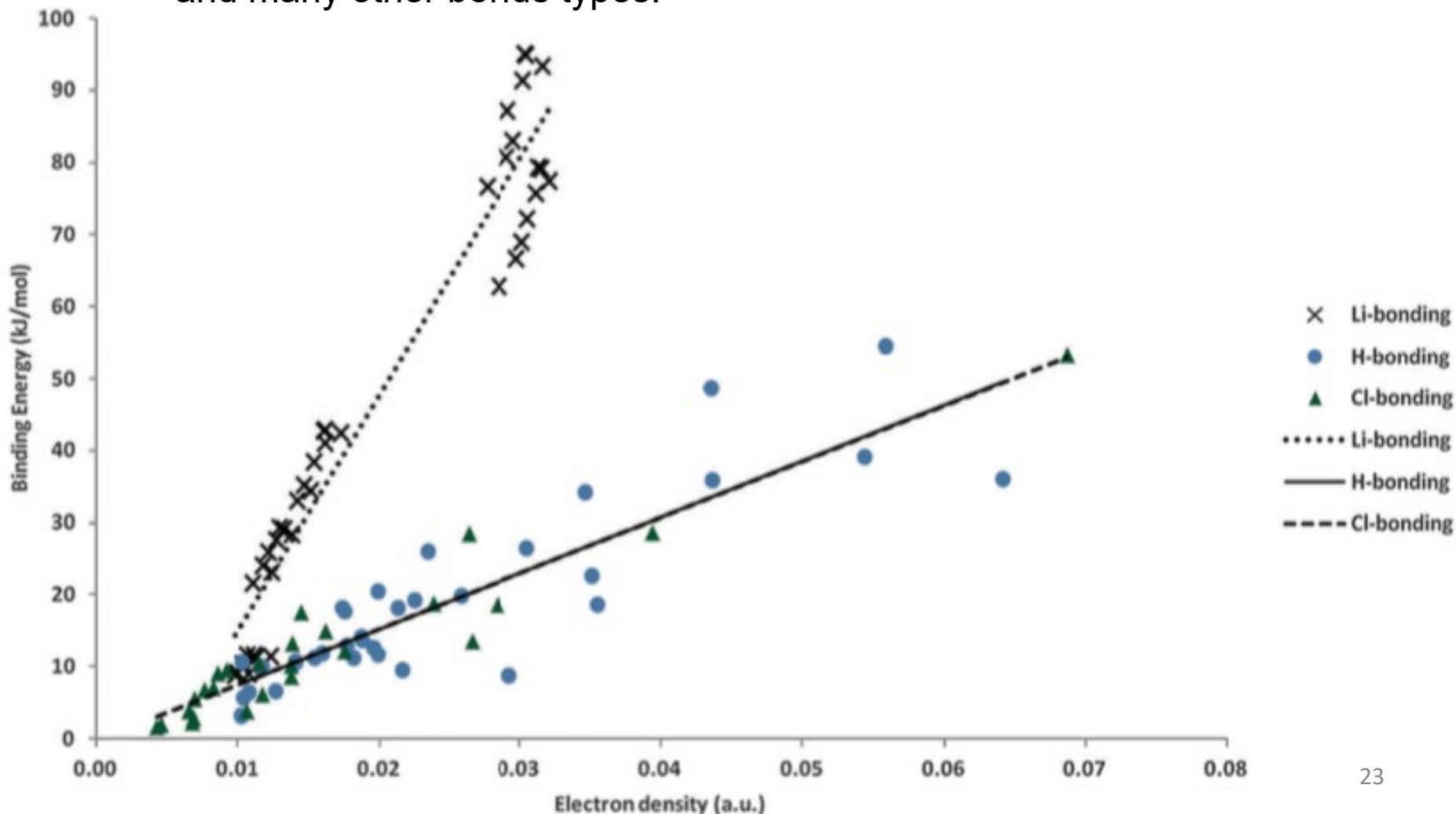


2.5. Using BCP properties to estimate bond energies

✓ *Espinosa*'s formula for hydrogen bonded complexes: $E_{HB} = \frac{1}{2} V(\vec{r}_c)$

(*Chem. Phys. Lett.* 285 (1998) 170)

✓ and many other bonds types:



2.6. Reaction mechanisms

- ✓ Chemical reactions generally involve bond forming and bond breaking
- ✓ From a topological point of view, one can follow the evolution of the molecular graph along the reaction path
- ✓ One will see *creation* and *annihilation* of critical points, in particular of (3,-1) ones
- ✓ These events always fulfill the Poincaré-Hopf relationship:

$$n_{(3,-3)} - n_{(3,-1)} + n_{(3,+1)} - n_{(3,+3)} = \begin{cases} 1 & \text{for molecules} \\ 0 & \text{for periodic systems} \end{cases}$$

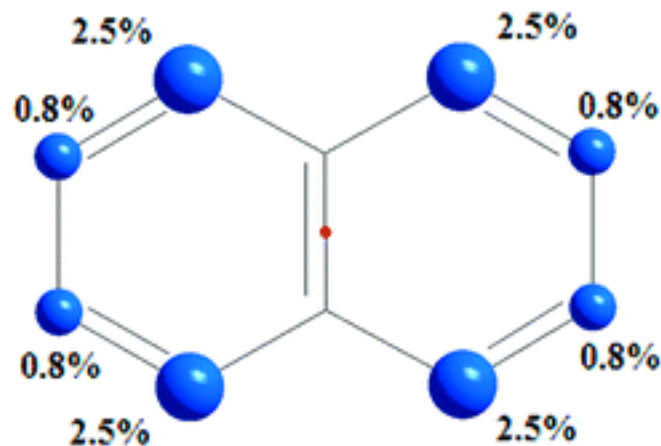
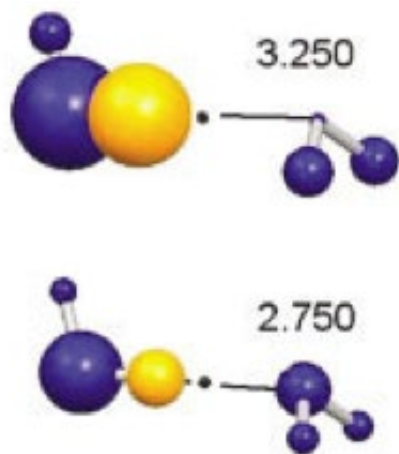
2.7. The source function

- ✓ How to understand the influence of each atom on a given bond ?
- ✓ Using one of Green's theorem:

$$\rho(\vec{r}_c) = \sum_{atoms A} S(A) \text{ with } S(A) = -\frac{1}{4\pi} \int_{\Omega_A} \frac{\nabla^2 \rho(\vec{r}')}{\|\vec{r}_c - \vec{r}'\|} d^3 r'$$

(Chem. Phys. Lett. 287 (1998) 233)

- ✓ Examples:



(J. Comput. Chem. 24 (2003) 422)

-
1. The QTAIM partition
 2. Local critical point properties
 - 3. Integrated atomic properties**
 4. Energy decompositions
 5. QTAIM in practice

3.1. Atomic properties

- ✓ Any local function g can be integrated over an atomic basin Ω_A :

$$g(A) = \int_{\Omega_A} g(\vec{r}) d^3r$$

- ✓ Atomic *population*: $N(A) = \int_{\Omega_A} \rho(\vec{r}) d^3r$

- ✓ Atomic *charge*: $q(A) = Z_A - N(A)$

- ✓ Atomic *reactivity* indices (link QTAIM-conceptual DFT using Fukui functions):

$$\text{Electrophilicity}(A) = \int_{\Omega_A} f^+(\vec{r}) d^3r$$

$$\text{Nucleophilicity}(A) = \int_{\Omega_A} f^-(\vec{r}) d^3r$$

(Chem. Phys. Lett. 527 (2012) 67)

3.2. Dipole moments

QTAIM atomic charges and molecular dipole moment

By definition:
$$\vec{\mu}^{tot} = \sum_i Z_i \vec{R}_i - \int \rho(\vec{r}) \vec{r} d^3r$$

QTAIM partition over atomic basins Ω_i

$$\vec{\mu}^{tot} = \sum_i Z_i \vec{R}_i - \underbrace{\sum_i \left(\int_{\Omega_i} \rho(\vec{r}) \vec{r} d^3r \right)}$$

$$- \sum_i \left(\int_{\Omega_i} \rho(\vec{r}) (\vec{r} - \vec{R}_i) d^3r \right) - \sum_i \underbrace{\left(\int_{\Omega_i} \rho(\vec{r}) \vec{R}_i d^3r \right)}$$

$$N_i \vec{R}_i$$

Population of atomic basin Ω_i

3.2. Dipole moments

QTAIM partition over atomic basins Ω_i

$$\vec{\mu}^{tot} = \sum_i Z_i \vec{R}_i - \sum_i \left(\int_{\Omega_i} \rho(\vec{r}) (\vec{r} - \vec{R}_i) d^3r \right) - \sum_i N_i \vec{R}_i$$

And finally:

$$\vec{\mu}^{tot} = \underbrace{\sum_i q_i \vec{R}_i}_{\text{Point Charge Contributions}} - \underbrace{\sum_i \left(\int_{\Omega_i} \rho(\vec{r}) (\vec{r} - \vec{R}_i) d^3r \right)}_{\text{Intra-atomic Polarization Contributions}}$$

Point Charge
Contributions

$$\vec{\mu}_i^q$$

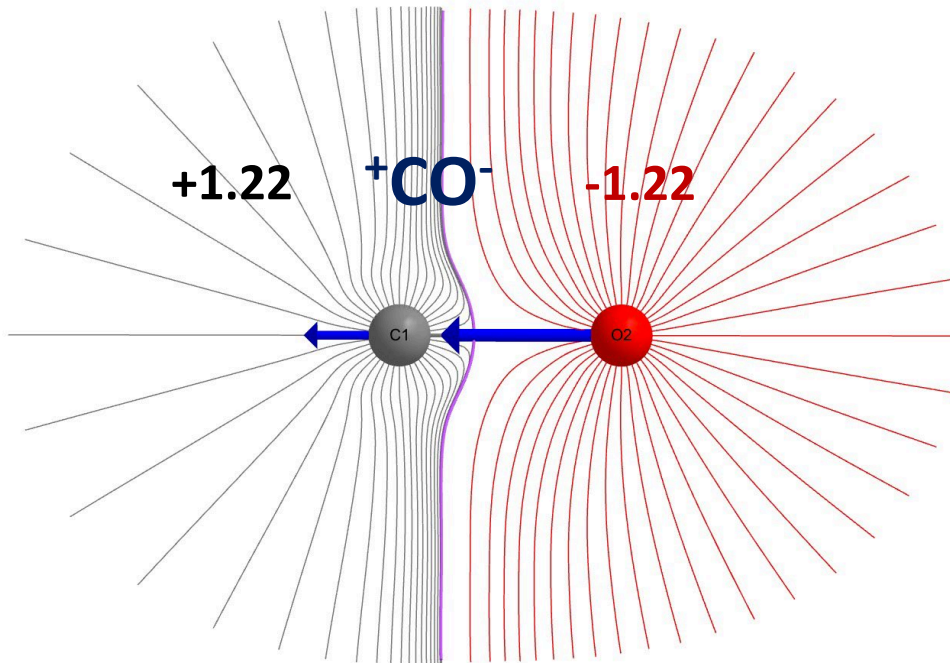
Intra-atomic
Polarization Contributions

$$\vec{\mu}_i^{intra}$$

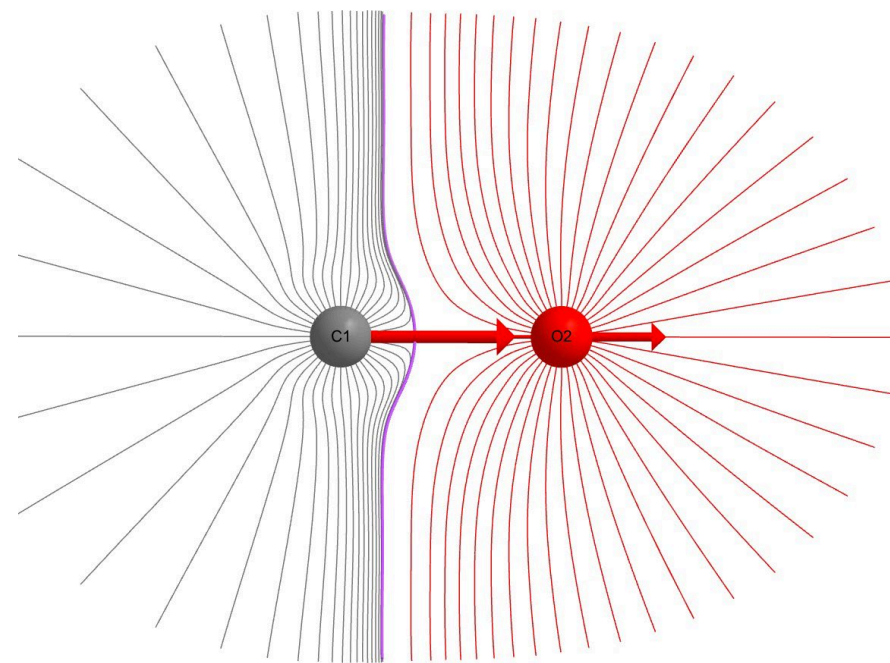
3.2. Dipole moments

QTAIM atomic charges and molecular dipole moment

A famous example: **CO** molecule



$$\sum_i \vec{\mu}_i^q \text{ (point charge contributions)}$$

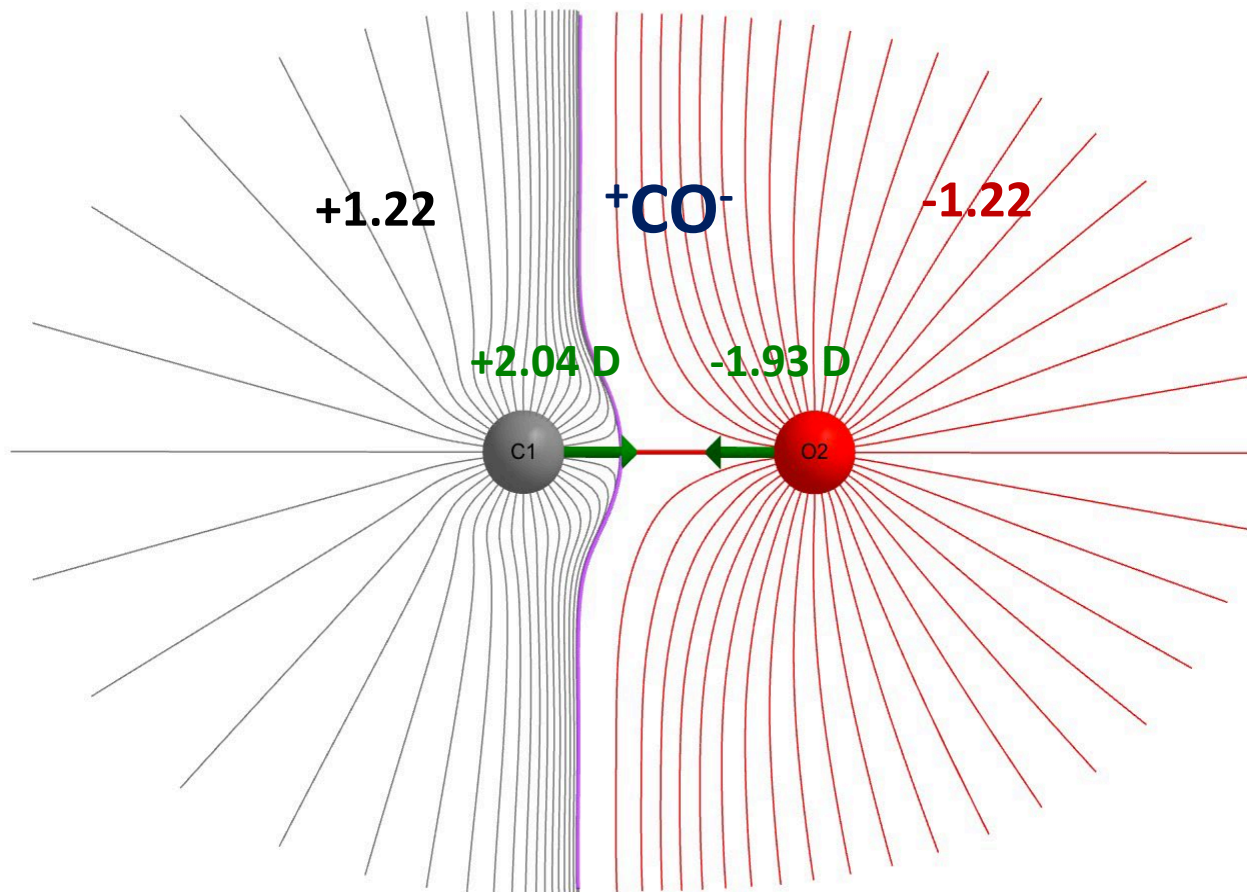


$$\sum_i \vec{\mu}_i^{intra} \text{ (counter polarization)}$$

3.2. Dipole moments

QTAIM atomic charges and molecular dipole moment

$$\vec{\mu}^{tot} = \sum_i (\vec{\mu}_i^q + \vec{\mu}_i^{intra})$$



*Atomic Charges
in agreement with
electronegativity
difference*

$$\|\vec{\mu}^{tot}\| = 0.112 \text{ D}$$



3.3. Delocalization indices

- ✓ Kind of QTAIM “*bond index*” defined from the 2-RDM:

$$DI(A, B) = 2 \left| \int_{\Omega_A} \int_{\Omega_B} (\rho_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) - \rho(\vec{r}_1)\rho(\vec{r}_2)) d^3r_1 d^3r_2 \right|$$

(*J. Phys. Chem. A* 103 (1999) 304)

- ✓ Measures the number of *electron pairs delocalized* between two atoms,
- ✓ Enables to recover Lewis picture
- ✓ Examples (at the HF level):

$$\delta(H, H)_{H_2} = 1.0$$

$$\delta(C, C)_{C_2H_6} = 0.99$$

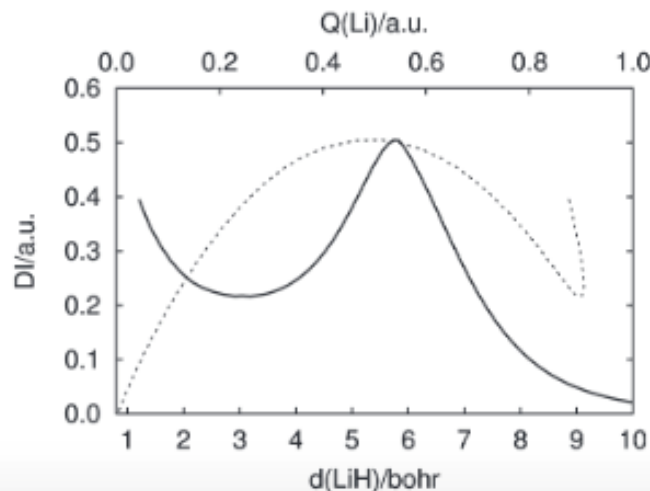
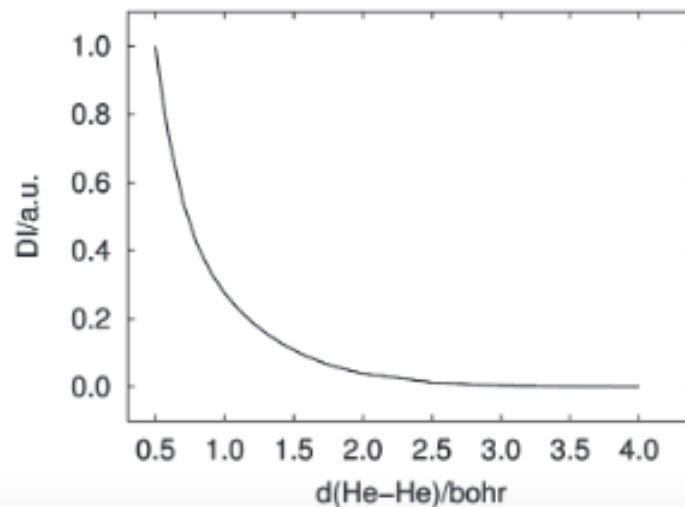
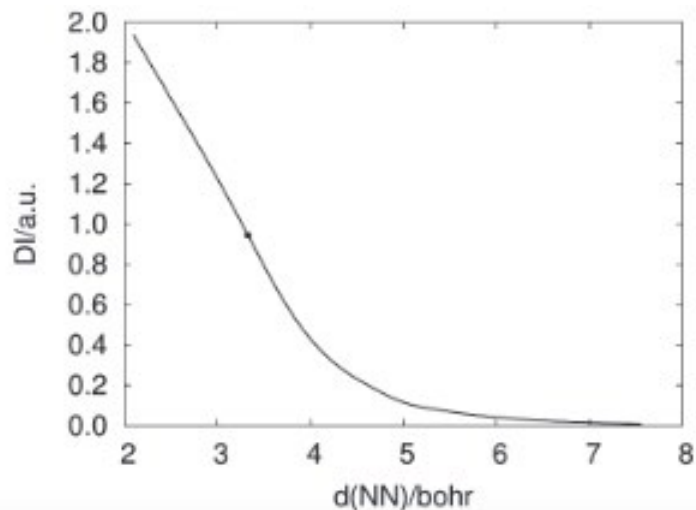
$$\delta(C, C)_{C_6H_6} \approx 1.39$$

$$\delta(C, C)_{C_2H_4} \approx 1.89$$

- ✓ Electron correlation tends to slightly decrease DI values

3.3. Delocalization indices

- ✓ The evolution of DIs with distance gives insight into bond nature



(J. Chem. Theory Comput. 7 (2011) 1704)

4.1. Virial atomic energies

- ✓ Quantum *virial* theorem for the exact wavefunction::

$$E_{mol} = -T_e - \sum_i X_i \frac{\partial E_{mol}}{\partial X_i}$$

- ✓ At an *equilibrium* geometry: $E_{mol} = -T_e$

- ✓ Two forms of kinetic energy:

$$\begin{aligned} T_e \left[\left\{ \varphi_i^{NO} \right\} \right] &= \int_{R^3} \underbrace{-\frac{1}{2} \sum_{i=1}^{+\infty} n_i^{NO} \varphi_i^{NO}(\vec{r}) \nabla^2 \varphi_i^{NO}(\vec{r})}_{K(\vec{r})} d^3 r \\ &= \int_{R^3} \underbrace{\frac{1}{2} \sum_{i=1}^{+\infty} n_i^{NO} \left\| \nabla \varphi_i^{NO}(\vec{r}) \right\|^2}_{G(\vec{r})} d^3 r \end{aligned}$$

4.1. Virial atomic energies

✓ But we have: $K(\vec{r}) = \nabla^2 \rho(\vec{r}) + G(\vec{r})$

✓ The zero-flux condition gives through Ostrograsky-Gauss theorem:

$$\int_{\Omega_A} \nabla^2 \rho(\vec{r}) d^3 r = \oiint_{\Sigma_A} \nabla \rho(\vec{r}) \cdot \vec{n}(\vec{r}) d\Sigma = 0 \quad (\text{Integration accuracy : } Lap(A) \sim 10^{-3} \text{ a.u.})$$

✓ So that: $\underbrace{\int_{\Omega_A} K(\vec{r}) d^3 r}_{K(A)} = \underbrace{\int_{\Omega_A} G(\vec{r}) d^3 r}_{G(A)}$

✓ And: $T_e = \sum_A K(A) = \sum_A G(A)$

✓ The atomic kinetic energy is *unambiguously* determined with QTAIM atoms !

4.1. Virial atomic energies

- ✓ Bader's original definition of the *atomic energy* at equilibrium geometry:

$$E(A) = -K(A) = -G(A)$$

- ✓ So that:

$$E_{mol} = \sum_A E(A)$$

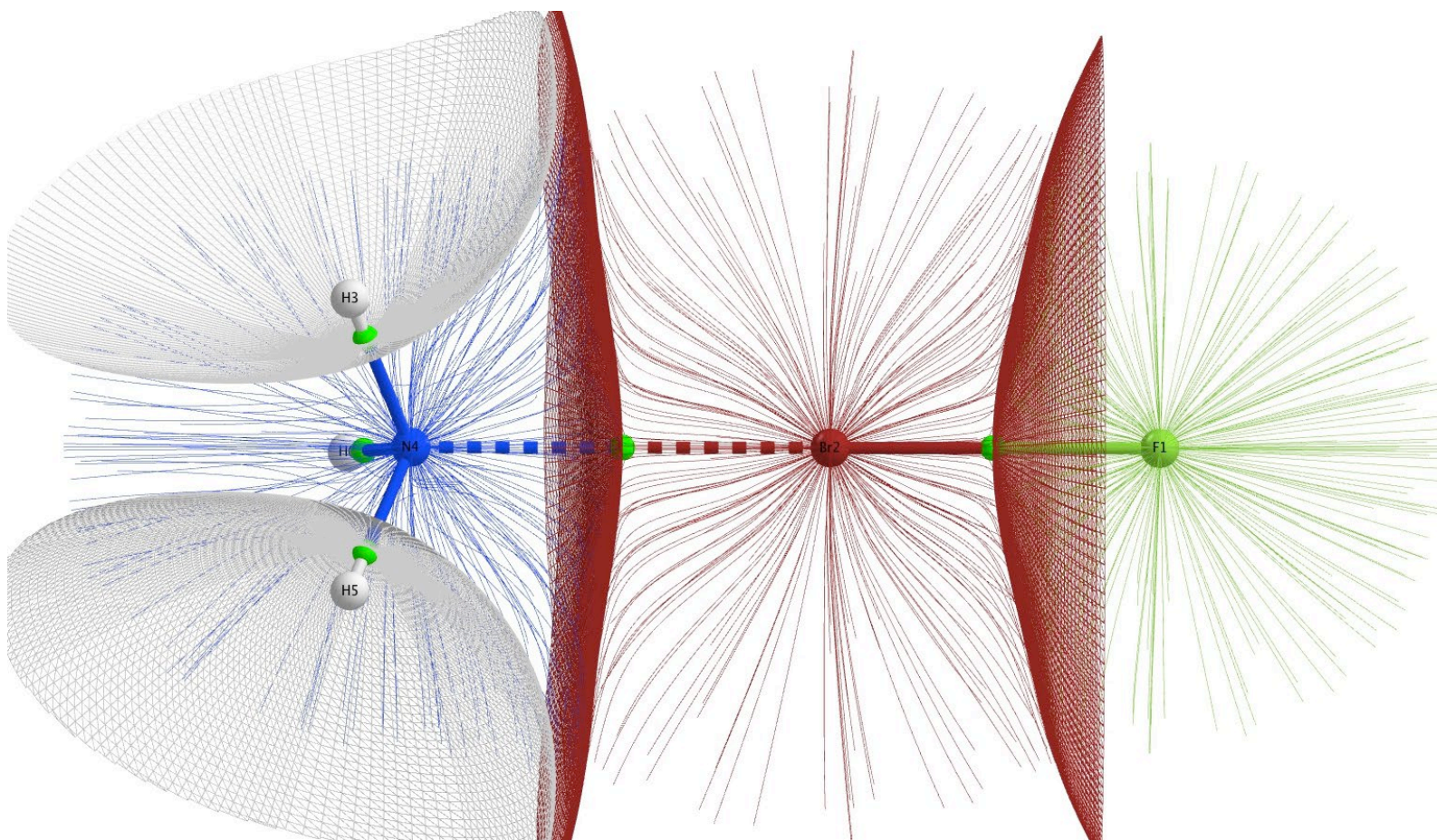
- ✓ In practice one will use approximate wavefunctions. A *scaling* approach is then often used:

$$E(A) = -\kappa K(A) = -\kappa G(A)$$

- ✓ κ is chosen so that we recover the calculated molecular energy by summation

4.2. The interacting quantum atoms approach (IQA)

- ✓ Based on real space partitioned into atomic bassins Ω_A :



4.2. The interacting quantum atoms approach (IQA)

- ✓ An *exact* decomposition at *any* PES point:

(*J. Chem. Phys.* 120 (2004) 4581)

(*J. Chem. Theory Comput.* 1 (2005) 1096)

(*J. Chem. Theory Comput.* 2 (2006) 90)

$$E_{tot} = \sum_A E_A^{self} + \frac{1}{2} \sum_A \sum_{B \neq A} E_{AB}^{int}$$

- ✓ With: $E_{AB}^{int} = E_{AB}^{nn} + (E_{AB}^{en} + E_{AB}^{ne}) + E_{AB}^{ee}$

“covalency”

- ✓ In particular:

$$E_{AB}^{ee} = \underbrace{\int_{\Omega_A} \int_{\Omega_B} \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{\|\vec{r}_1 - \vec{r}_2\|} d^3 r_1 d^3 r_2}_{E_{AB}^{eeCoul} = \frac{q_A q_B}{R_{AB}} + \text{multipoles}} - \underbrace{\int_{\Omega_A} \int_{\Omega_B} \frac{|\rho_1(\vec{r}_1; \vec{r}_2)|^2}{\|\vec{r}_1 - \vec{r}_2\|} d^3 r_1 d^3 r_2}_{E_{AB}^x} + E_{AB}^c$$

$$\int_{\Omega_A} \int_{\Omega_B} \frac{\rho_1(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2)}{\|\vec{r}_1 - \vec{r}_2\|} d^3 r_1 d^3 r_2$$

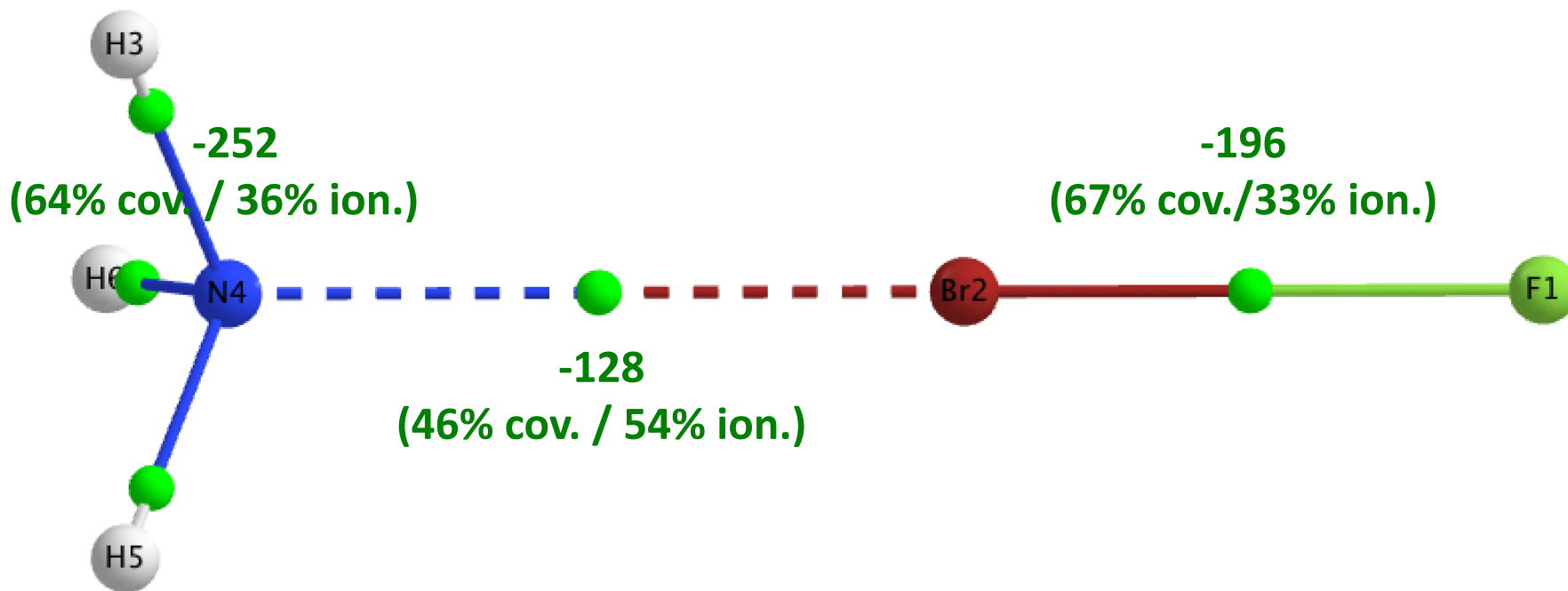
- ✓ But approximate in KS-DFT...

(*Phys. Chem. Chem. Phys.* 16 (2014) 14539)

(*Mol. Phys.* 114 (2016) 1285)

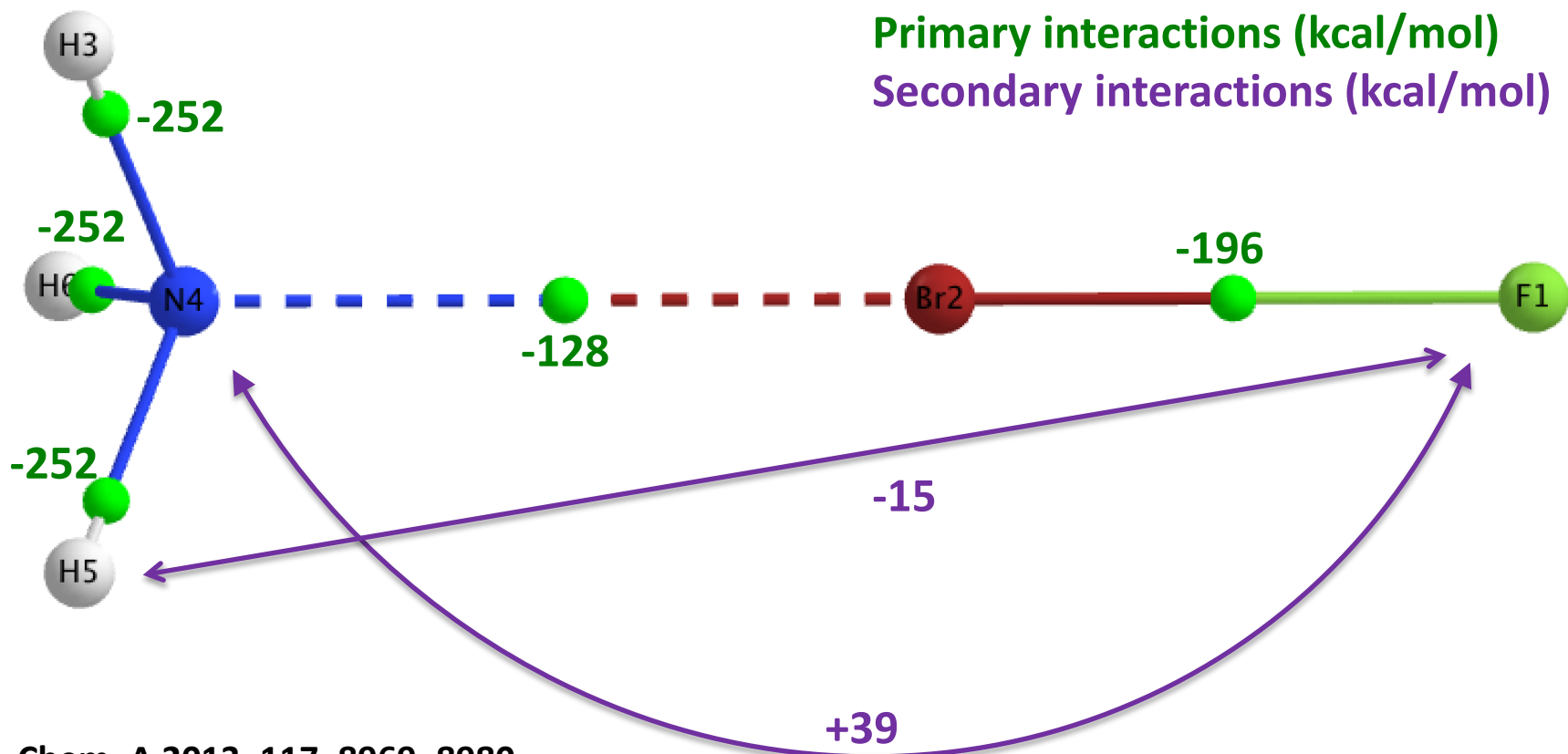
4.2. The interacting quantum atoms approach (IQA)

IQA energy decomposition (partial)
(all values in kcal/mol)



4.2. The interacting quantum atoms approach (IQA)

IQA energy decomposition (partial)
(all values in kcal/mol)



4.3. The many faces of binding energies

- ✓ Between two fragments:

$$E_{SCF}^{bind} = E(F_1 \dots F_2) - E(F_1) - E(F_2)$$

- ✓ It includes:

- interactions between each atoms pair whatever they belong to the same fragment or not
- changes inside each atom (intraatomic contributions)

- ✓ As a pure measure of interaction between F_1 and F_2 (with a BCP linking atoms X_1 and X_2) without the need for any reference:

$$E_{IQA}^{inter} = \sum_{A \in F_1} \sum_{B \in F_2} E_{IQA}^{AB} = \underbrace{E_{IQA}^{X_1 X_2}}_{primary} + \underbrace{\sum_{A \neq X_1 \in F_1} \sum_{B \neq X_2 \in F_2} E_{IQA}^{AB}}_{secondary}$$

(*J. Phys. Chem. A* 117 (2013) 8969)

Conclusions

- ✓ QTAIM provides a *physically* rigorous definition of atoms-in-molecules based on the electron density gradient field (experimental or theoretical)
- ✓ It is composed of two complementary approaches:
 - a *local* one that focuses on critical points properties
 - an *integrated* one that enables to evaluate atomic properties
- ✓ It affords a wide arsenal of *descriptors* for studying chemical interactions
- ✓ *Energy decompositions* are also available and informative
- ✓ Obviously this document is very far from being comprehensive
- ✓ **Other** interesting atom-in-molecules definitions exist, among them:
 - Hirshfeld
 - Fuzzy
 - Parr