Electron density distribution analysis

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Electron density analysis

- Introduction
- QTAIM
- NCI
- ELF

QTAIM

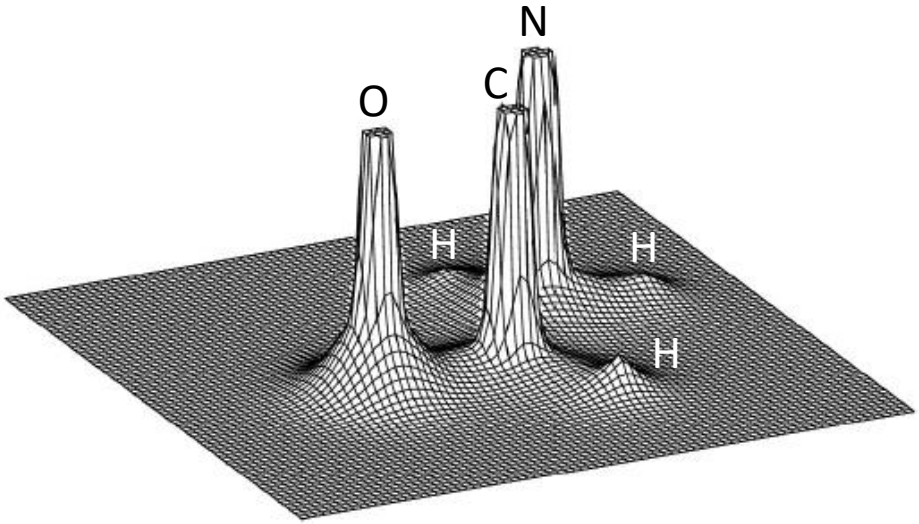
The traditional way of approaching the theoretical basis of chemistry is though the wavefunction and the molecular orbitals obtained through approximate solutions to the Schrödinger wave equation

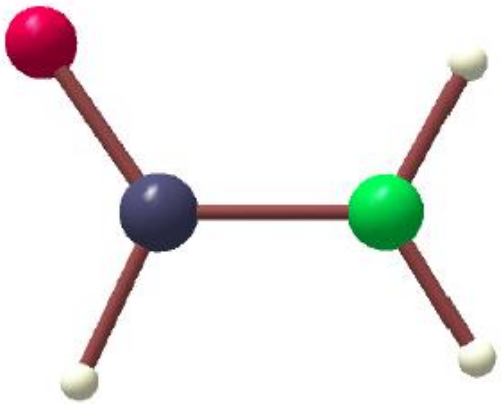
$$H\Psi = E\,\Psi$$

The Hohenberg-Kohn theorem confirmed that **the density, ρ(r), is the fundamental property that characterizes the ground state** of a system - once $\rho(r)$ is known, the energy of the system is uniquely defined, and from there a diverse range of molecular properties can, in principle, be deduced.

Thus a knowledge of $\rho(r)$ opens the door to understanding of all the key challenges of chemistry. $\rho(r)$ is a quantum-mechanical observable is **both experimentally and theoretically accessible**.

QTAIM



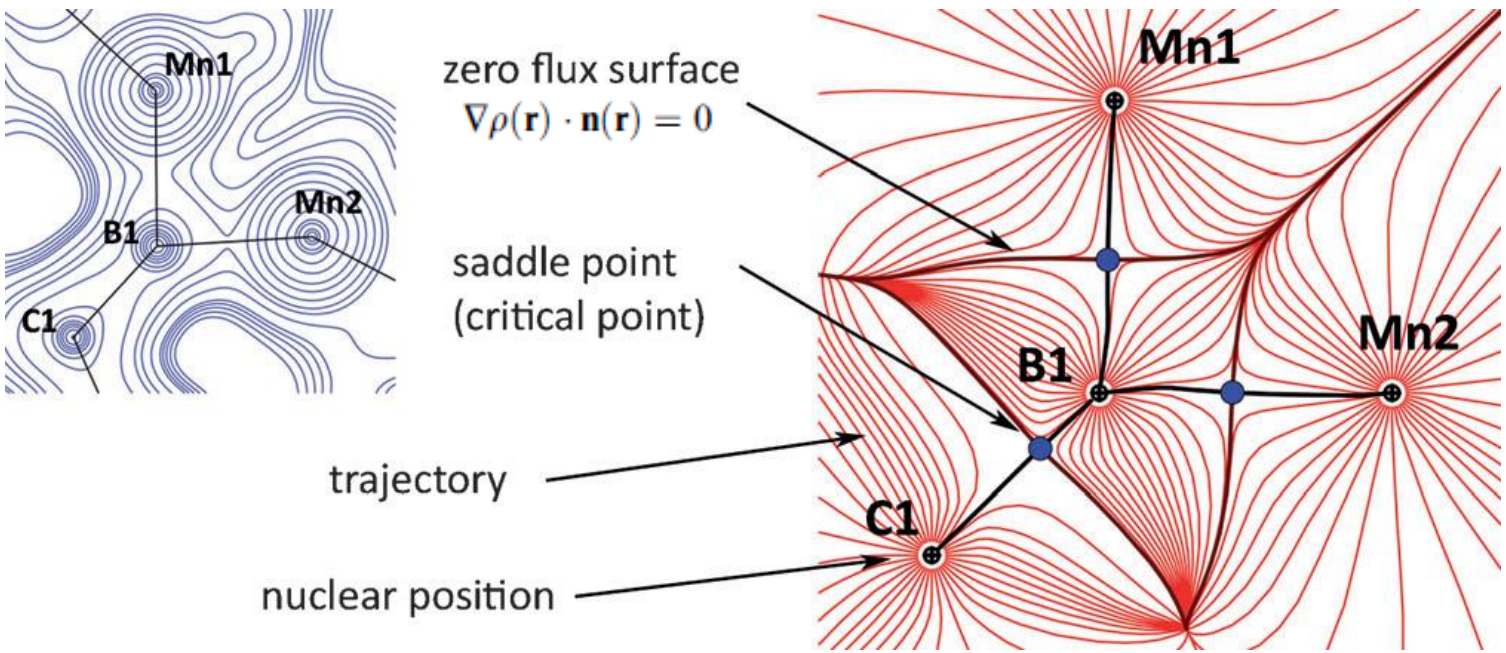


- A representation of the total charge density $\rho(r)$ in the plane of the formamide molecule. This is a typical picture of $\rho(r)$ where the distribution is dominated by the electrostatic attraction of the electrons for the positively charged nuclei.
- The maxima occur at the nuclear sites and $\rho(r)$ decays in a nearly spherical manner away from the nuclei.
- The other obvious features are the saddle points between the nuclei.

QTAIM

- A quantitative way to analyse the topology of $\rho(r)$ is to consider the gradient $\nabla\rho(r)$. At critical points this gradient vanishes.

Electron density map $\rho(\vec{r})$



Electron density gradient $\nabla\rho(\vec{r})$

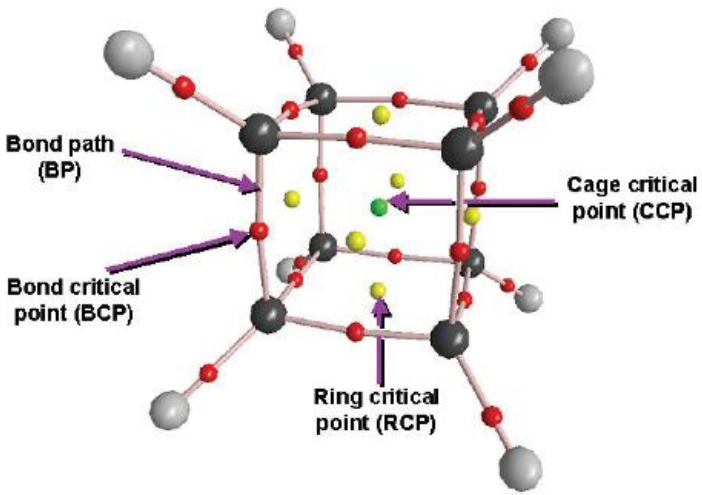
At critical points (CPs):
$\nabla\rho(\vec{r}) = 0$

QTAIM

Hessian:

$$\mathcal{H}(x,y,z) = \begin{bmatrix} \frac{\partial^2 f}{\partial x^2} & \frac{\partial f}{\partial y \partial x} & \frac{\partial^2 f}{\partial z \partial x} \\ \frac{\partial^2 f}{\partial x \partial y} & \frac{\partial^2 f}{\partial y^2} & \frac{\partial^2 f}{\partial z \partial y} \\ \frac{\partial^2 f}{\partial x \partial z} & \frac{\partial^2 f}{\partial y \partial z} & \frac{\partial^2 f}{\partial z^2} \end{bmatrix}$$

The CPs are designated as ($\boldsymbol{\omega}$, $\boldsymbol{\sigma}$), where $\boldsymbol{\omega}$ is rank of CP and $\boldsymbol{\sigma}$ is its signature

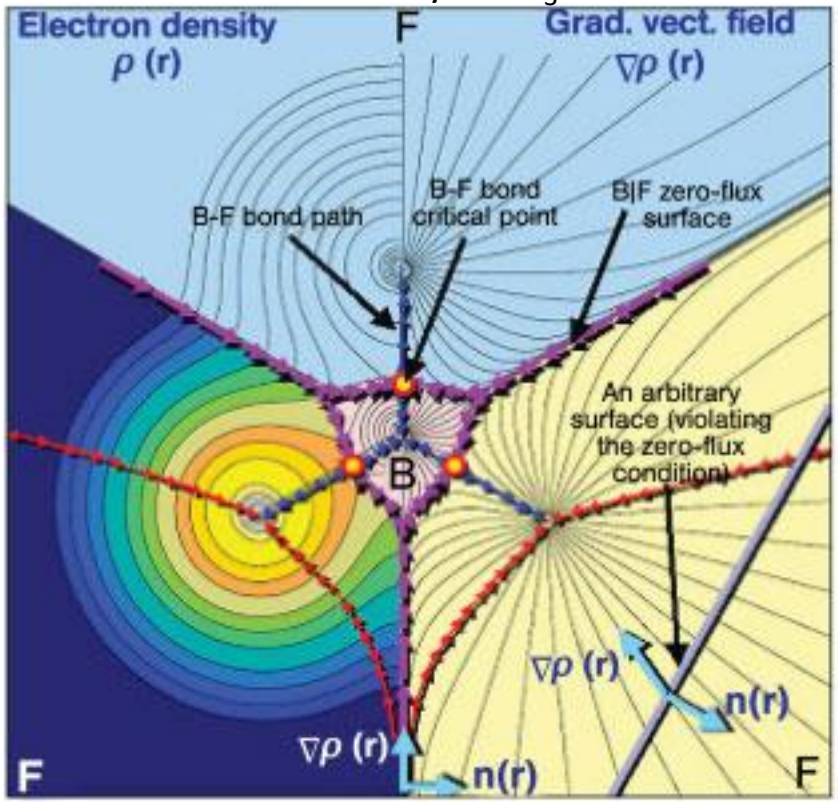


Critical points:

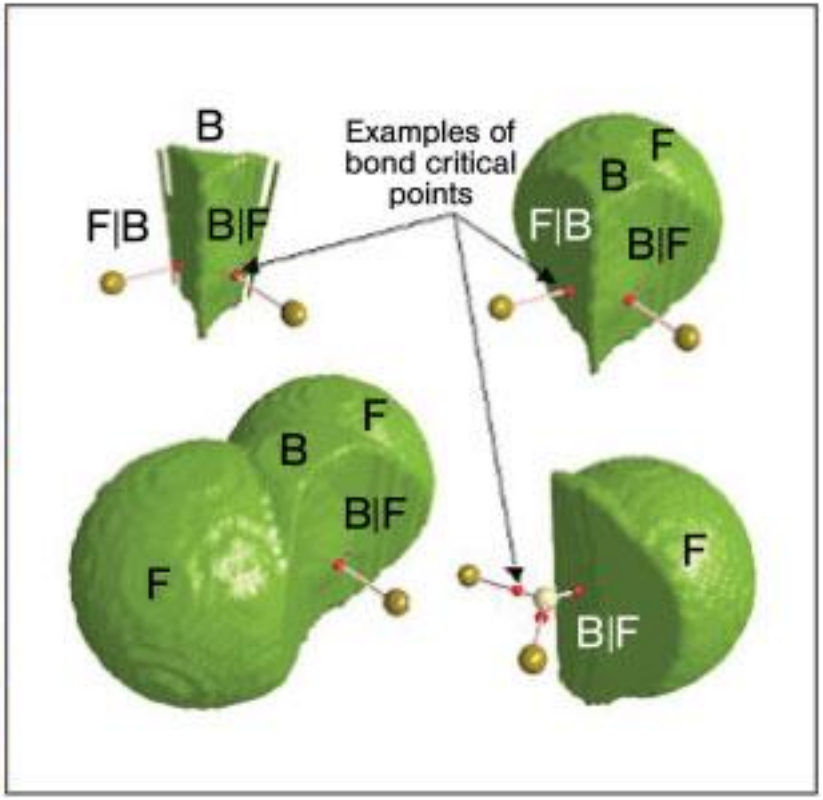
- (3, -3) Nucleus
- (3, -1) Bond Critical point (BCP)
- (3,+1) Ring Critical point (RCP)
- (3,+3) Cage Critical point (CCP)

R. F. W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press: Oxford, U.K., 1990.

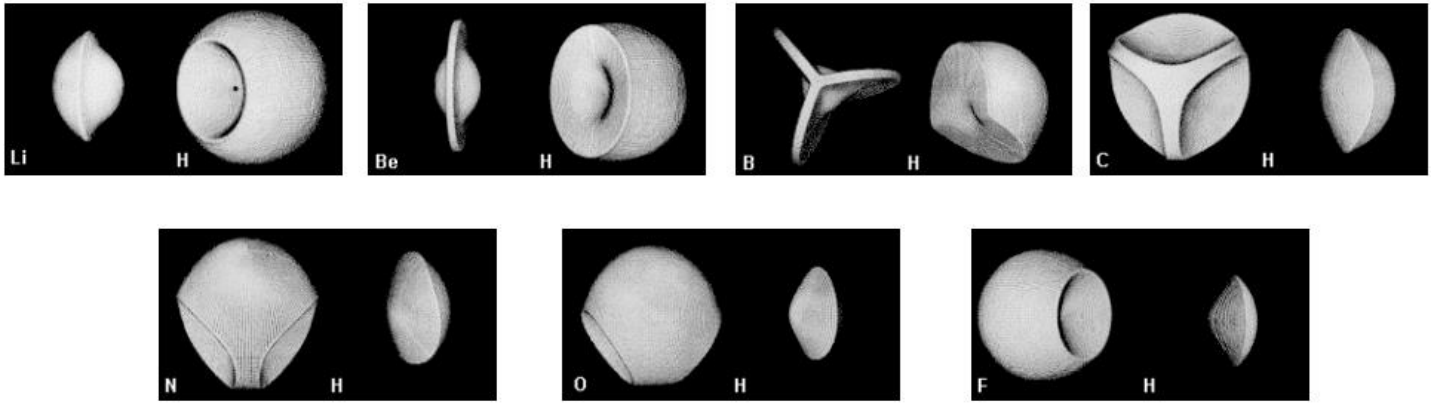
The electron density and the gradient vector field of the density of BF_3



Density of atoms and groupings of atoms in BF_3



The 2nd-row hydrides: AH_n, where A = Li, Be, B, C, N, O, F



Atomic properties obtaining using QTAIM:

1. Electron population $N(\Omega)$ - subtraction of the nuclear charge give the Bader atomic charge $q(\Omega)$. This is an unambiguous method of determining atomic charges !

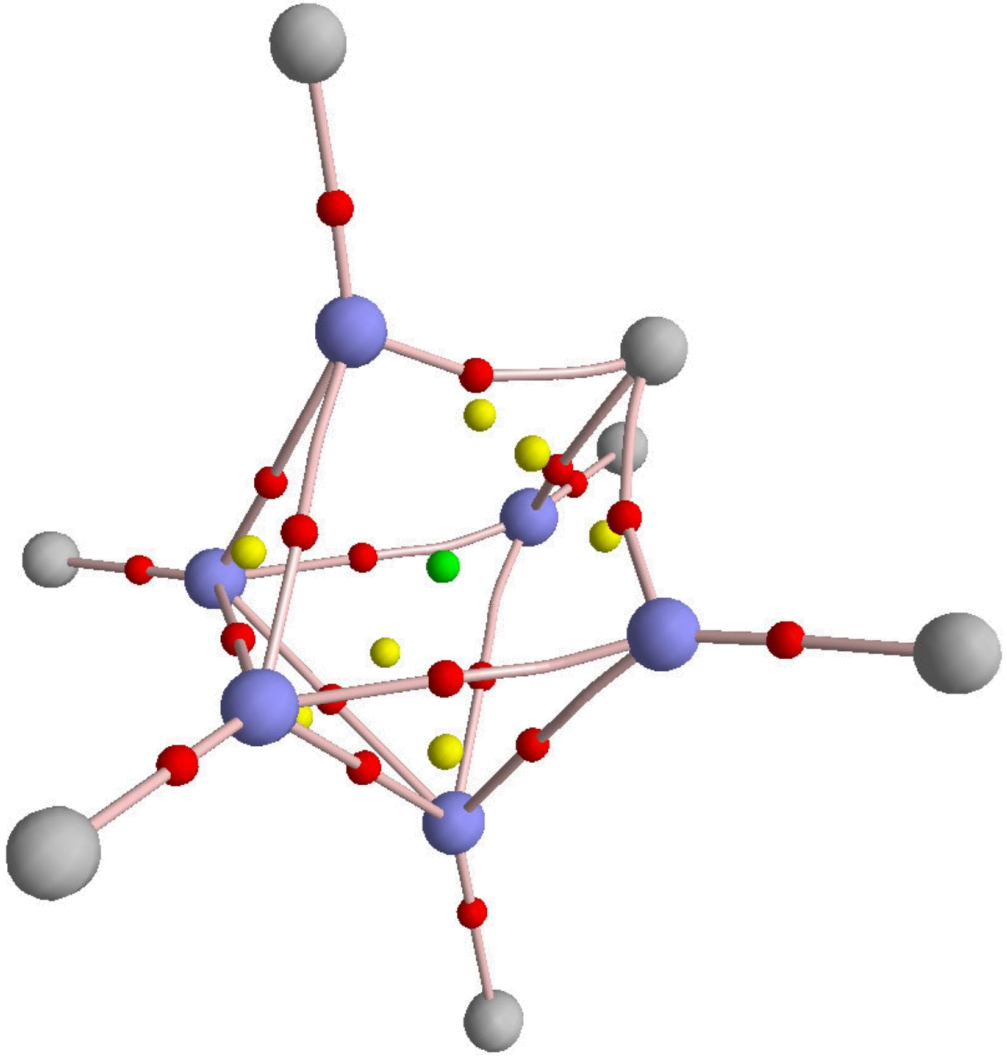
2. Atomic volume $\mathrm{Vol}(\Omega)$ - the volume of space inside the interatomic surface. Since (for molecules in the gas phase) part of the interatomic surface is terminated at infinity, it is usual to terminate integration at the level 0.001 a.u. Usually this is closely similar to the van der Waals volume, and it generally encloses more than 99% of the electron population.

3. Atomic Laplacian $L(\Omega)$ - this property should vanish, and the actual magnitude is used as a gauge for the accuracy of integration.

4. Atomic energy $E(\Omega)$ - Baders analysis provides a unique method for obtaining (additive) atomic energies.

5. Other properties, the atomic dipolar $\mu(\Omega)$ or quadrupolar $\underline{Q}(\Omega)$ polarisations.

QTAIM: molecular graph

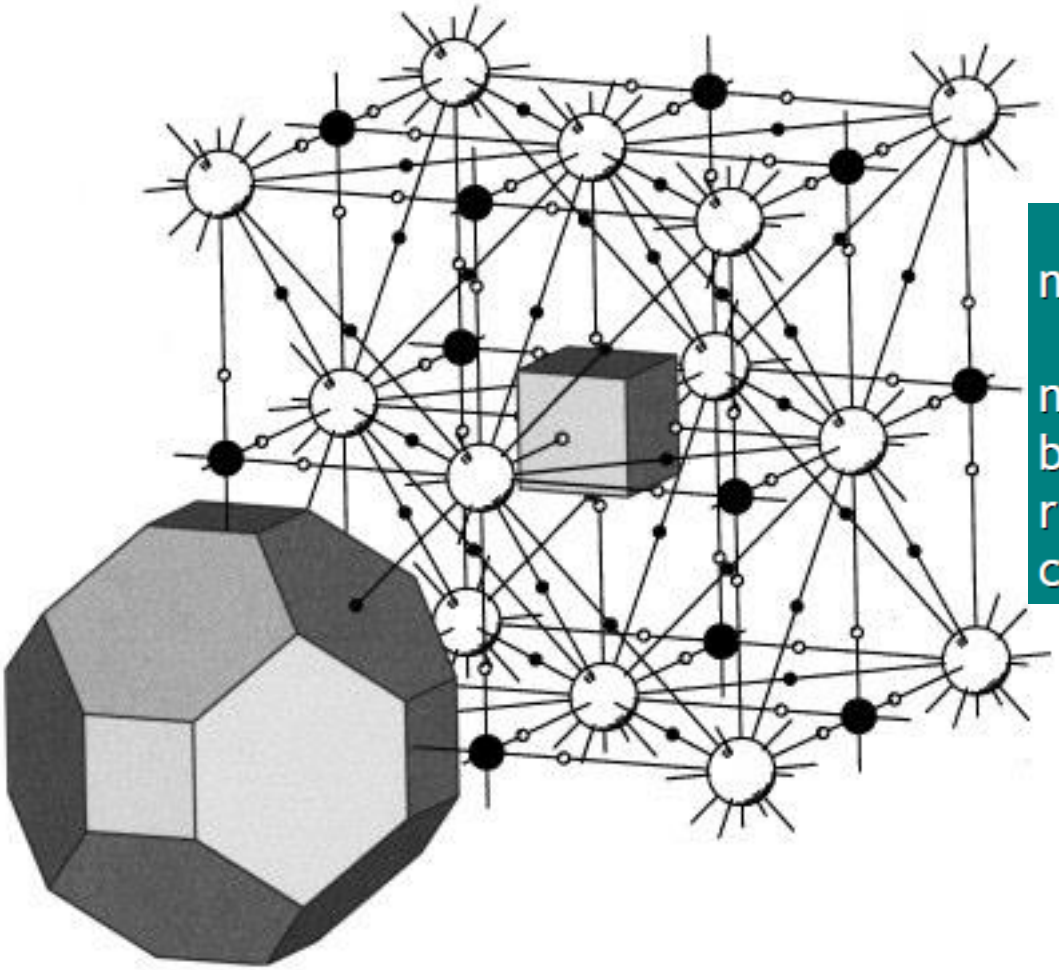


$n - b + r - c = 1$

n = number of (3,-3) cp's
b = number of (3,-1) cp's
r = number of (3,+1) cp's
c = number of (3,+3) cp's

$13 - 18 + 7 - 1 = 1$!!

QTAIM: topology in crystals

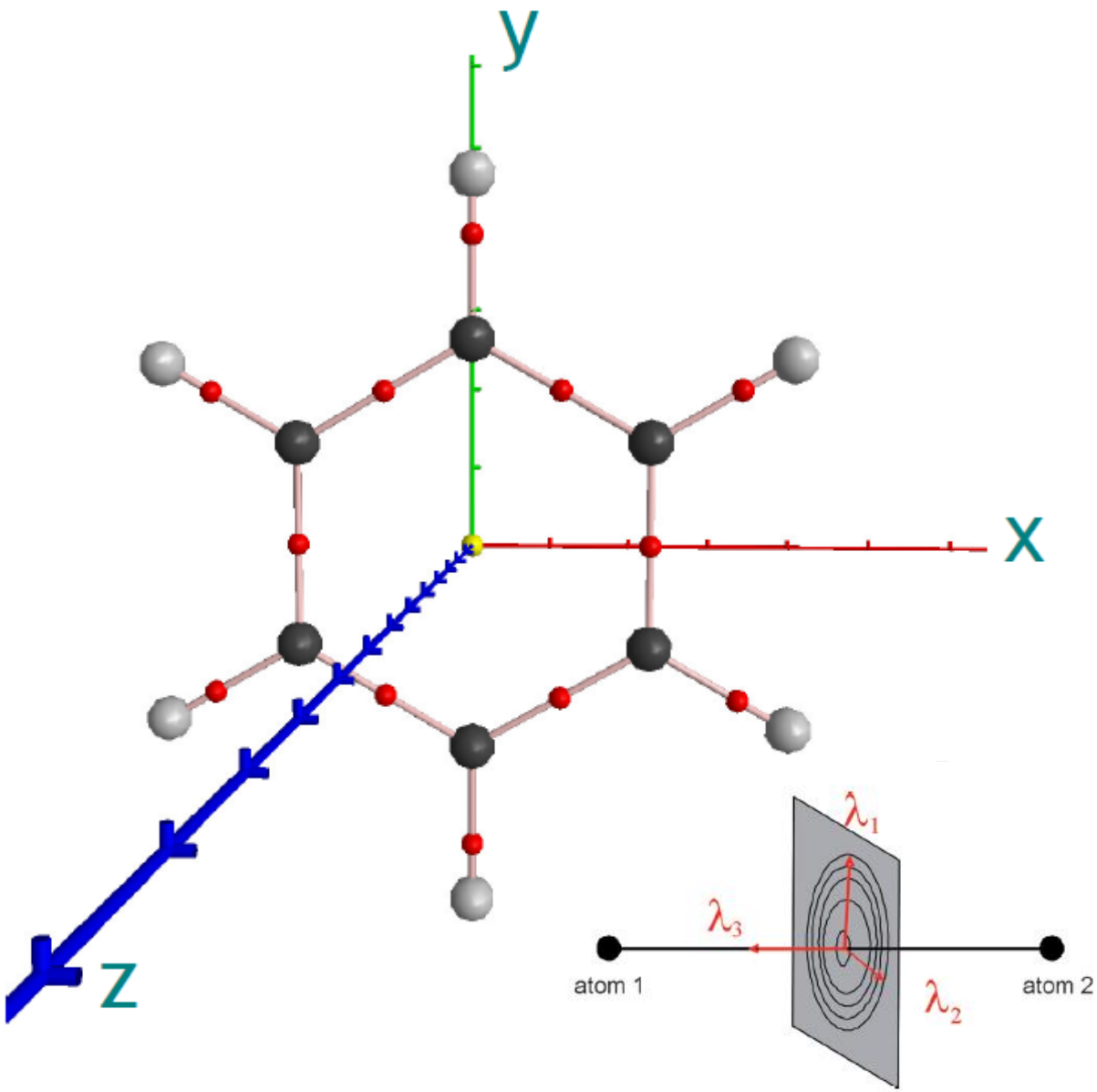


$$n - b + r - c = 0$$

$n \geq 1$, $b \geq 3$, $r \geq 3$, $c \geq 1$

n = number of (3,-3) cp's
b = number of (3,-1) cp's $\rightarrow$ faces
r = number of (3,+1) cp's $\rightarrow$ edges
c = number of (3,+3) cp's $\rightarrow$ vertices

Bond ellipticity



$\varepsilon = \lambda_1/\lambda_2 - 1$

C–C bond

Rho(r) 2.084
Lap(r) −20.791
Eigenvalues
λ_1 −15.599
λ_2 −12.990
λ_3 7.797
ε 0.201 (π–bond)

C–H bond

Rho(r) 1.901
Lap(r) −23.379
Eigenvalues
λ_1 −18.033
λ_2 −17.728
λ_3 12.382
ε 0.017 (cylindrical)

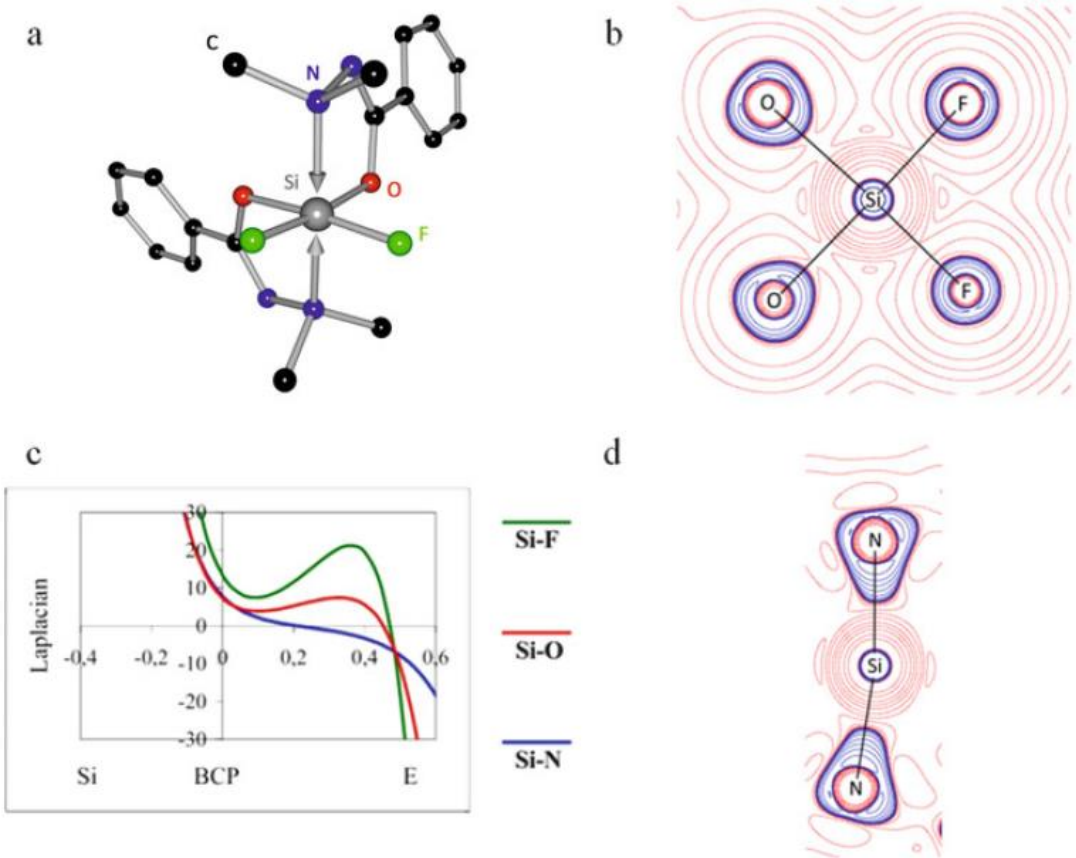
Units in Å

Closed shell and open shell interactions

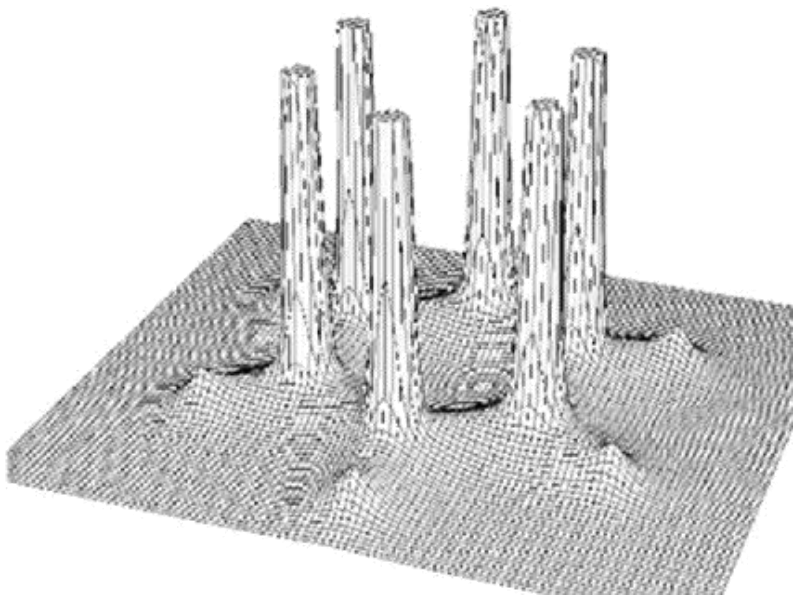
Properties at the BCP	Covalent	Closed shell
Electron density $\rho(\mathbf{r})$	High	Low
Laplacian $\nabla^2\rho(\mathbf{r})$	Negative	Positive
$\eta = \lvert\lambda_1\rvert/\lambda_3$	Bigger than unity	Smaller than unity
Total energy density $H(\mathbf{r})$	Negative	Positive

Closed shell and open shell interactions

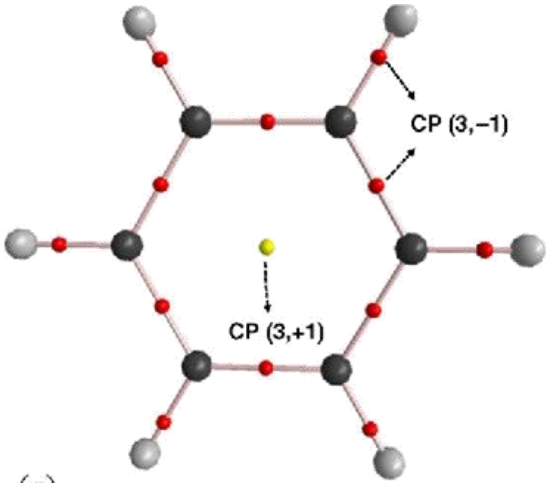
Bond	$\rho(\mathbf{r}_{BCP})$ [eÅ^{-3}]	$\nabla^2\rho(\mathbf{r}_{BCP})$ [eÅ^{-5}]	H_{BCP}	G_{BCP}/ρ_{BCP}	η
Si ← N	0.501(16)	7.78(3)	−0.011	1.23	0.20
Si–O	0.766(13)	7.37(3)	−0.052	1.14	0.29
Si–F	1.015(13)	13.47(3)	−0.076	1.43	0.26



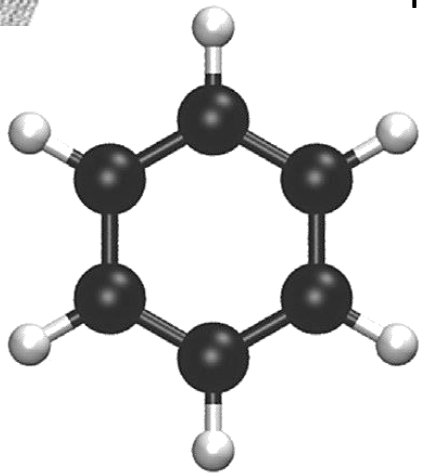
From electronic density to chemical structure



Electron density



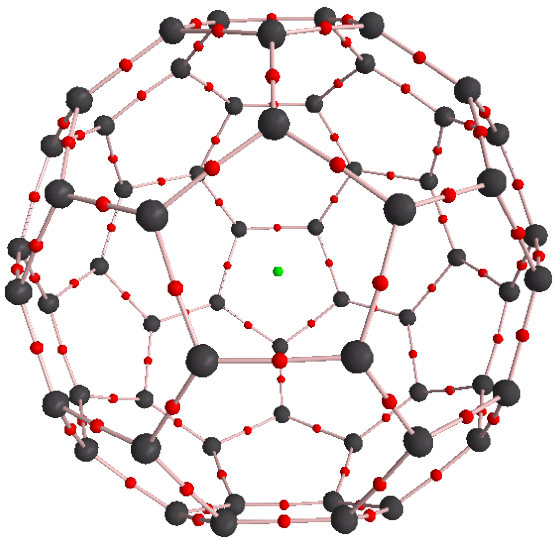
Topology of electron density



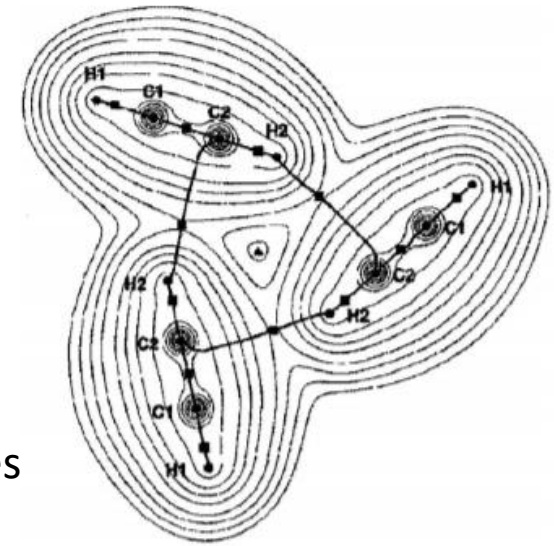
Chemical structure

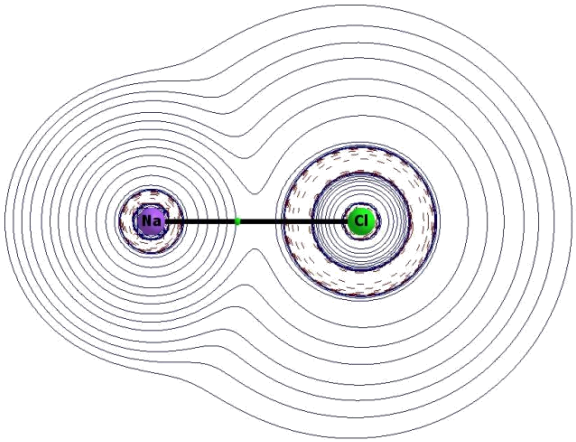
Kumar, P. S./*J. Chem. Sci.* 128 (2016): 1527-1536.

Limitations of QTAIM



Complicated for nonplanar structures



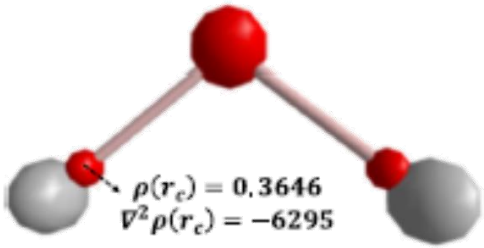


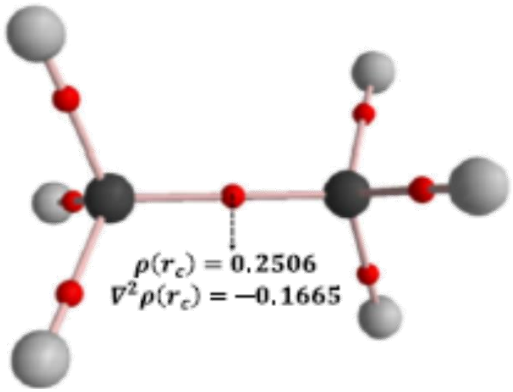
Don’t consider peculiarities of ionic and metallic bonding

Bonds between the neighboring molecules

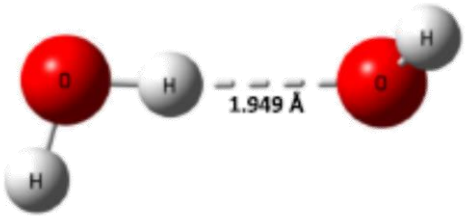
www.aim2000.de, P.L.A. Propelier / Cheminform. September 2005. 57 p.

Weak interactions: problems of QTAIM

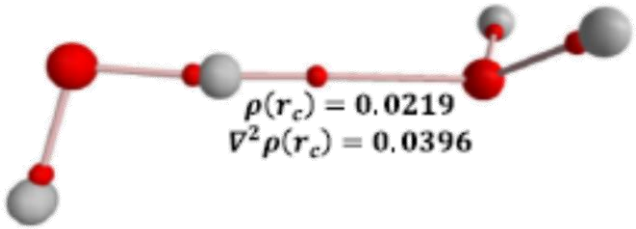




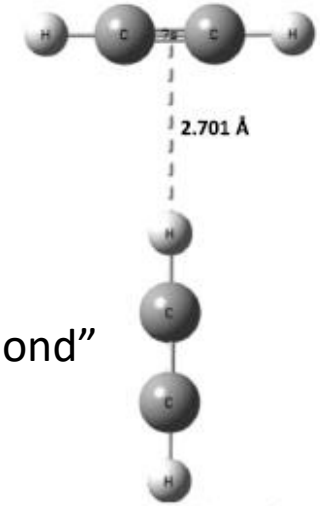
covalent bond



E_{int}= −4.33 k cal mol^{-1}

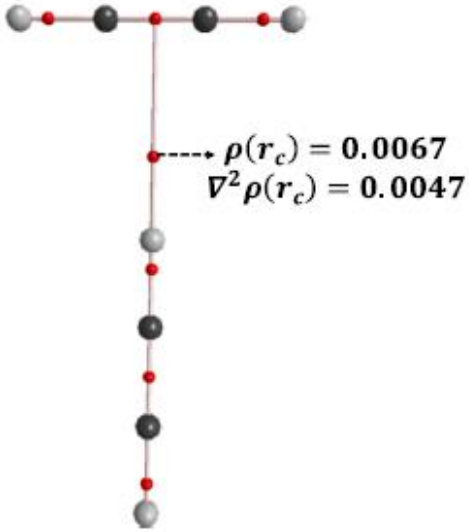


conventional hydrogen bond



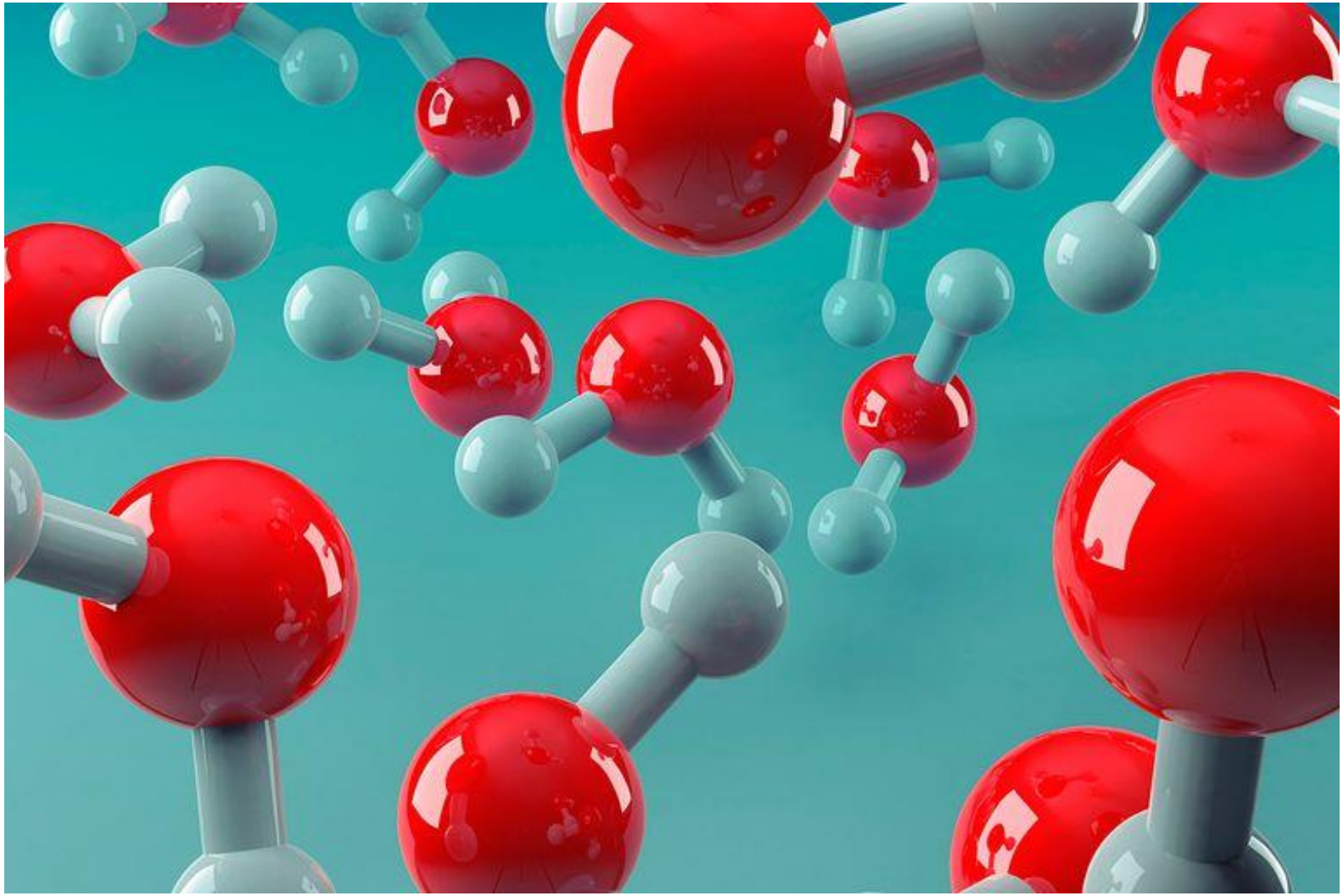
weak
“hydrogen bond”

E_{int}= −0.93 k cal mol^{-1}



Kumar, P. S./*J. Chem. Sci.* 128 (2016): 1527-1536.

NCI – non covalent interactions index



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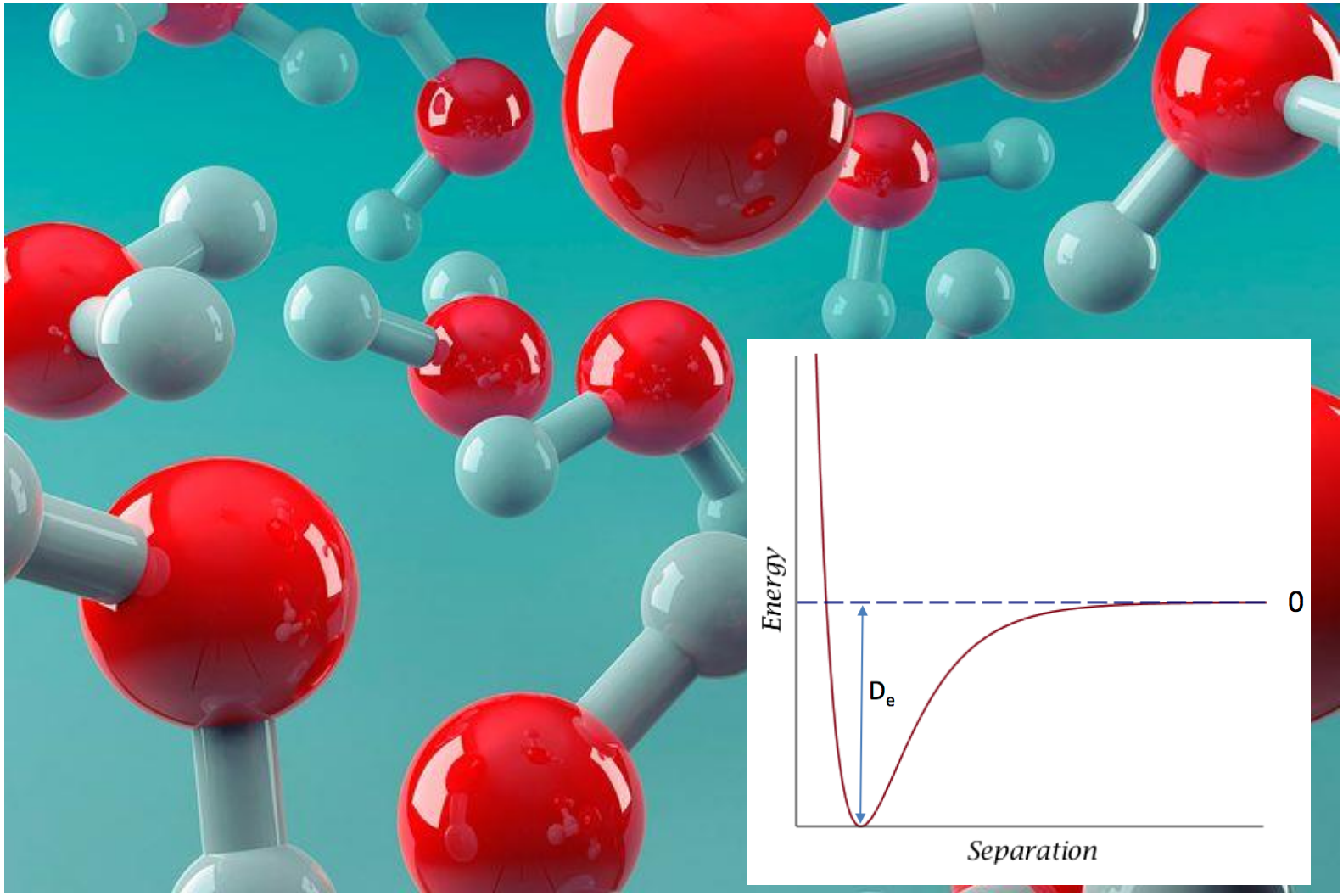

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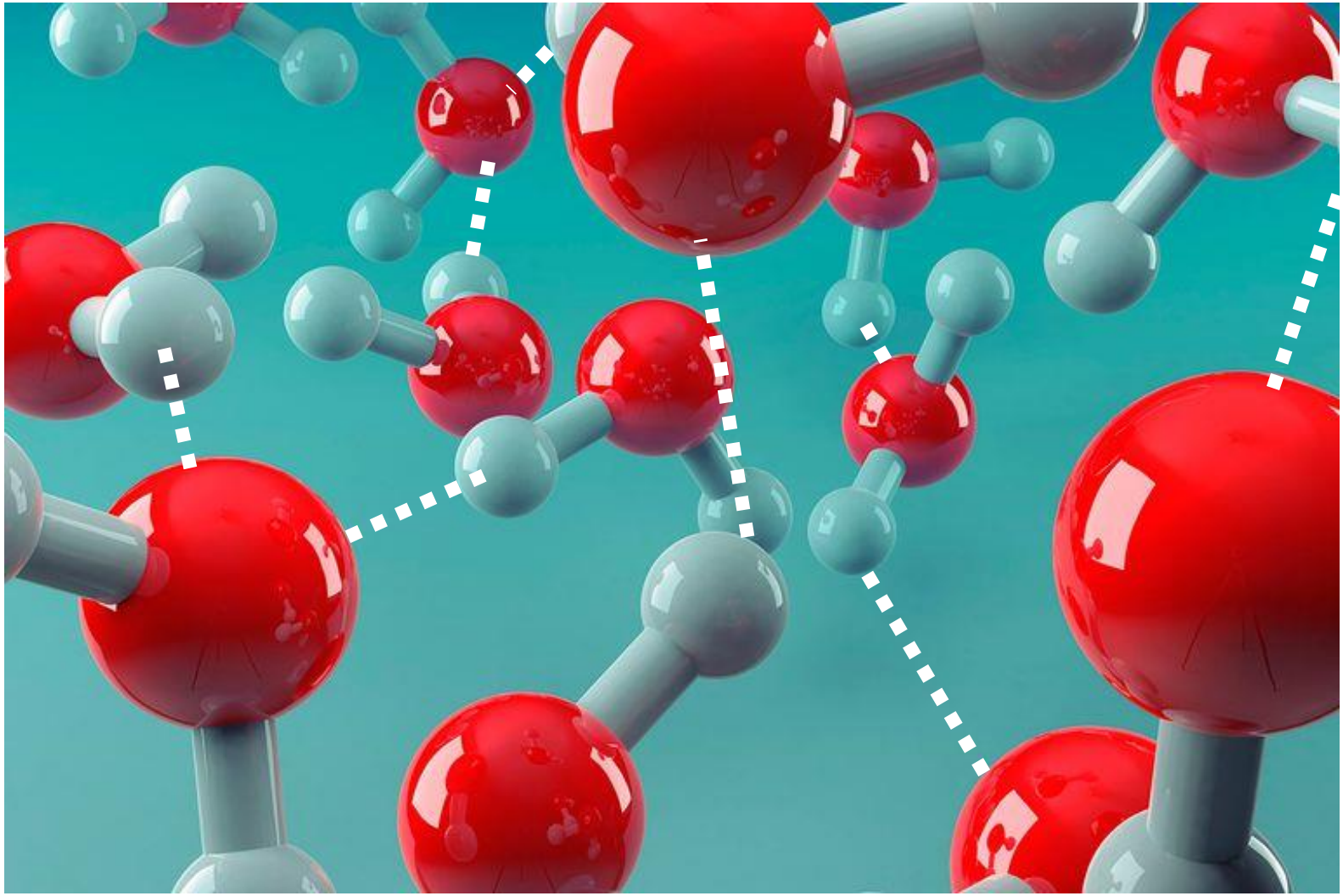

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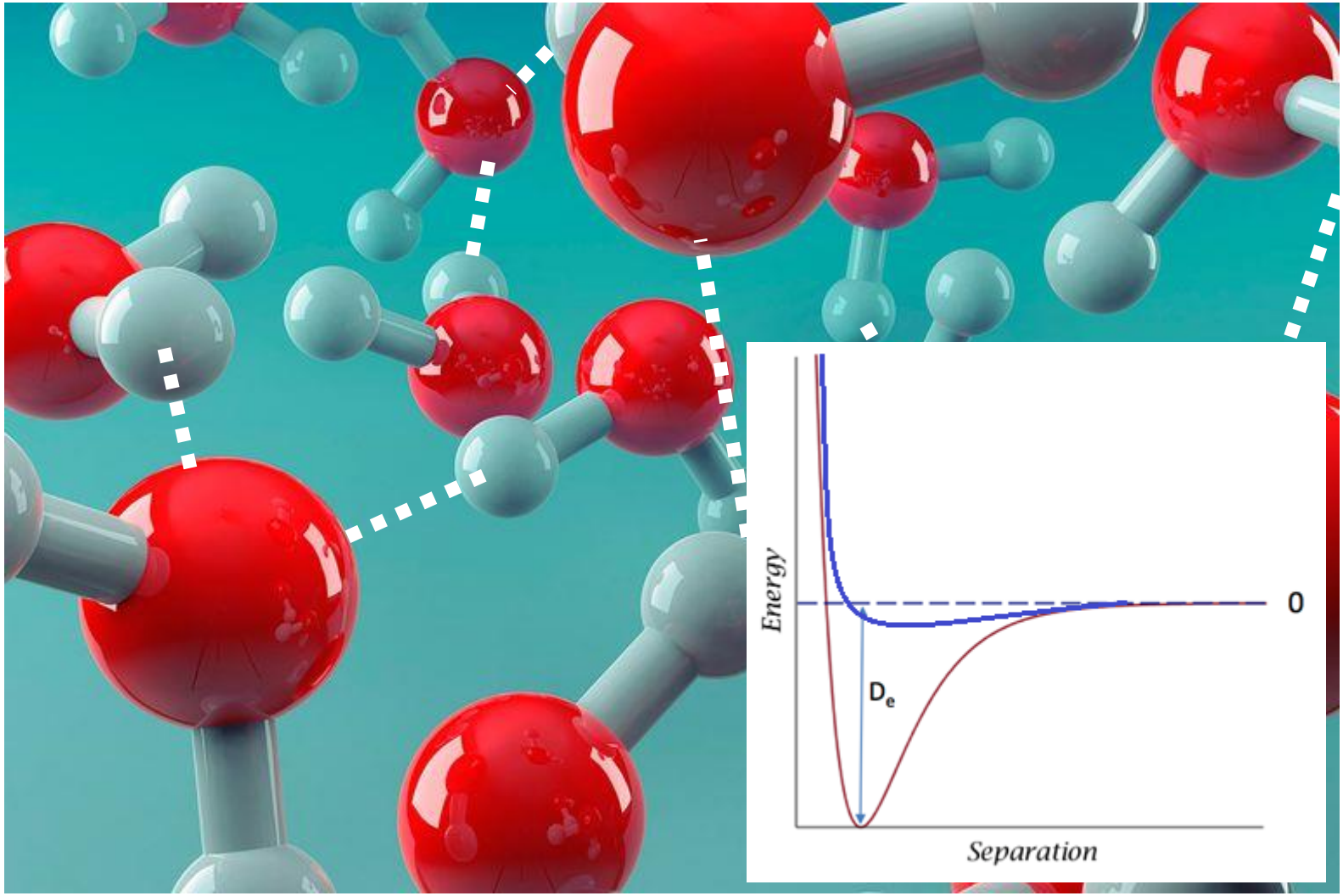
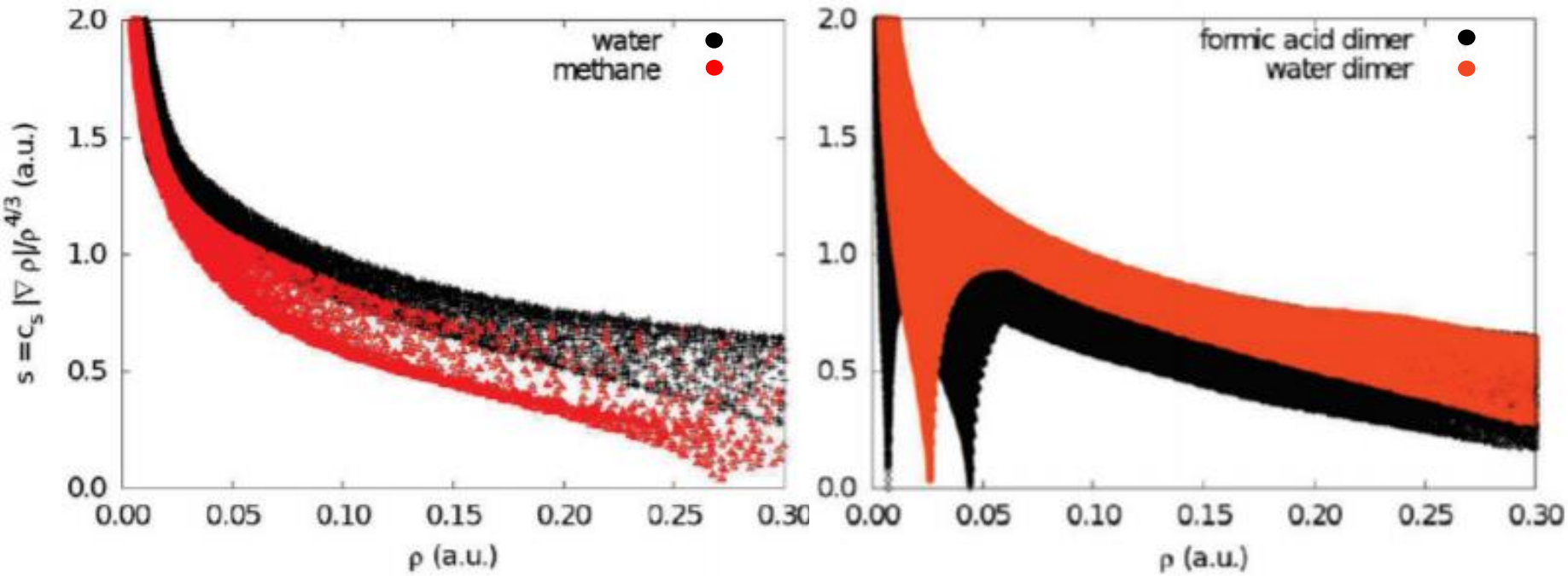


NCI – weak interactions detection

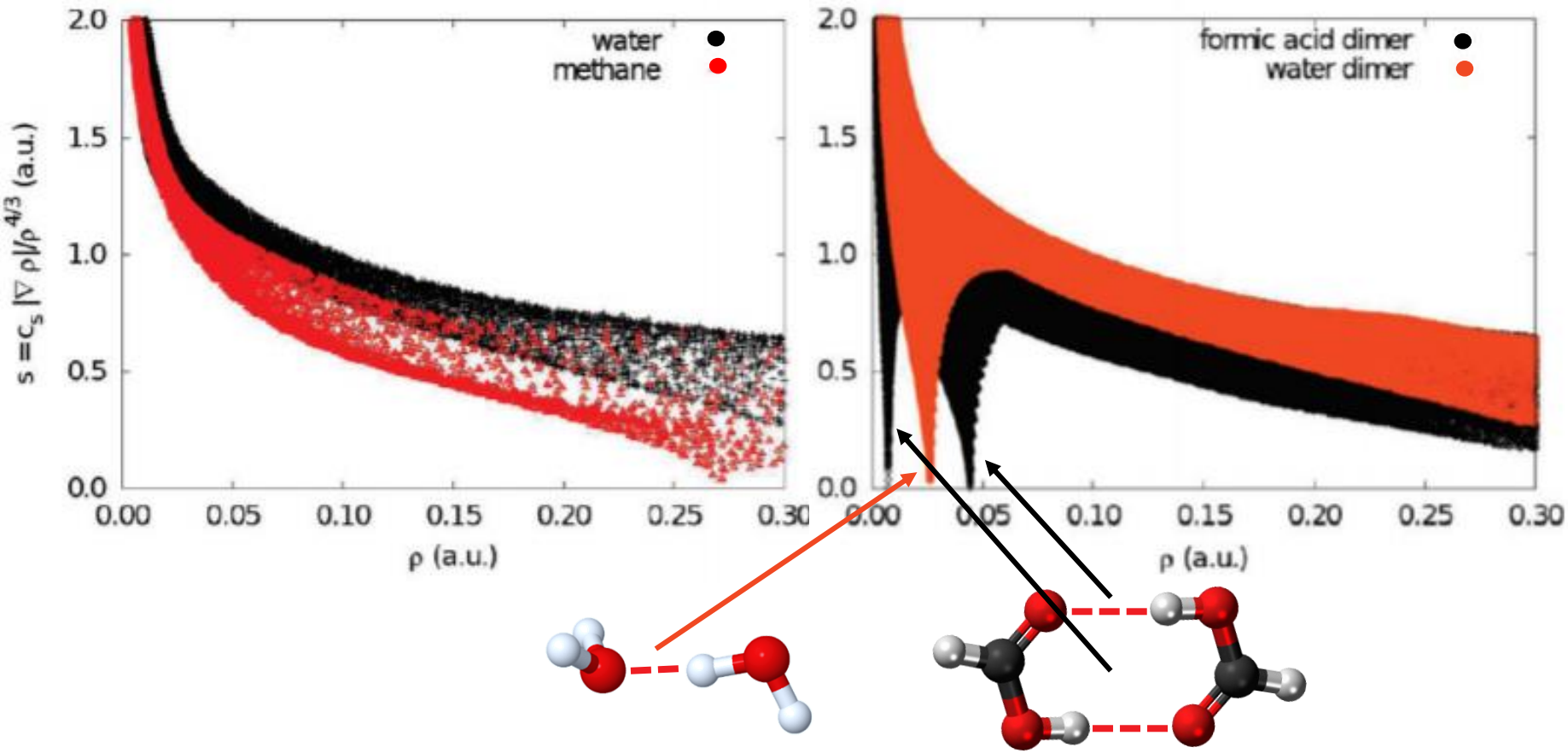


$$s \propto \frac{|\nabla \rho|}{\rho^{4/3}}$$

Reduced density gradient

J. AM. CHEM. SOC. 2010, 132, 6498–6506

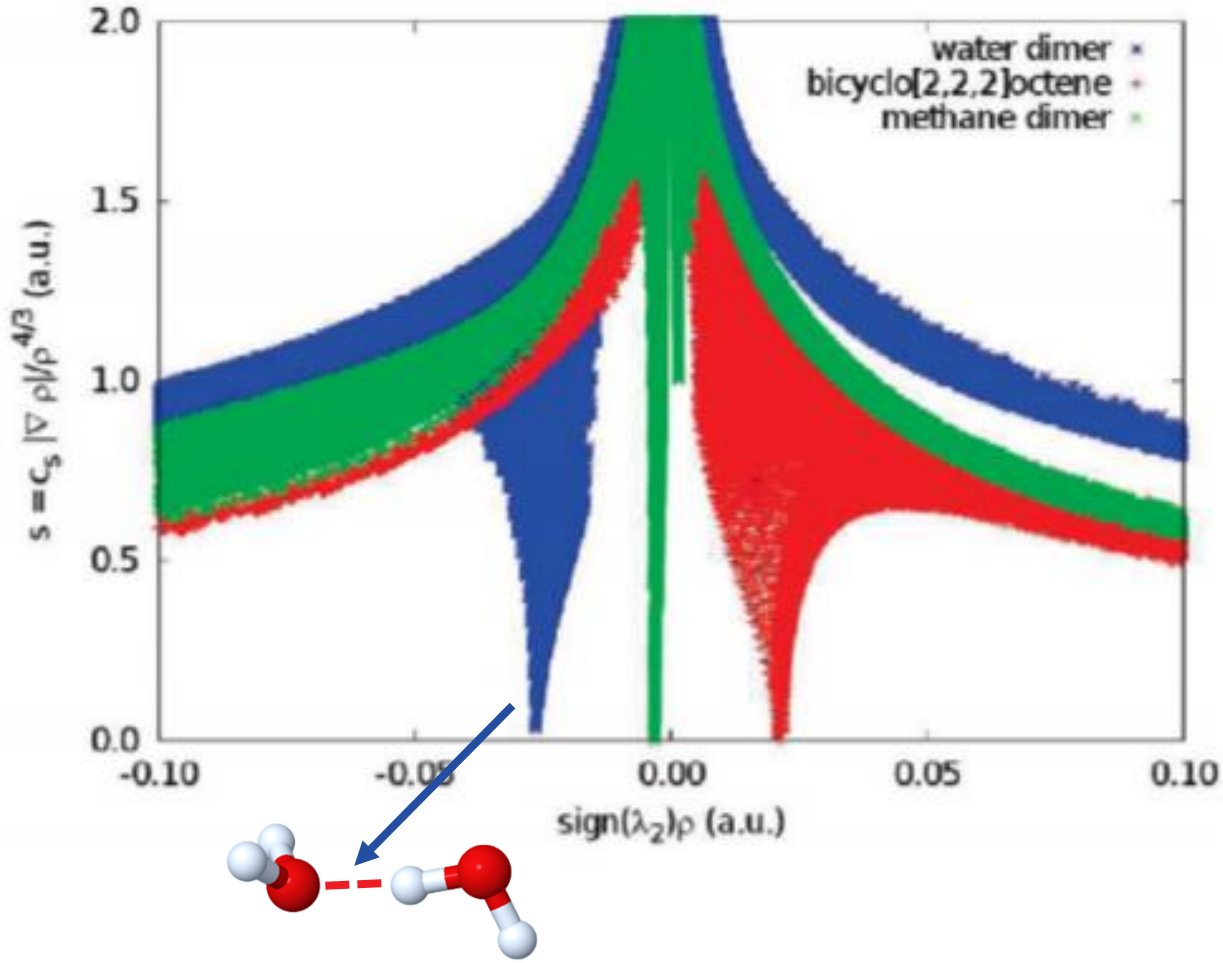
NCI – weak interactions detection



Noncovalent interactions can be isolated as regions with low density and low reduced gradient

J. AM. CHEM. SOC. 2010, 132, 6498–6506

NCI – identification of types of intermolecular interactions



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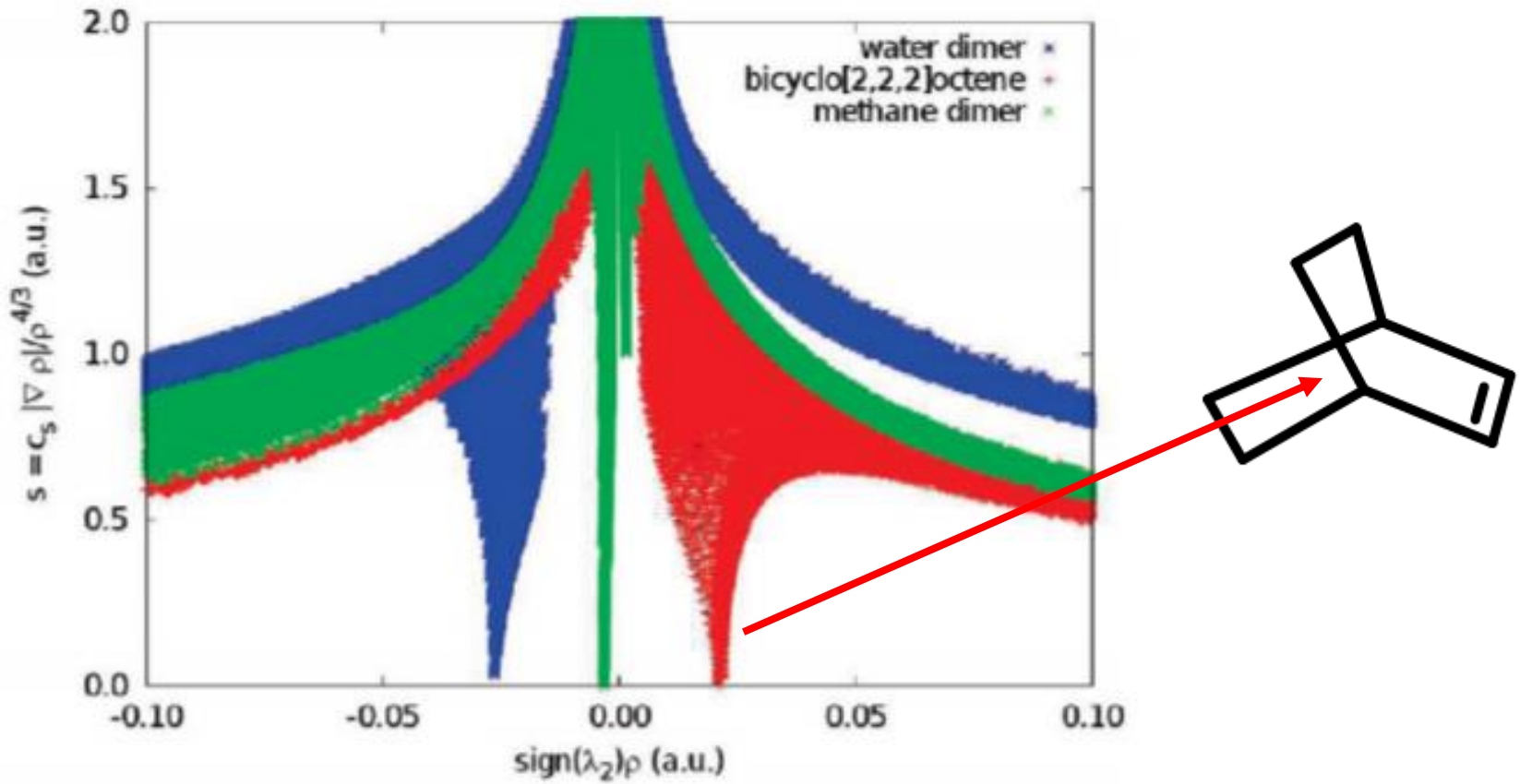

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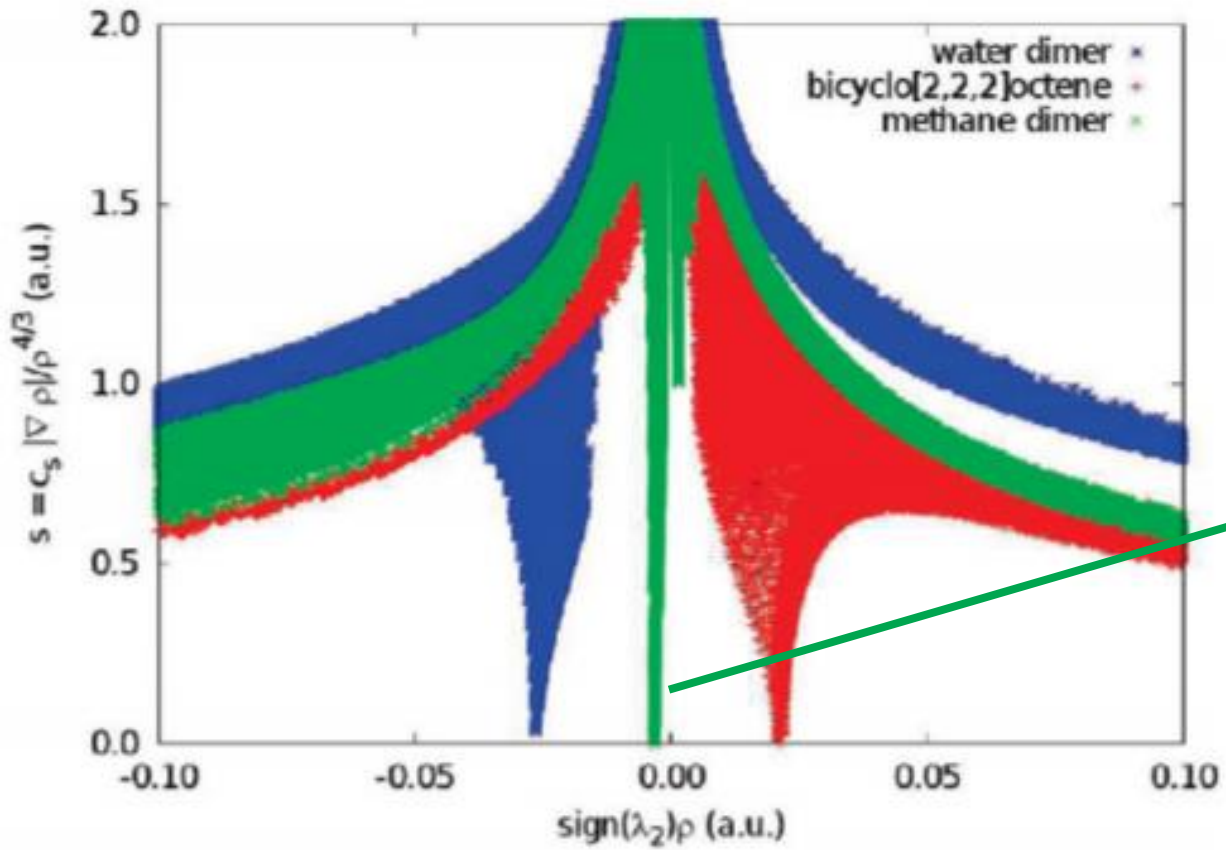
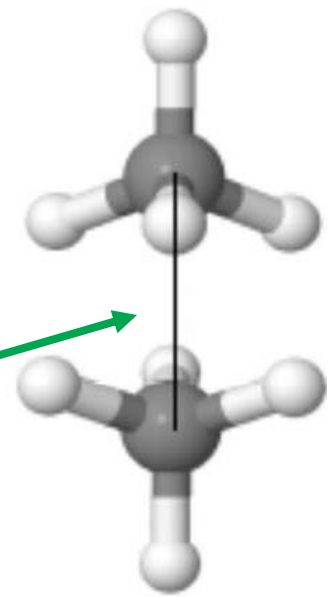
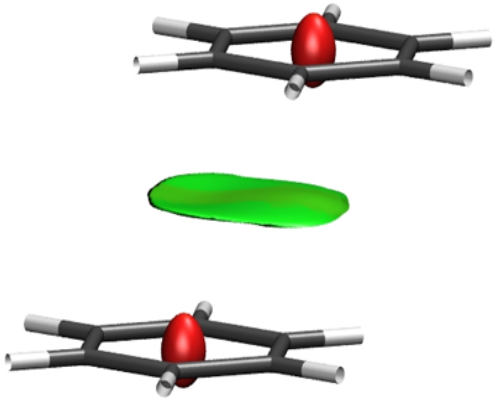


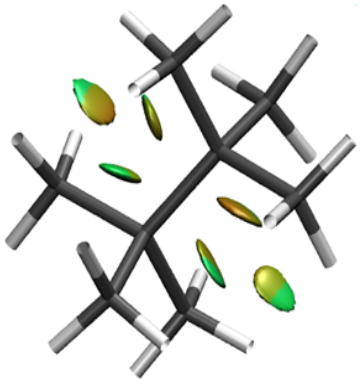


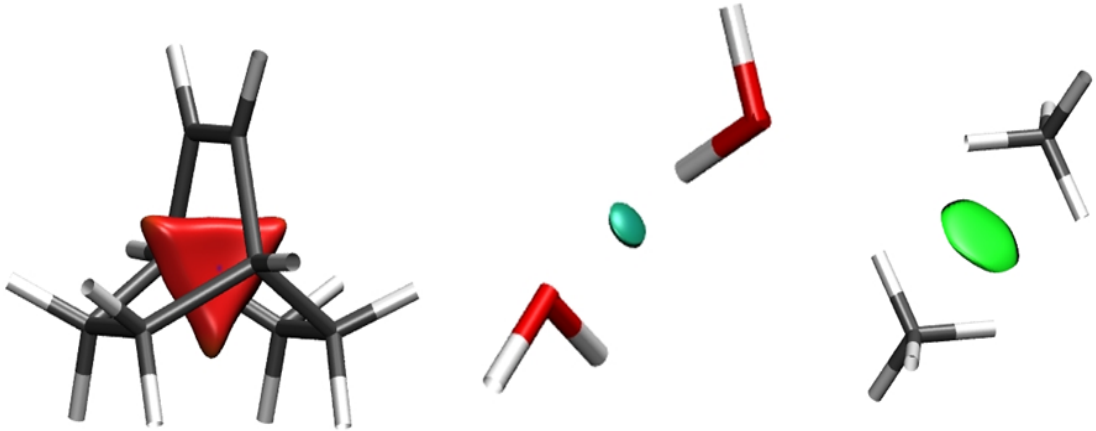
J. AM. CHEM. SOC. 2010, 132, 6498–6506

NCI visualization

Strong and attractive $\rho > 0 \quad \lambda_H > 0$
Weak $\rho \approx 0 \quad \lambda_H \approx 0$
Strong and repulsive $\rho > 0 \quad \lambda_H > 0$







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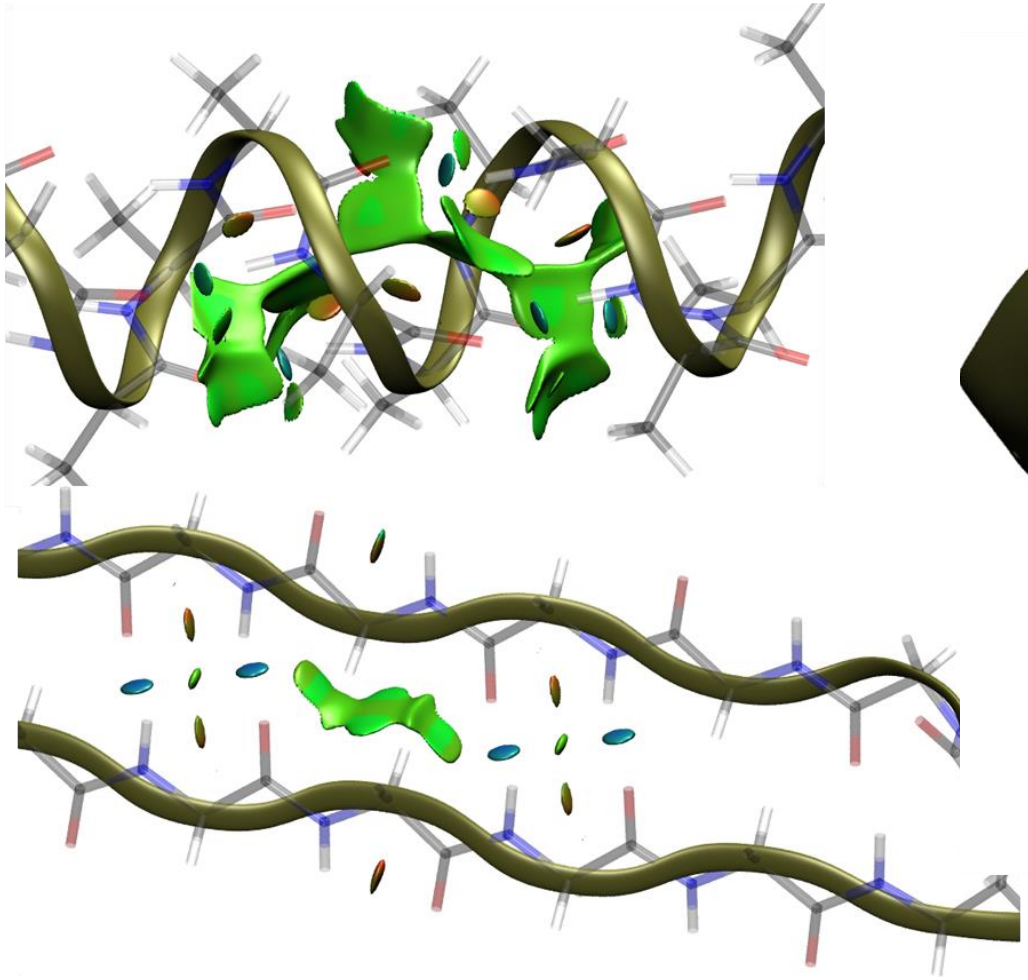
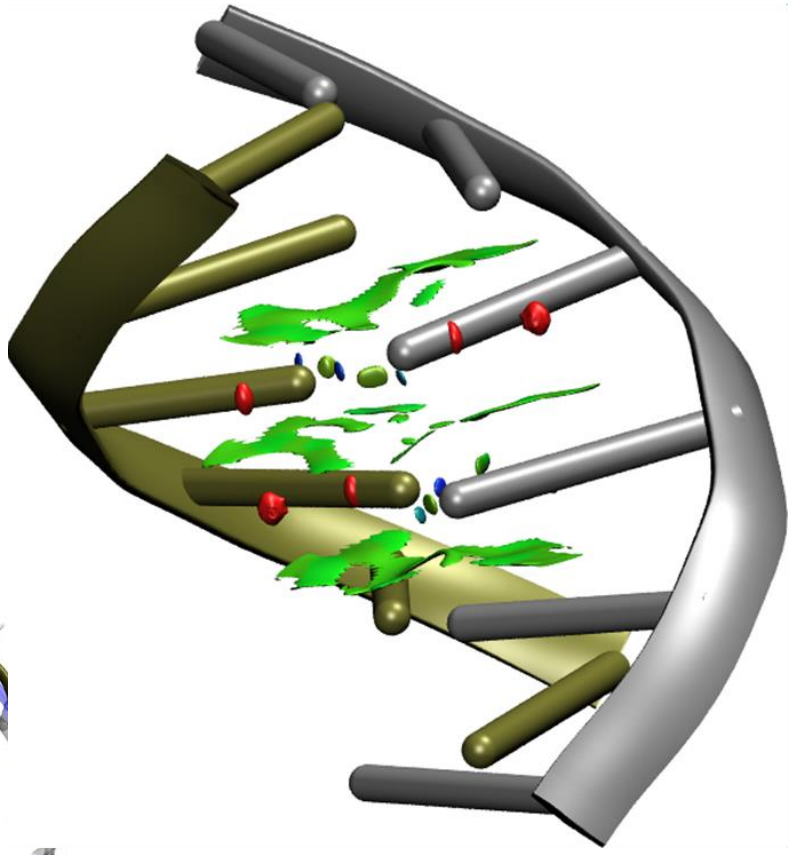
NCI for large systems

- Based on procrystal electron density distribution





J. AM. CHEM. SOC. 2010, 132, 6498–6506

ELF – electron localization function

$$\mathrm{ELF} = \left[1 + \left(\frac{T(r)}{T_h(r)}\right)^2\right]^{-1}$$

$$0 \leq \mathrm{ELF} \leq 1$$

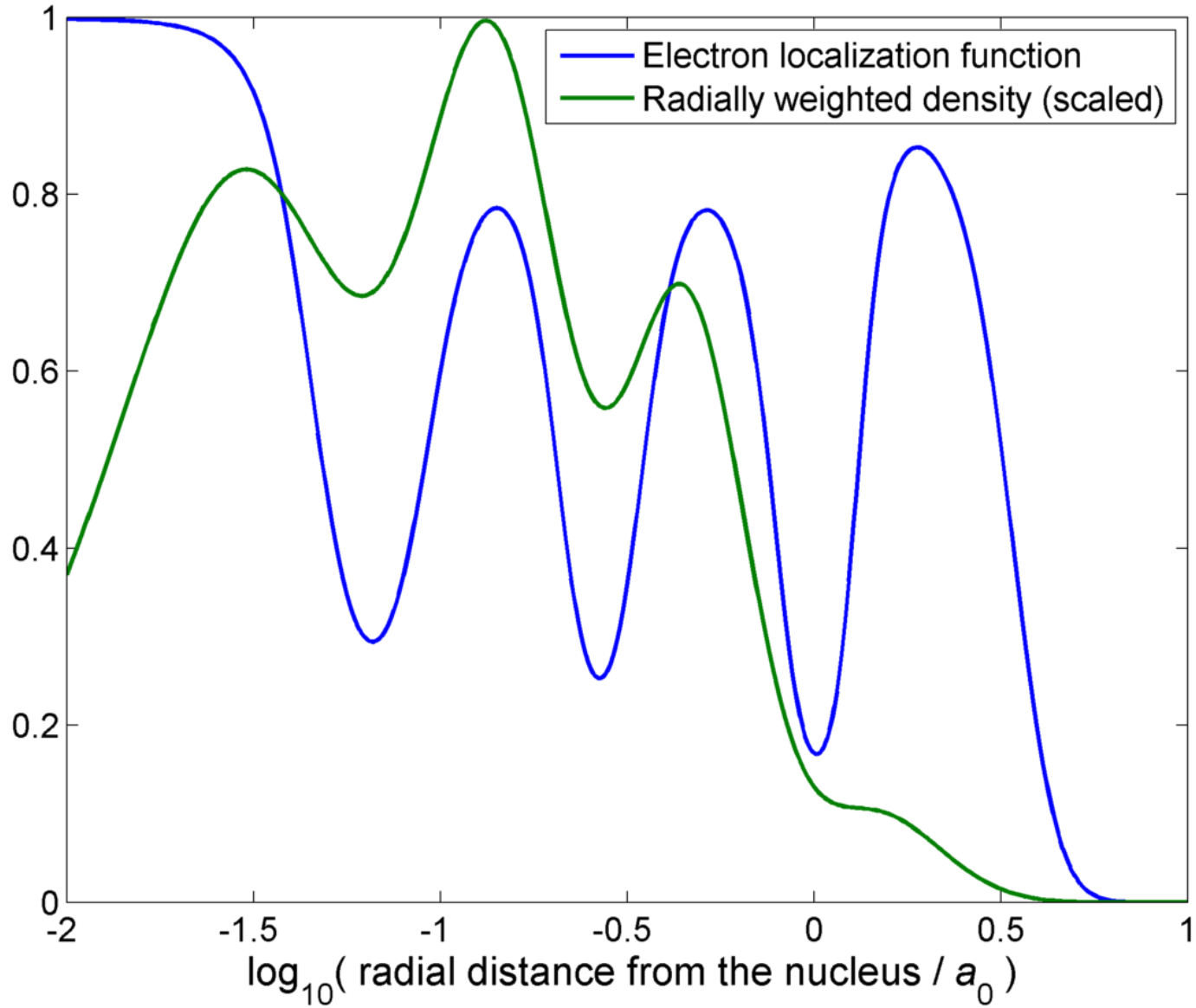
excess of local kinetic energy density due to the Pauli exclusion principle

kinetic energy density of homogeneous electron gas

ELF is **large** where the **Pauli repulsion** is **small**
(two electrons with anti-parallel spin are paired)
and it is small in the regions between electron pairs

Theoretical Aspects of Chemical Reactivity. 2006. P. 58

ELF – electron localization function



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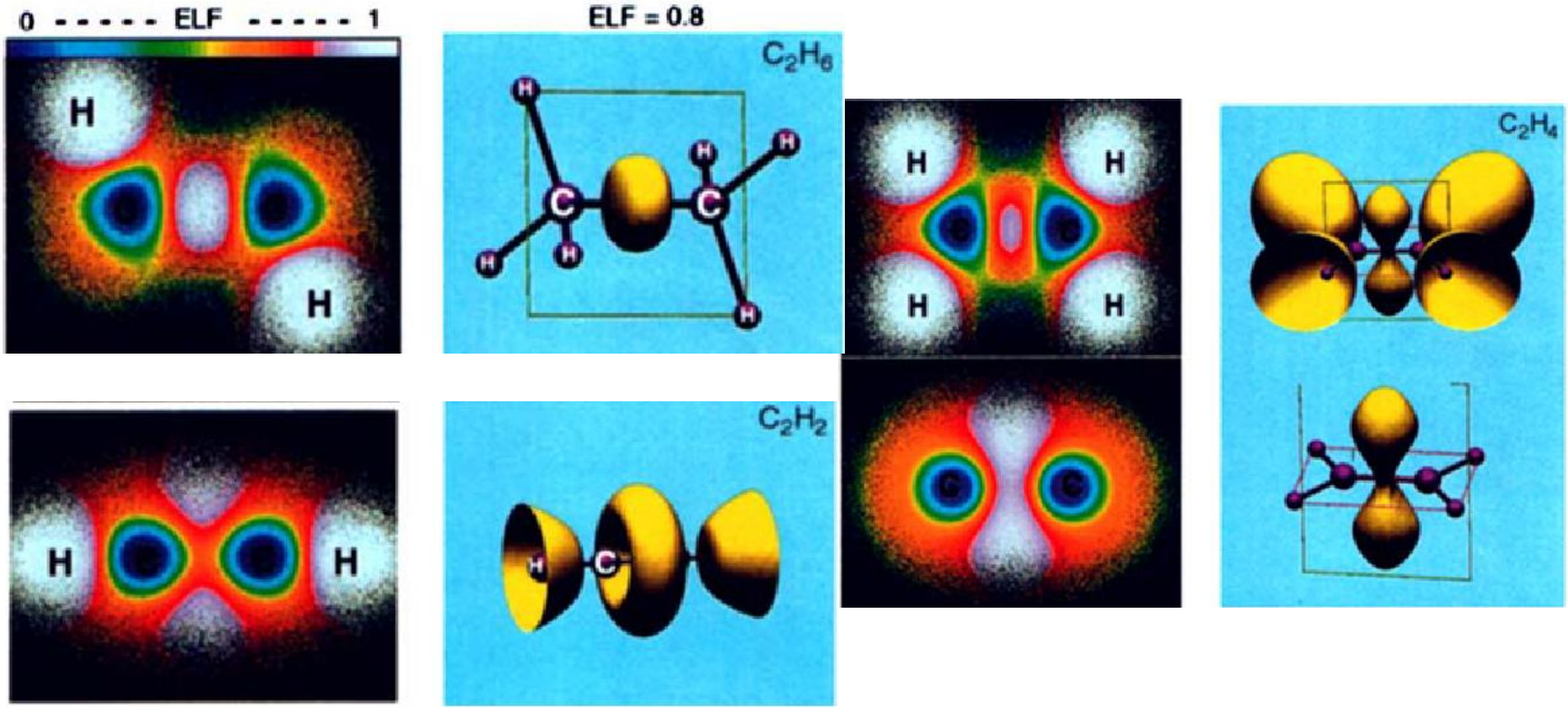
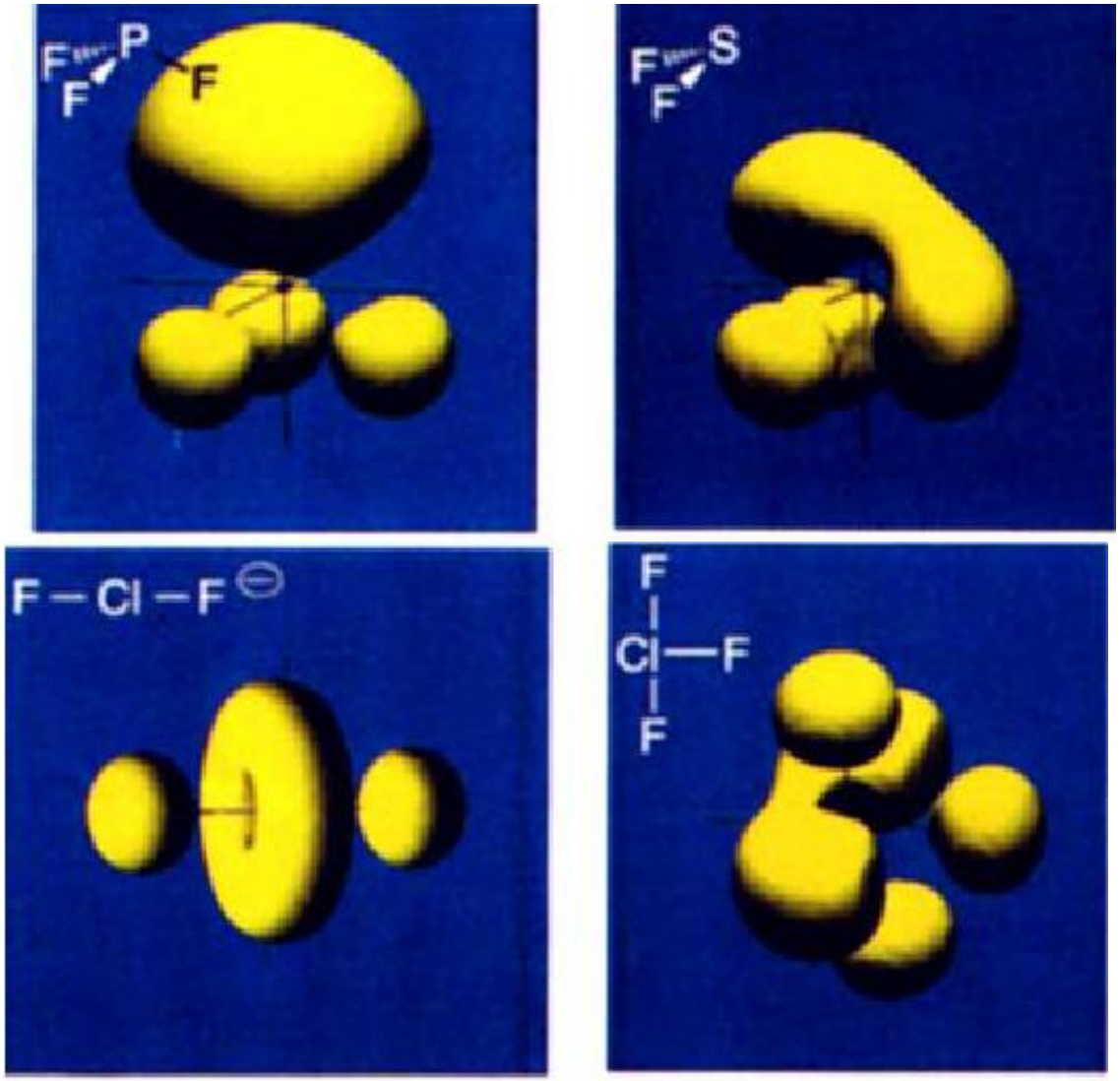


Savin, Andreas et al. “ELF: The Electron Localization Function.” (1997).

ELF – electron localization function



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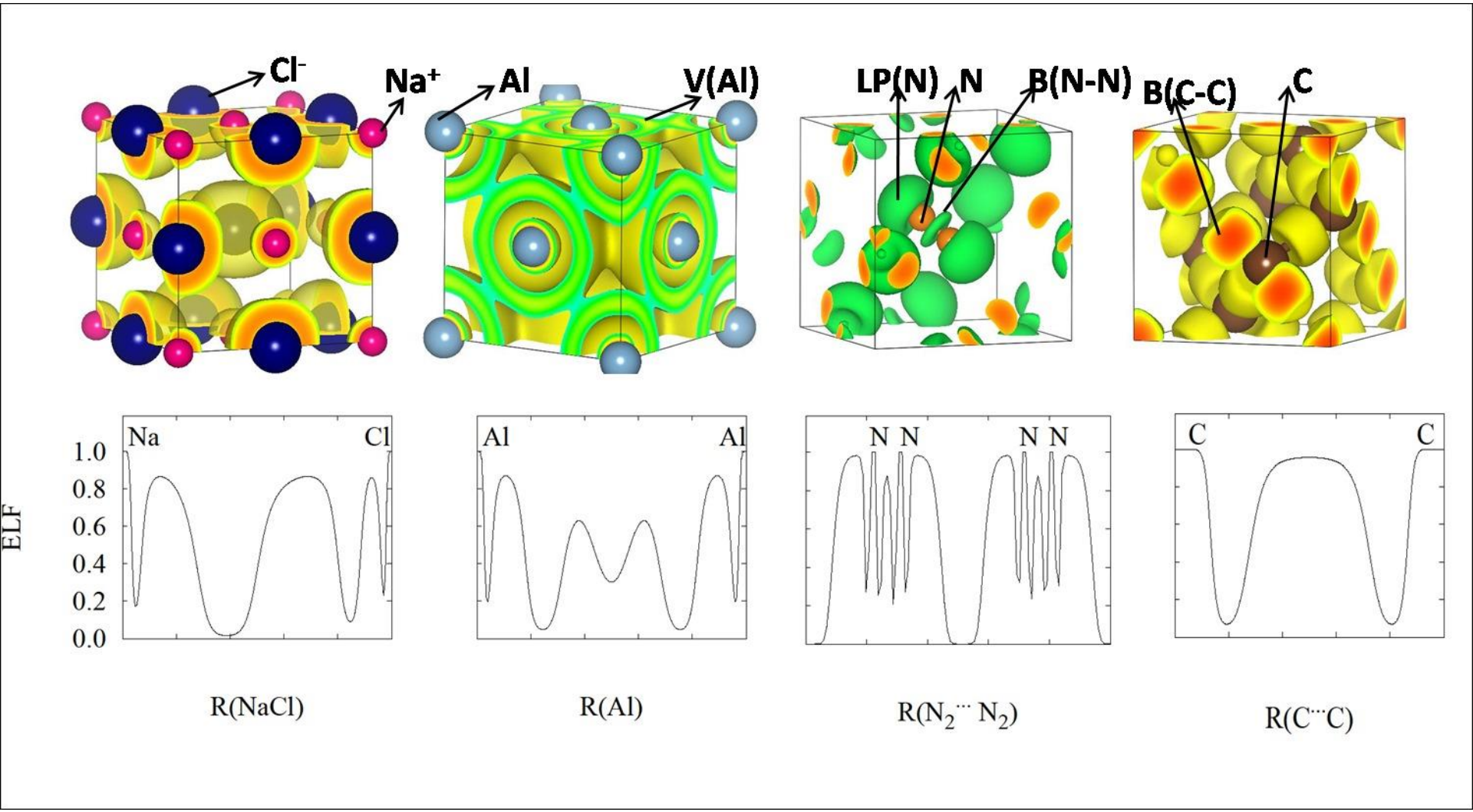

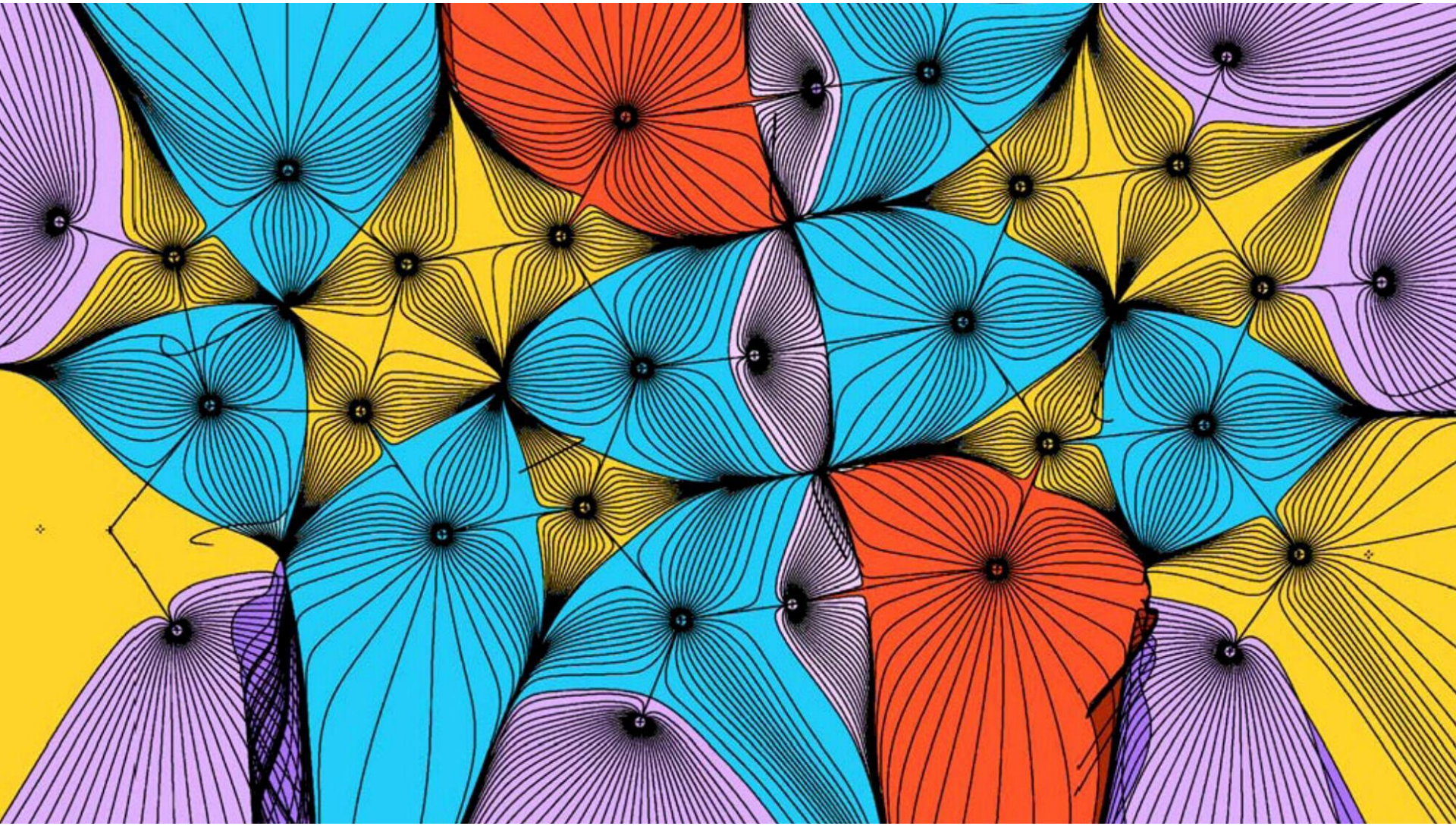

THANK YOU FOR YOUR ATTENTION!

Method	QTAIM	ELF	NCI
Function	density	Pauli kinetic energy density	Reduced density gradient
Chemical meaning	Atoms	Lewis pairs	Non covalent interactions
Critical points	Maxima=atoms	Maxima=Lewis pairs	Minima=NCIs
Regions	Atoms	Lewis pairs	Non covalent interactions