

Quantum Theory of Atoms in Molecules

by

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Are There “Atoms” in Molecules

- A Physicist Response:
NO! There is no operator in QM describing such a things!
- A Chemist Response:
Yes! I am classifying many reactions based on “functional groups” there must be something!
- **My Recommendation:**
- **An Skeptic Response:**
Maybe!

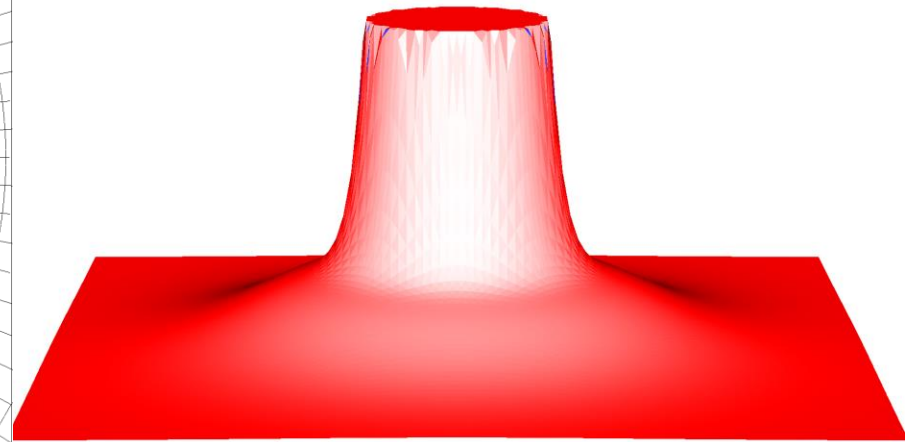
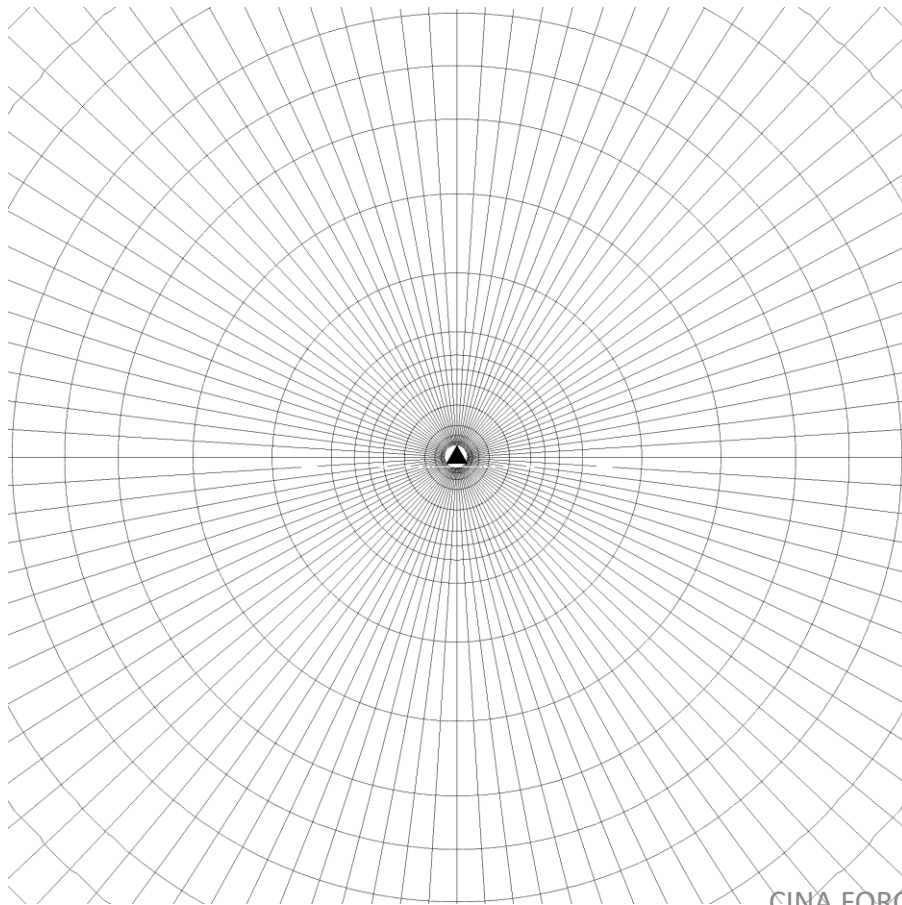


How To Define an Atom in a Molecule?

- There are various approaches based on orbital view point but the lecturer's recommendation is electron density-based approaches!
- Electron density is a 3-dimensional function in contrast to wavefunction which is $4N$ -dimensional per N electrons.
- There are various approaches for definition of atoms in molecules based on electron density, here we focus on the topological approach for defining an atom in a molecule; the QTAIM approach.

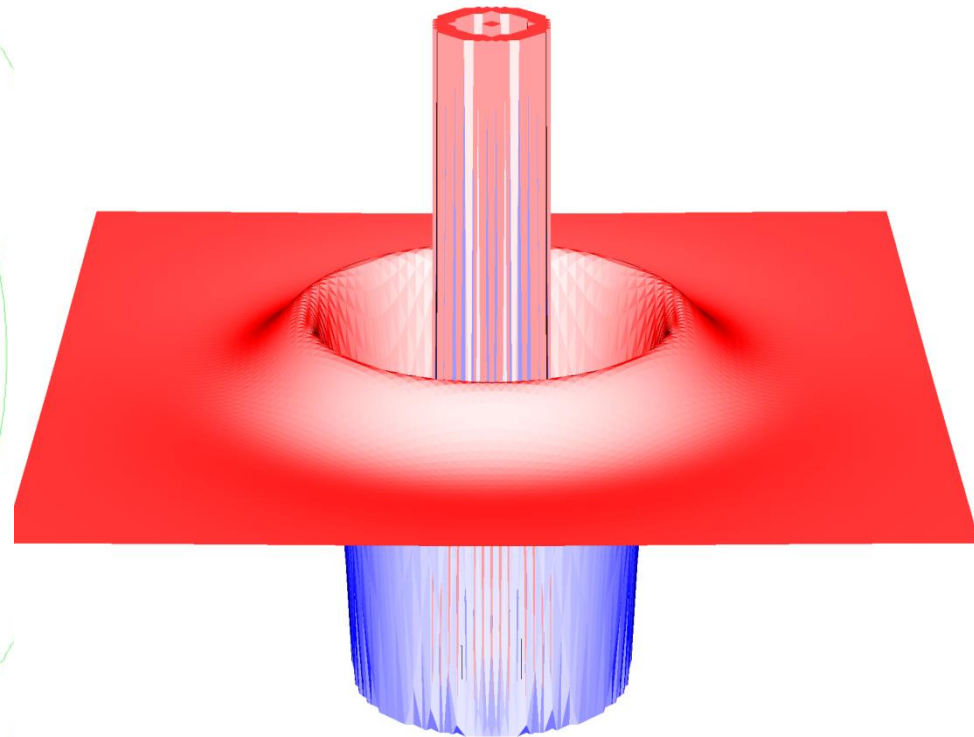
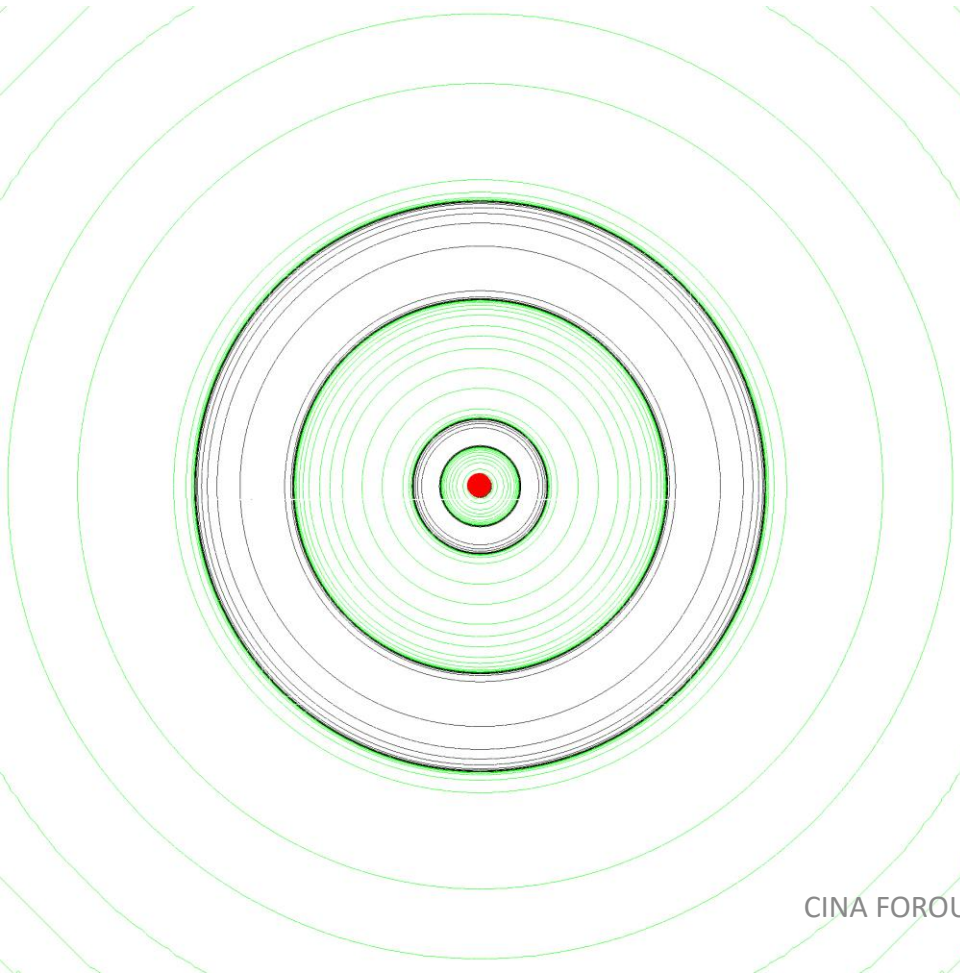
The Free Atom in the Context of QTAIM

- The electron density distribution



The Free Atom in the Context of QTAIM

- The Laplacian of electron density.

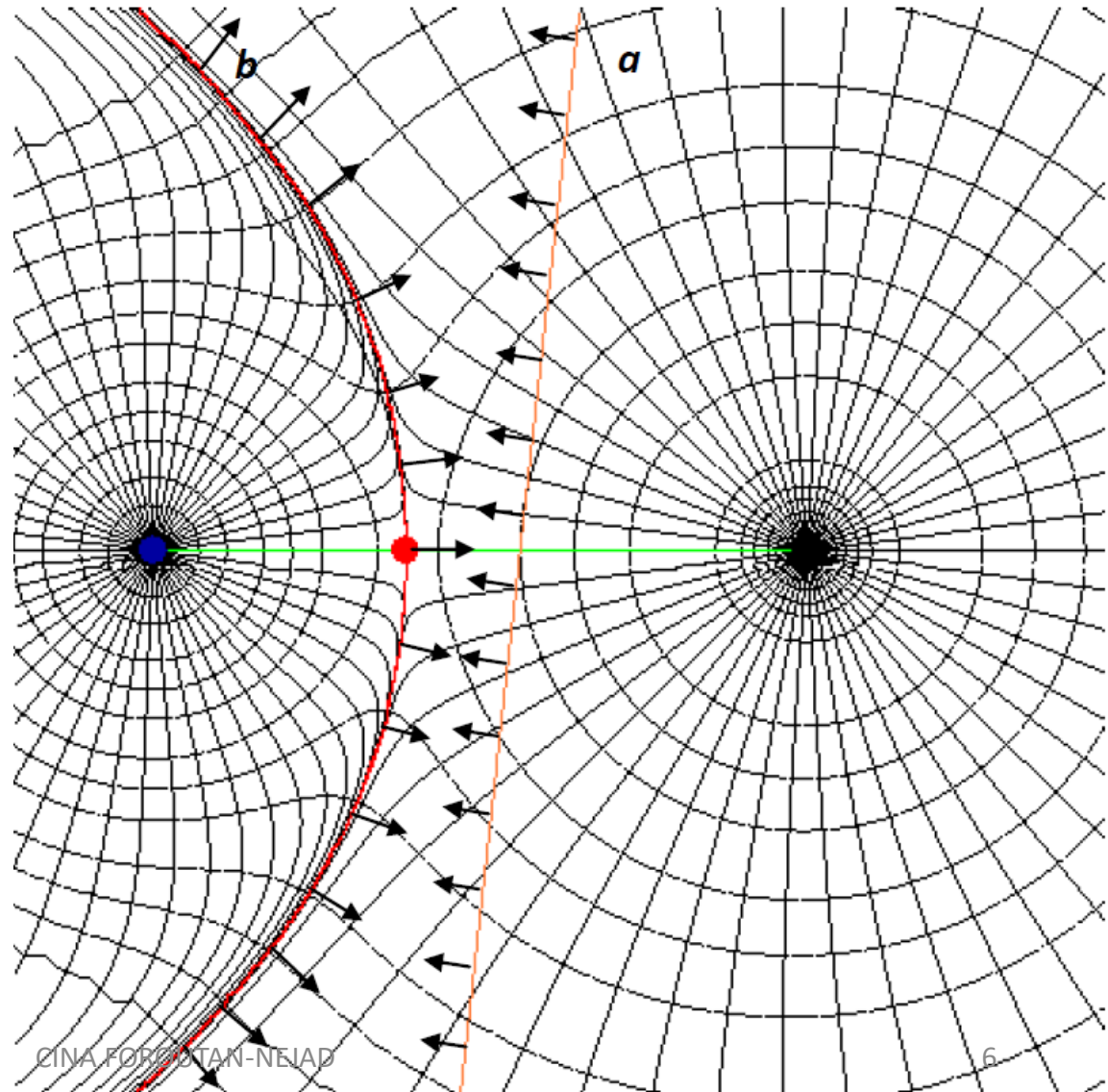


Atoms in a Molecule

An atomic boundary should satisfies this equation:

$$\nabla \vec{\rho} \cdot \vec{n} = 0$$

Where n is the normal vector to the interatomic surface



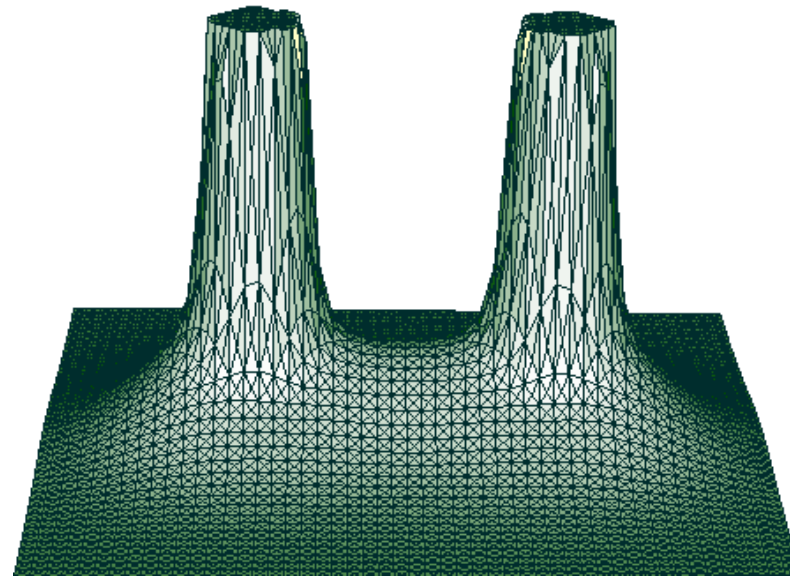
What is a Critical Points in QTAIM?

A critical point, CP, is a point at which

$$\nabla \vec{\rho} = 0$$

Four different types of CP could be found in a molecular space of a molecule. Each CP can be introduced by a *rank* and a *signature*, (r, s) .

Rank represents the number of non-zero diagonal eigenvalues of the Hessian matrix of the Laplacian of electron density. Signature denotes local curvatures of the CP with respect to the x , y and z directions.



Critical Points of QTAIM

- A (Non)-Nuclear Attractor or (3,-3) CP is a point in which electron density is maximum with respect to all directions (x , y , z).
- A Bond CP or (3,-1) CP is a point in which electron density is minimum with respect to the maximum density path, connecting two (3,-3) points but maximum respecting to the rest of directions
- A Ring or (3,+1) CP is a point on a surface which is minimum in electron density on that surface but maximum with respect to the path perpendicular to the surface
- A Cage or (3,+3) CP is a point which is minimum with respect to all other points around it.

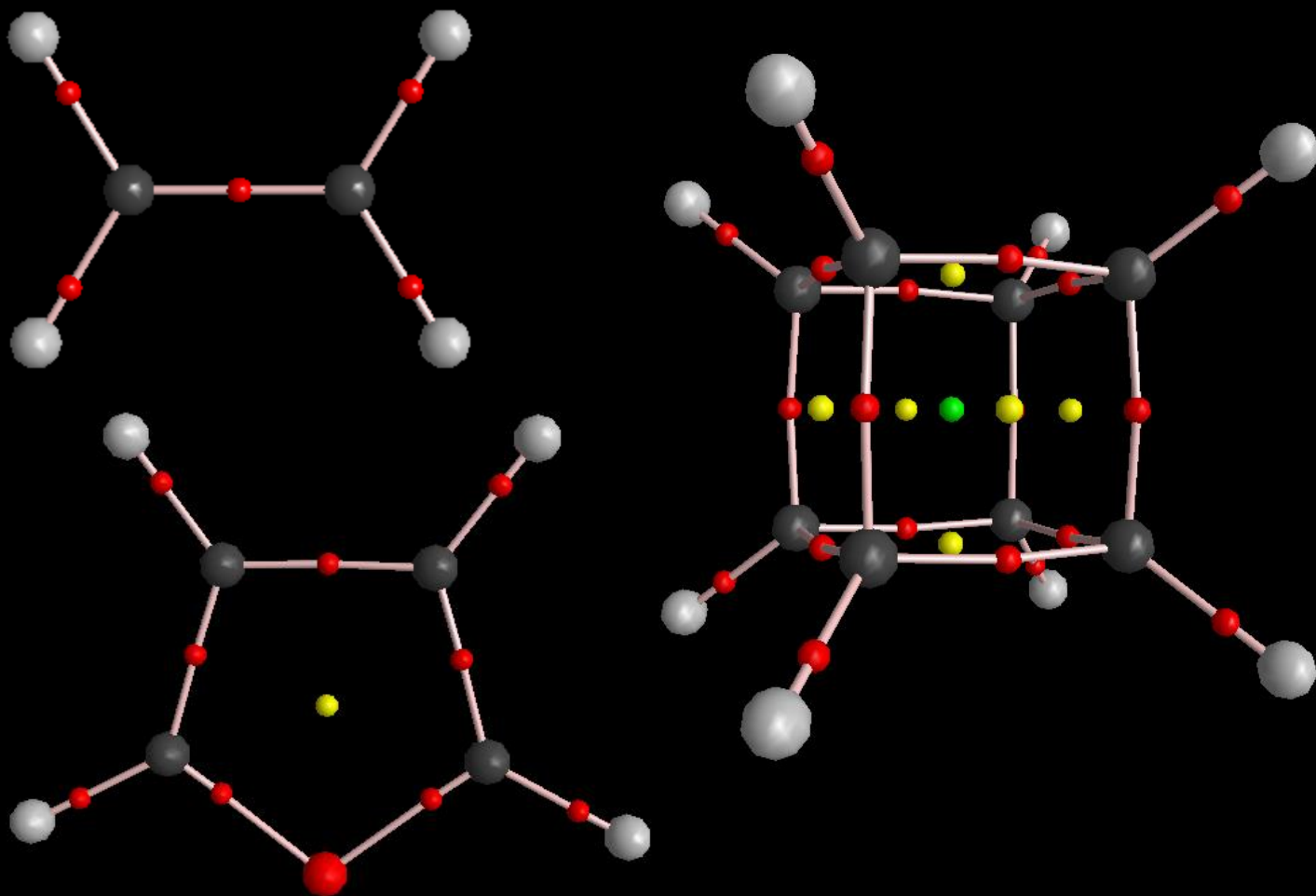
Critical Points of QTAIM; a Summary

Full Name	Acronym	λ_1	λ_2	λ_3	(r, s)
(Non)-Nuclear Attractor	(N)NA	–	–	–	$(3, -3)$
Bond (Line) Critical Point	B(L)CP	–	–	+	$(3, -1)$
Ring Critical Point	RCP	–	+	+	$(3, +1)$
Cage Critical Point	CCP	+	+	+	$(3, +3)$

Poincare-Hopf rule:

$$(N)NA - B(L)CP + RCP - CCP = 1$$

Critical Points and Bond Paths of QTAIM



Bonding in the Context of QTAIM

Presence of BP or AIL between two atoms was first introduced as the necessary and sufficient conditions for presence of chemical bond. In QTAIM terminology each bond could be classified either as *Shared* or *Closed Shell*.

If in a (3,-1) CP, $\nabla^2\rho < 0$, then the corresponding bond could be classified as *Shared*.

In contrary, if in a (3,-1) CP $\nabla^2\rho > 0$, then the corresponding bond is classified as a *Closed Shell* interaction.

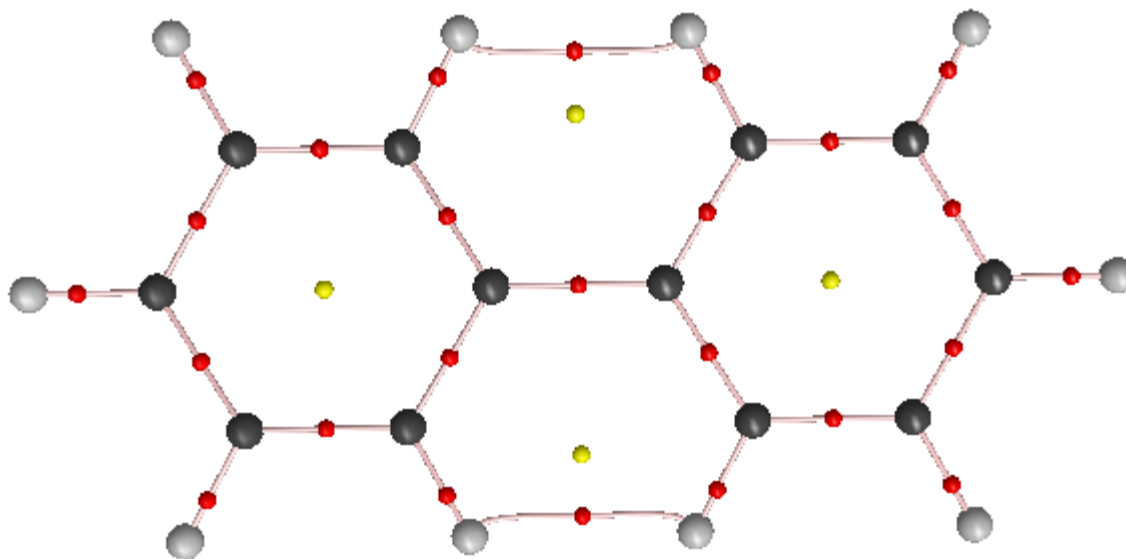
Shared interactions usually are found between *covalently* bonded atoms. *Closed Shell* interactions usually correspond to *ionic* and *van der Waals* bonds.

Bonding in the Context of QTAIM

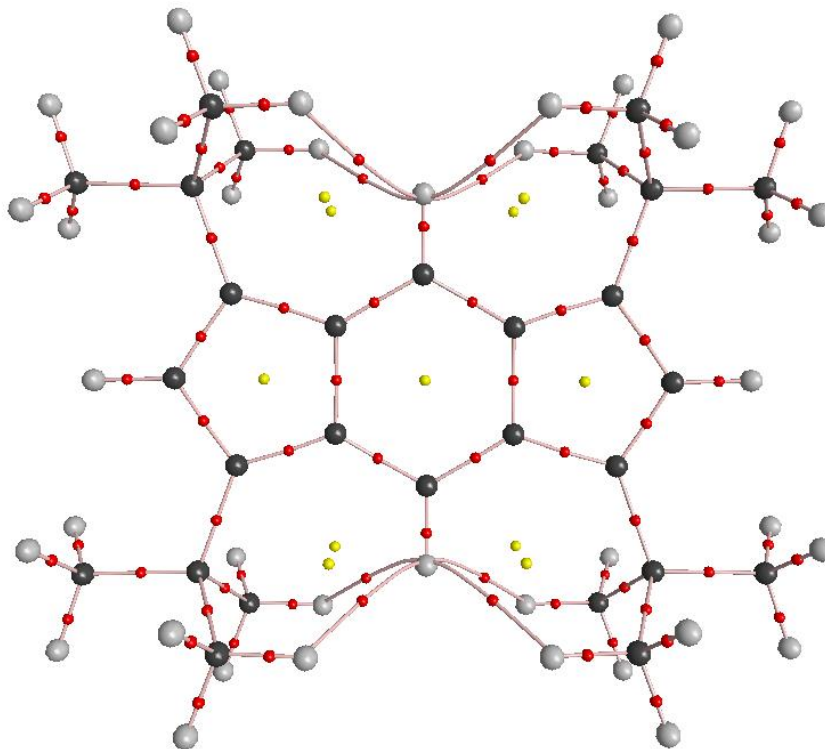
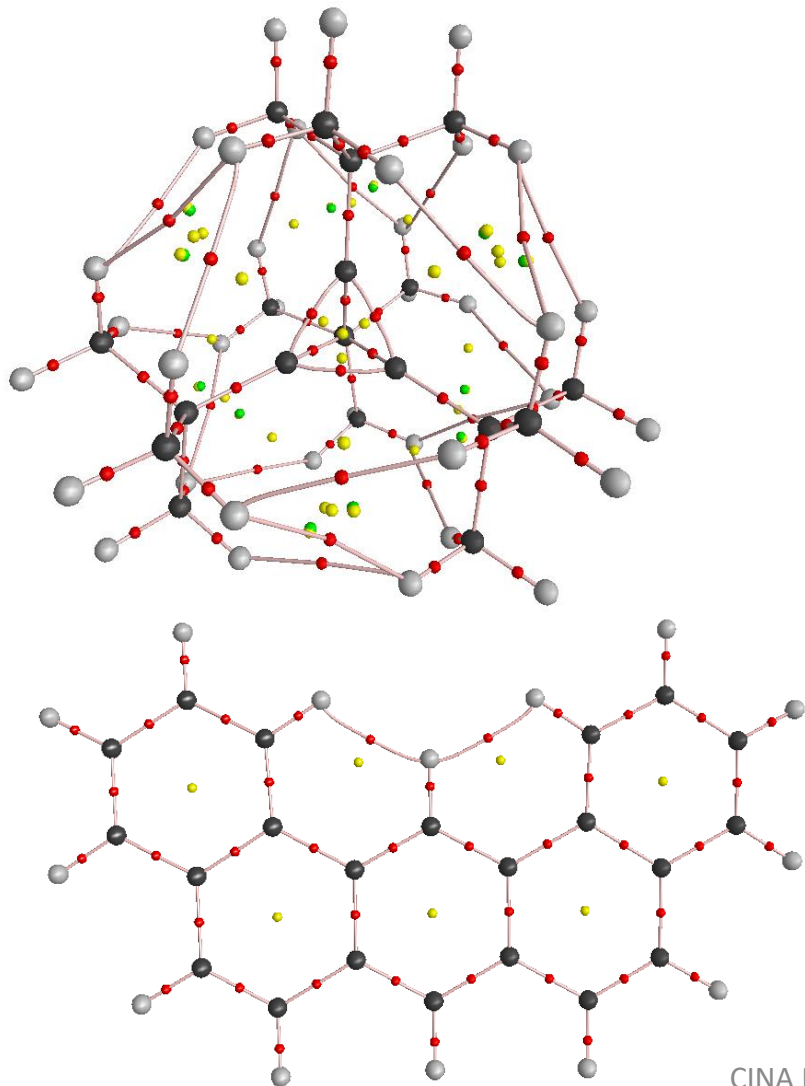
Properties	Description & Application
$\rho(\mathbf{r})$	Electron Density; in homologous series a higher $\rho(\mathbf{r})$ means stronger bond. $\rho(\mathbf{r})$ could be used for defining the bond order.
$L(\mathbf{r})$	$-1/4 \nabla^2 \rho(\mathbf{r})$; definition of charge concentration/depletion and discriminating bonds as <i>Shared</i> or <i>Closed Shell</i>
$K(\mathbf{r})$	$-\frac{1}{4} N \int d\tau [\psi^* \nabla^2 \psi + \psi \nabla^2 \psi^*]$, Hamiltonian Kinetic Energy
$G(\mathbf{r})$	$-\frac{1}{4} N \int d\tau \nabla \psi^* \cdot \nabla \psi$, Lagrangian Kinetic Energy; $G(\mathbf{r}) = K(\mathbf{r}) - L(\mathbf{r})$
$G(\mathbf{r})/\rho(\mathbf{r})$	Defines the local kinetic energy per electron; a value bigger than unity denotes presence of ionic-type of bonding, less than unity denotes presence of covalent-type bonds
$V(\mathbf{r})$	If the Virial ratio in a molecule is exactly 2 then $V(\mathbf{r}) = -K(\mathbf{r}) = H(\mathbf{r})$, the Energy Density. Negative values represent covalency and vice versa
$\epsilon(\mathbf{r})$	$\frac{\lambda_1}{\lambda_2} - 1$, Bond Ellipticity; defines the preferred directional distribution of electron density in (3, -1) CP

Bond Path or Line Path?

It was shown that B(L)Ps may appear in unexpected positions! A good example is the bond critical point between two hydrogen atoms of a planar biphenyl.



Unexpected BPs! H-H Bonding Controversy...



The Quantum Atom

- The Gauss Divergence Theorem:
if Ω is a region in space, bounded by a surface S , V is a vector field defined in Ω and n is the normal vector to S , then:

$$\iiint_{\Omega} dV \nabla \cdot V = \iint_S dS V \cdot n$$

This theorem is valid since integration and differentiation are inverse operators.

- A Quantum Atom is a region in space in which

$$\iiint_{\Omega} dV \nabla^2 \rho = 0 \text{ since}$$

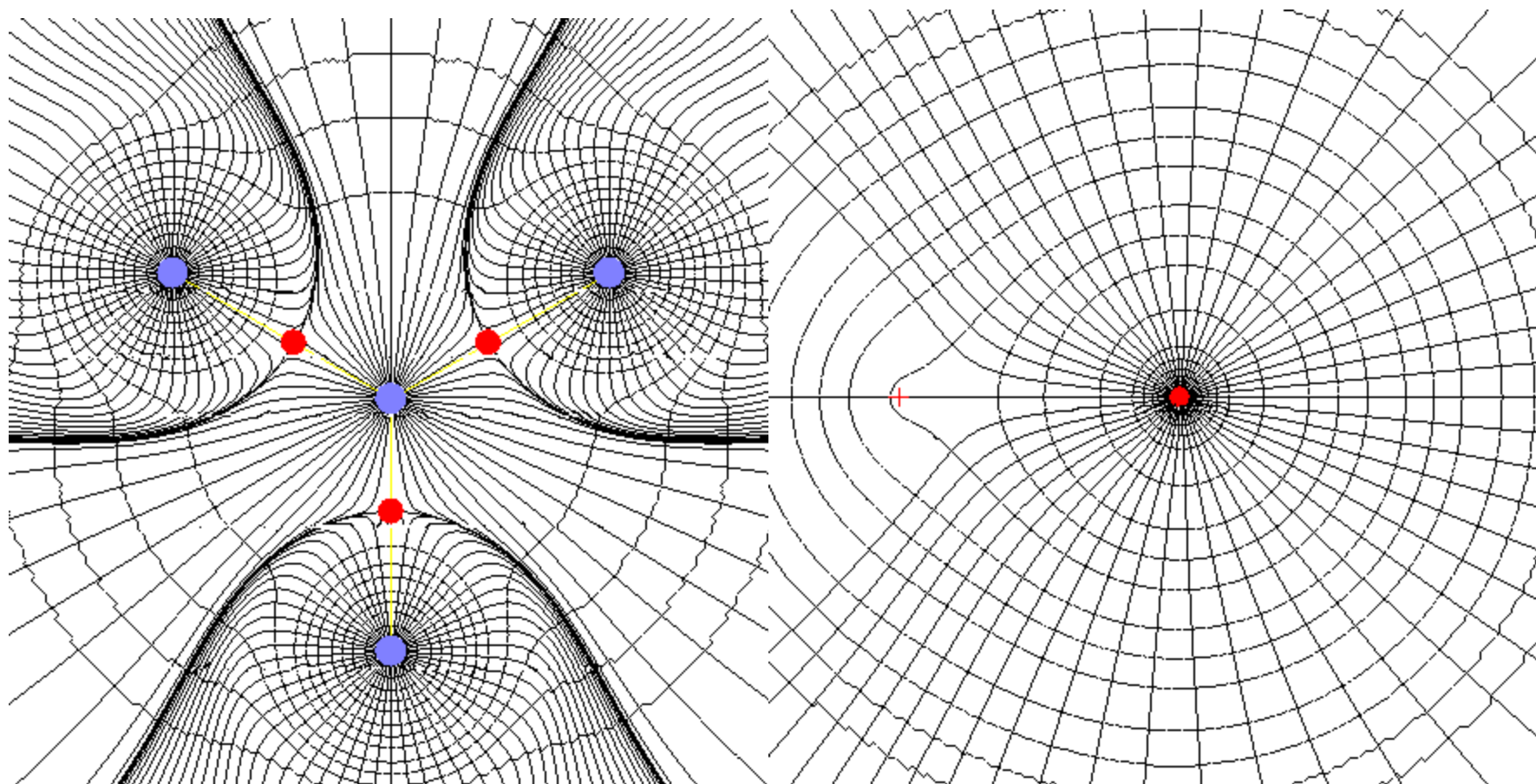
$$\iiint_{\Omega} dV \nabla^2 \rho = \iiint_{\Omega} dV \nabla \cdot \nabla \rho = \iint_S dS \nabla \rho \cdot n$$

- The $\iint_S dS \nabla \rho \cdot n$ is simply integration over the zero-flux surface of a topological atom.

Atomic Properties

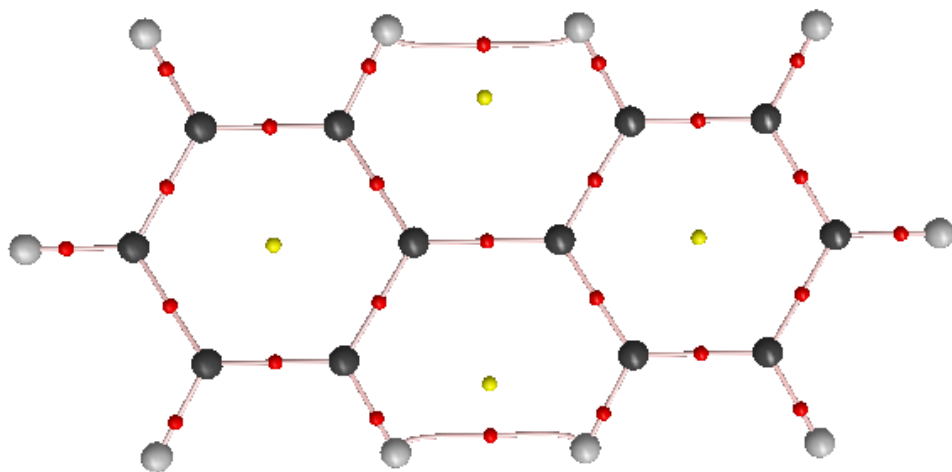
- Atomic Energy, $E(\Omega)$
- Atomic Charge, $q(\Omega)$
- Atomic Volume, $\text{Vol}(\Omega)$
- Atomic Multiple Electric Moments, $\mu(\Omega)$,
 $Q(\Omega)$
- Atomic Magnetizability, $\chi(\Omega)$
- Localization and Delocalization Indices, $\lambda(\Omega)$,
 $\delta(\Omega|\Omega')$

Non-Nuclear Attractors and United Atoms; Beyond Classical Chemistry!

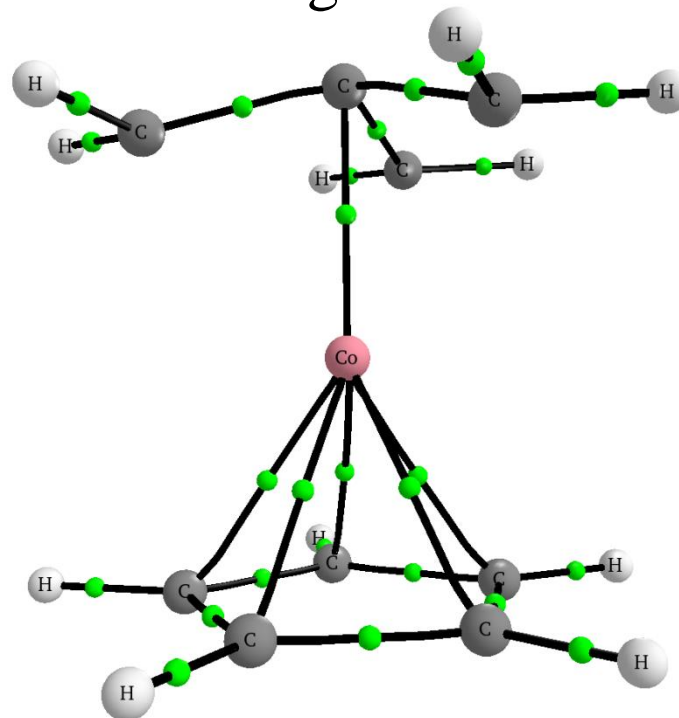


Two Problematic Types of MG

I. Unexpected Bond Paths^[1-3]



II. Missing Bond Paths^[4-6]



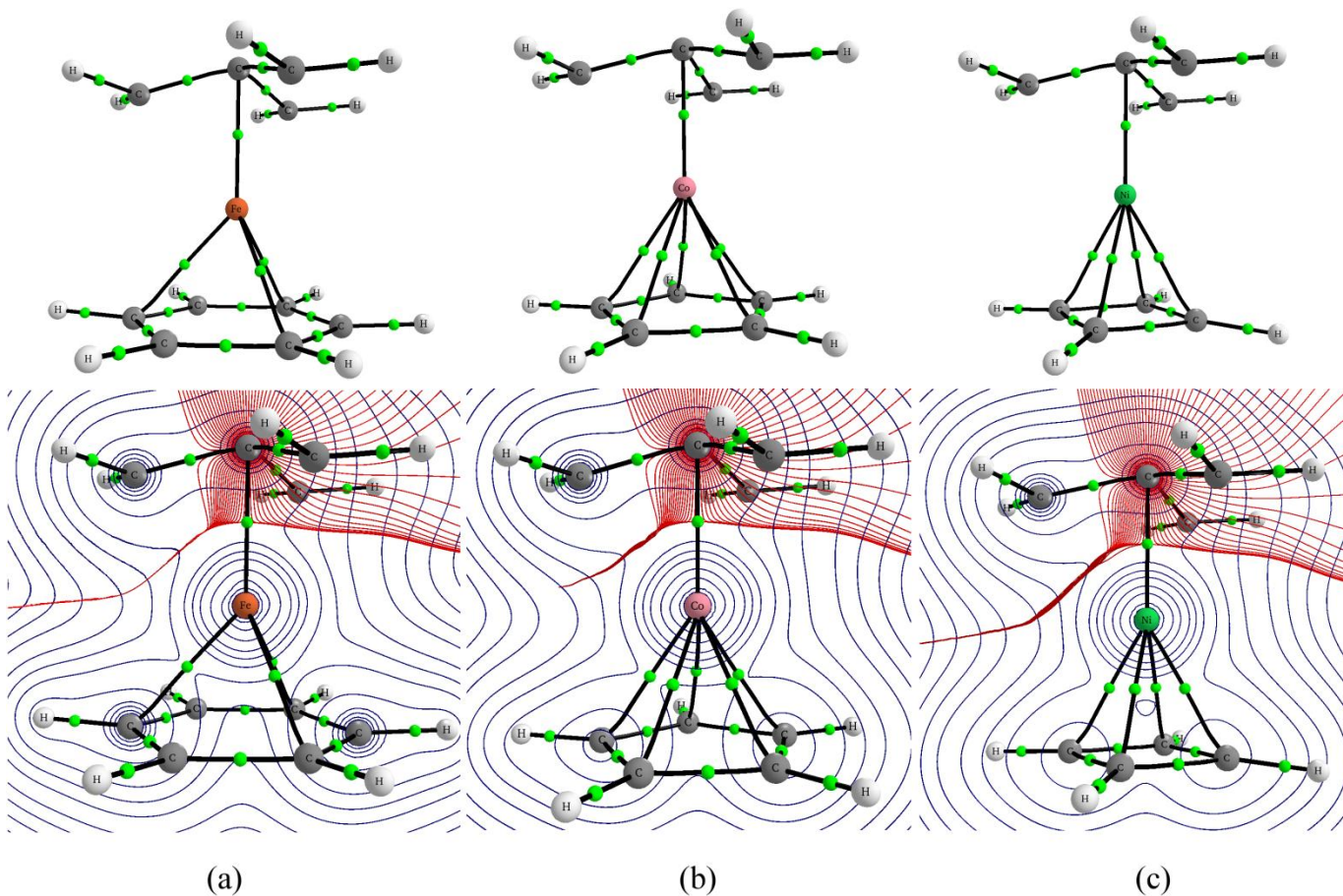
1. C. F. Matta, J. Hernandez-Trujillo, T.-H. Tang, R. F. W. Bader, *Chem. Eur. J.*, 2003, 9, 1940.
2. J. Poater, M. Sola, M. Bickelhaupt, *Chem. Eur. J.*, 2006, 12, 2889.
3. R. F. W. Bader, *Chem. Eur. J.*, 2006, 12, 2896.
4. J. Farrugia, C. Evans, M. Tegel, *J. Phys. Chem. A* 2006, 110, 7952.
5. M. Mousavi, G. Frenking, *J. Organomet. Chem.* 2013, 748, 2.
6. M. Mousavi, G. Frenking, *Organometallics* 2013, 32, 1743.

Dynamic vs. Static Molecular Graphs

- Distribution of electron density depends on the nuclear geometry so any change in the nuclear geometry is followed by sudden changes in the topology of electron density, i.e. molecular graph.
- In general, it is believed that finite geometry changes due to molecular vibrations/rotations do not affect molecular graph. Though, some exotic cases are known that break this general rule.^[7]
- The role of geometry in the distribution of the electron density for problematic cases of type II was investigated.

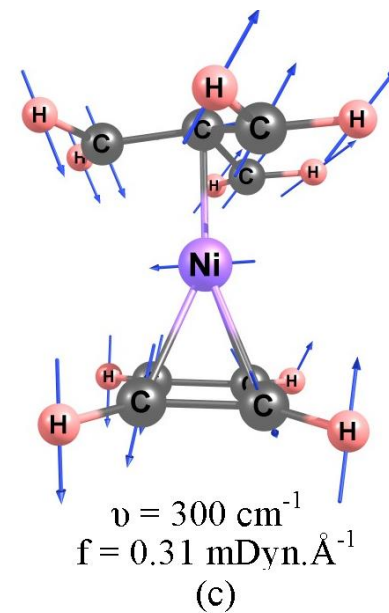
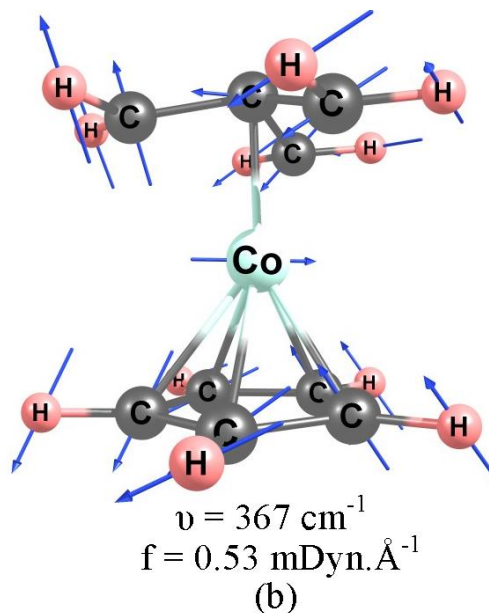
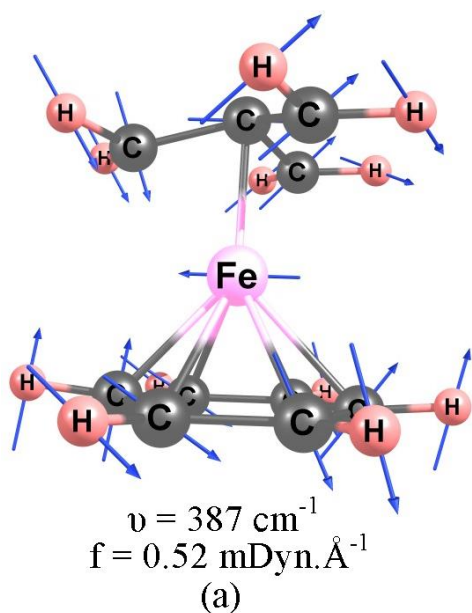
7. C. Foroutan-Nejad, G. H. Shafiee, A. Sadjadi, S. Shahbazian, Can. J. Chem. 2006, 84, 771.

Missing BP in TMM Complexes of TMs^[6]

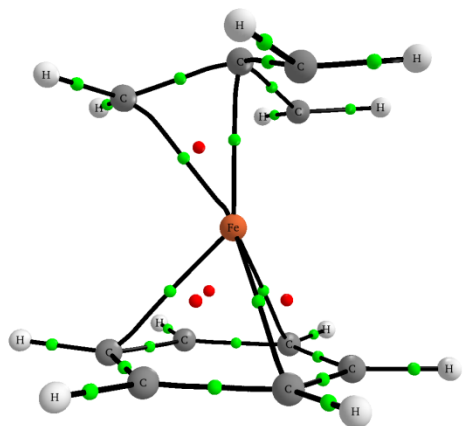


Missing BP in TMM Complexes of TMs^[6]

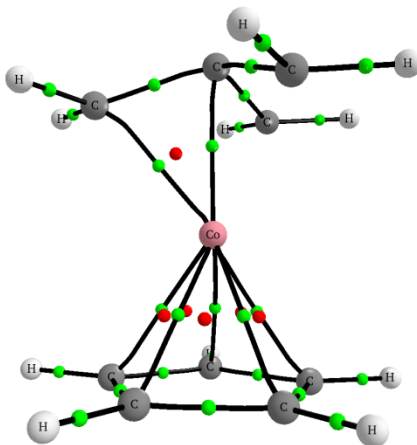
Geometry changes in low-force constant normal modes of TMM complexes were investigated.



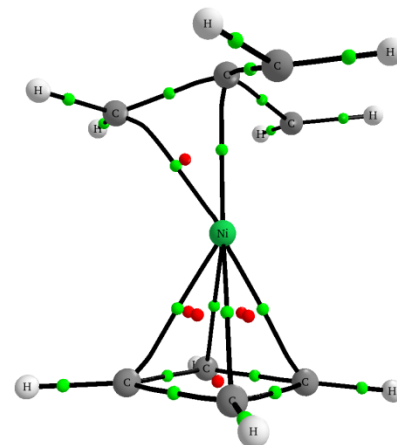
Missing BP in TMM Complexes of TMs^[6]



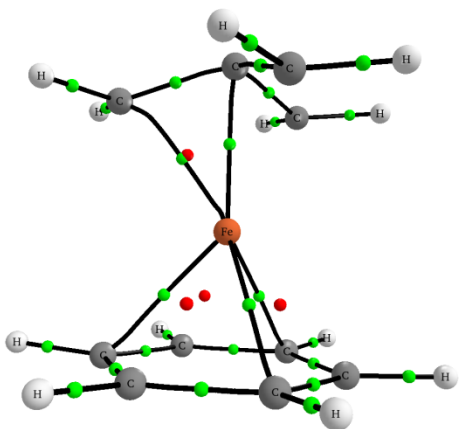
Fe: A



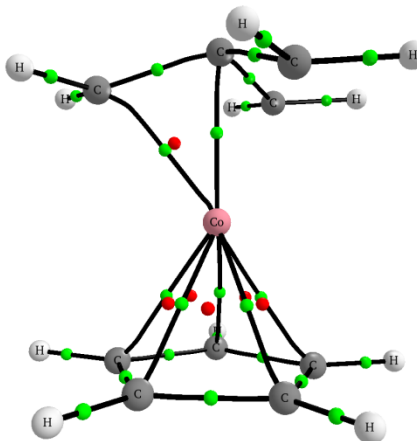
Co: A



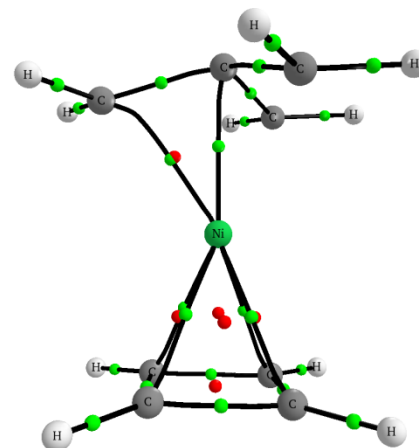
Ni: A



Fe: B, C



Co: B, C
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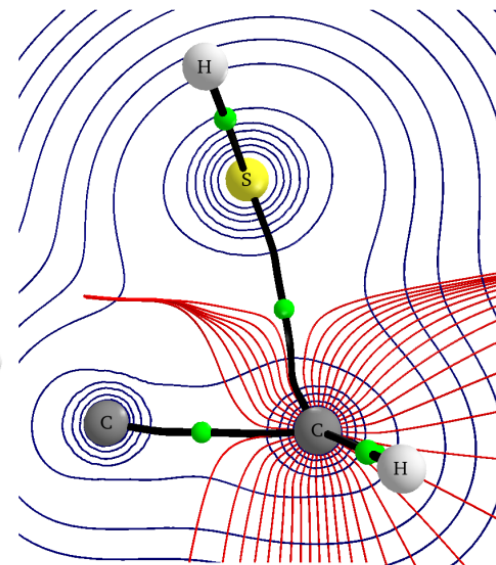
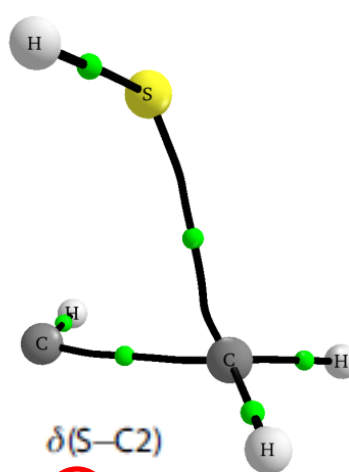


Ni: B, C

Missing BP in TMM Complexes of TMs^[6]

	Fe-C(t)	Fe-C(c)-C(t)	$\Delta E^{[b]}$	$\delta(\text{Fe-C(c)})$	$\delta(\text{Fe-C(t)})^{[c]}$
Fe-Opt	2.10	76.0	0.00	0.46	0.70
Fe-A	2.00	71.5	1.20	0.45	0.75
Fe-B	2.02	72.5	0.68	0.46	0.74
Fe-C	2.04	72.5	0.46	0.45	0.74
	Co-C(t)	Co-C(c)-C(t)	$\Delta E^{[b]}$	$\delta(\text{Co-C(c)})$	$\delta(\text{Co-C(t)})^{[c]}$
Co-Opt	2.07	75.5	0	0.47	0.69
Co-A	1.97	71.0	1.23	0.46	0.75
Co-B	1.99	72.0	0.72	0.46	0.73
Co-C	2.00	72.0	0.48	0.46	0.73
	Ni-C(t)	Ni-C(c)-C(t)	$\Delta E^{[b]}$	$\delta(\text{Ni-C(c)})$	$\delta(\text{Ni-C(t)})^{[c]}$
Ni-Opt	2.11	77.0	0	0.43	0.57
Ni-A	1.99	72.0	1.36	0.42	0.63
Ni-B	2.00	72.5	0.97	0.42	0.62
Ni-C	2.02	72.5	0.61	0.42	0.63

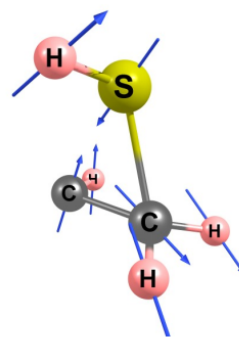
Another Example^[8,9]



	S-C1	S-C2-C1	$\Delta E^{[a]}$	$\delta(S-C1)$	$\delta(S-C2)$
Opt	2.01	72.8	0	0.60	0.79
A	1.92	69.0	0.73	0.68	0.78
B	1.94	69.0	0.41	0.67	0.76

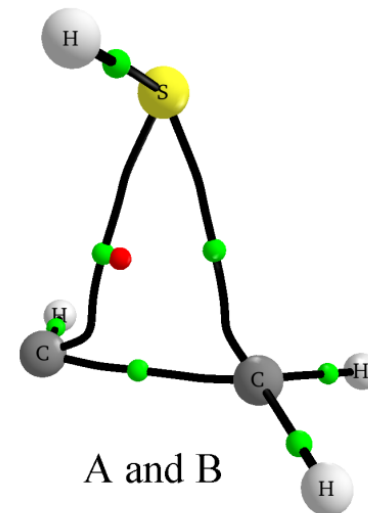
(a)

(b)



$$\nu = 360 \text{ cm}^{-1}$$

$$f = 0.63 \text{ mDyn. \AA}^{-1}$$

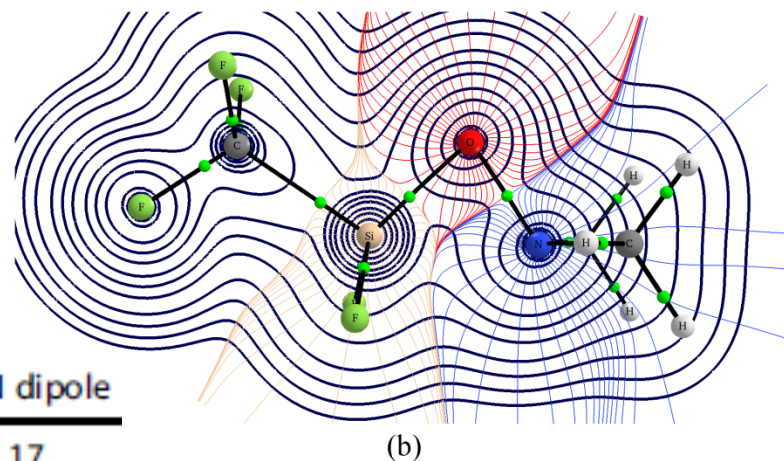
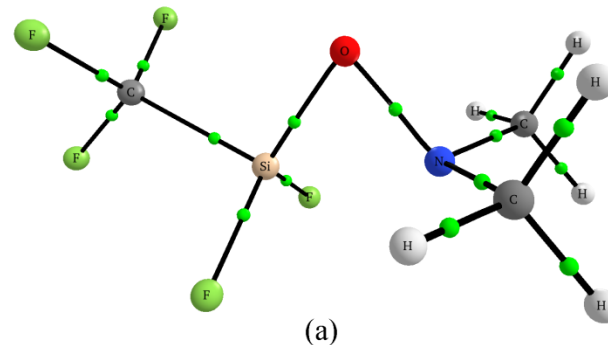


A and B

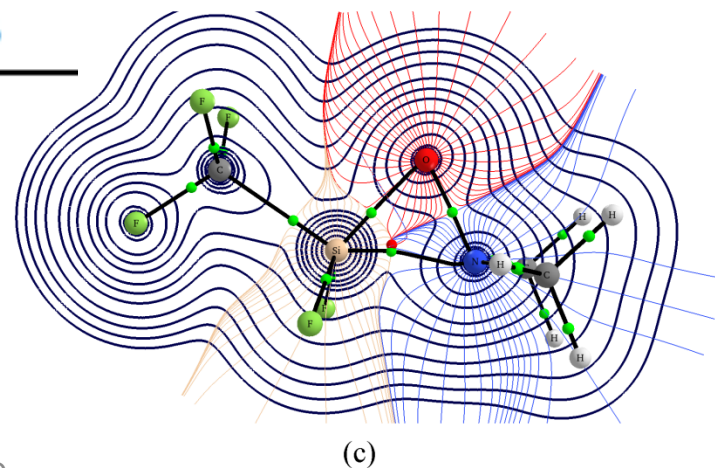
8. J. Henn, D. Leusser, D. Stalke, *J. Comput. Chem.* 2007, 28, 2317.

9. H. Jacobsen, *J. Comput. Chem.* 2009, 30, 1093.

Open Question: Ionic Interaction^[9]



	Si-N	Si-O-N	$\Delta E^{\text{[a]}}$	$\delta(\text{Si-N})$	Si charge	N charge	Si dipole	N dipole
Opt	2.06	81.3	0	0.10	3.19	-0.74	0.48	1.17
A	1.84	70.5	2.11	0.16	3.20	-0.85	0.50	0.96



[9] N. W. Mitzel, K. Vojinovic', R. Frçhlich, T. Foerster, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin, J. Am. Chem. Soc. 2005, 127, 13705.

Take Home Messages

- $(3, -1)$ CPs are not chemical bonds. A bond cannot appear and disappear by vibrations.
- In analogy with Ring and Cage Critical Points, $(3, -1)$ CPs are suggested to be called Line Critical Points (LCP) to avoid misunderstanding.
- Similarly, Bond Paths are suggested to be called Line Paths (LP).
- Electron Delocalization (Delocalization Index) is the best descriptor of covalency. It does not depend on presence or absence of LCPs.

Take Home Messages

- A new terminology was suggested to classify atoms in a molecule in three groups:
 - Non-neighbors, which are not connected by LCP/LP because have no common interatomic surface
 - Neighbors that are connected by an LCP
 - Passionate neighbors! These atoms are separated because a tiny atomic basin penetrates between them but they can form LCP in a non-equilibrium but low-energy structure.

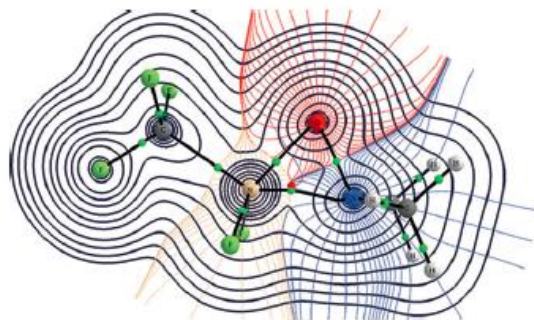
FULL PAPER

■ Bond Theory

*C. Foroutan-Nejad, S. Shahbazian,**
R. Marek 10140 – 10152



Toward a Consistent Interpretation of the QTAIM: Tortuous Link between Chemical Bonds, Interactions, and Bond/Line Paths



Let's look through a new window! Careful "reinterpretation" of the quantum theory of atoms in molecules (QTAIM) analysis dismisses many controversies in chemical applications of the theory. It is argued that the assumed equivalence between the bond paths and chemical bonds does not lead to a consistent interpretation of the theory. A new interpretation is proposed that does not assume the mentioned equivalence, and thus circumvents conceptual obstacles (see figure).

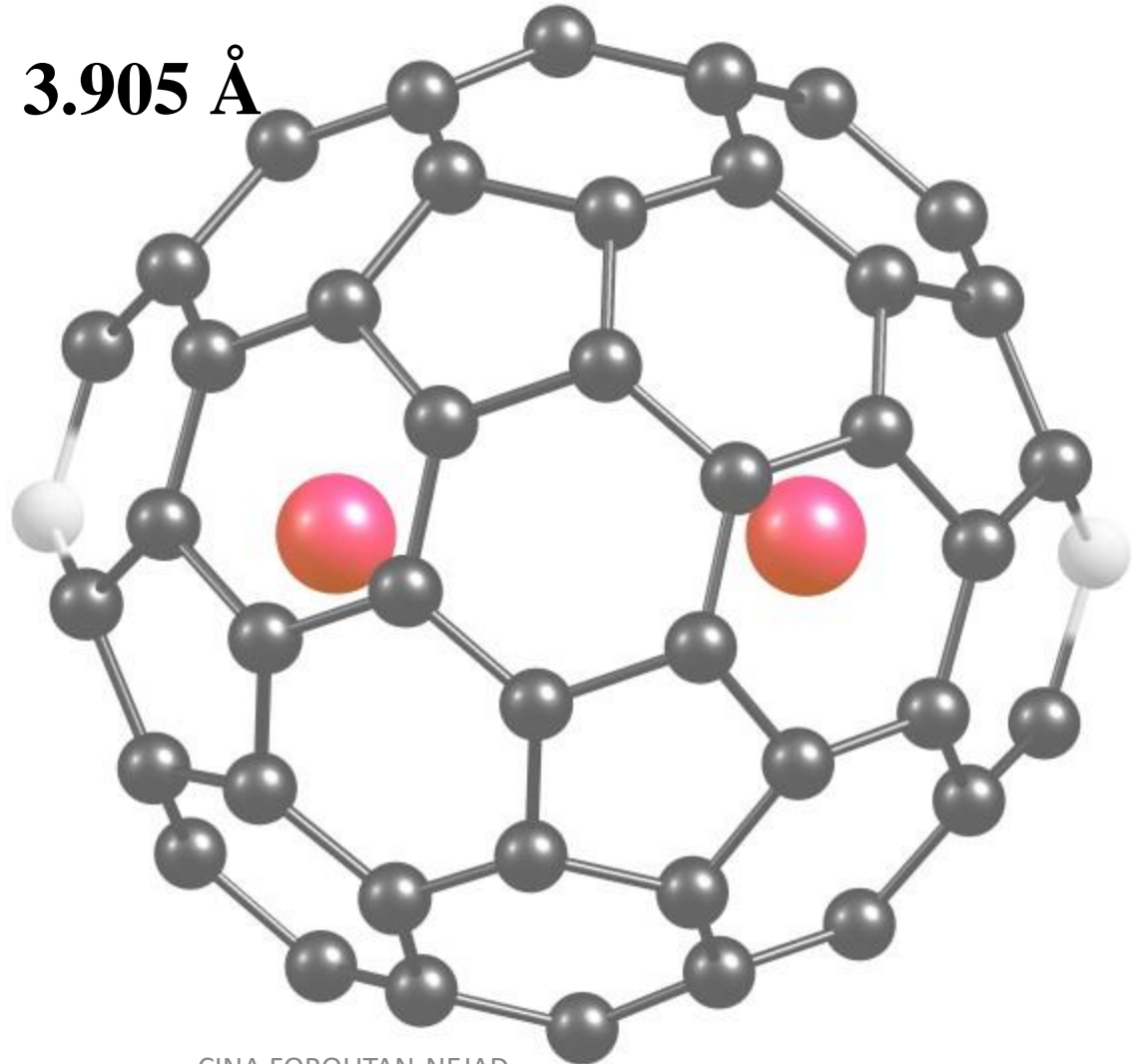
How to Identify a Chemical Bond?

- Do not rely on one descriptor
- Inspect both molecular orbitals and electron density
- Always compare your system with well-known systems
- See the next slides...

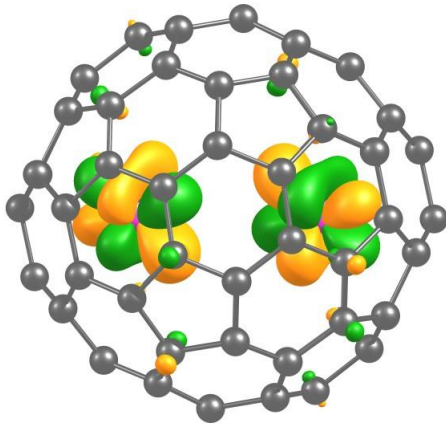
Are These Uranium Atoms Bonded?

U-U Distance: **3.905 Å**

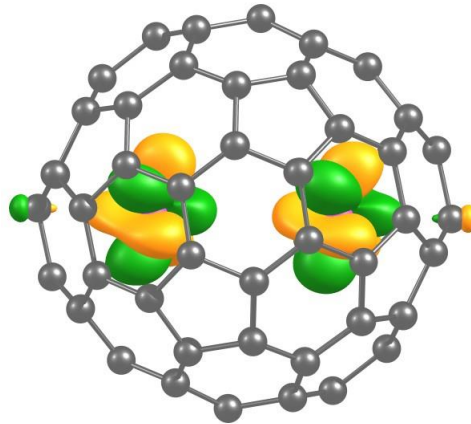
$U_2@C_{80}$



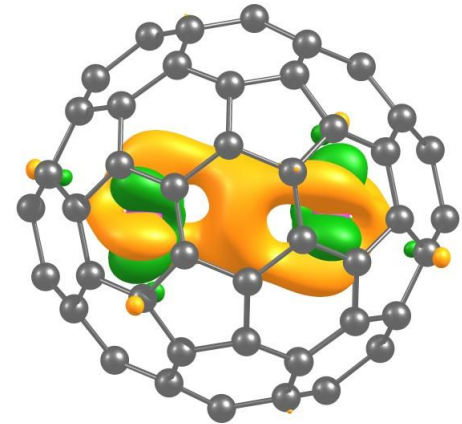
MO Analysis



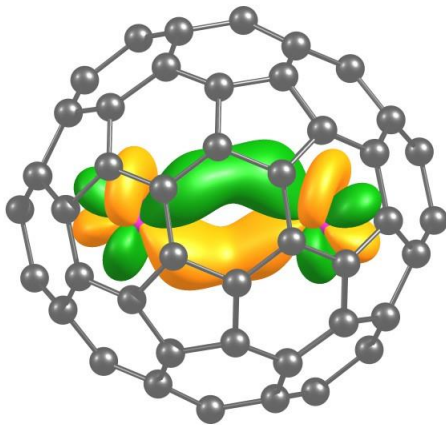
HOMO



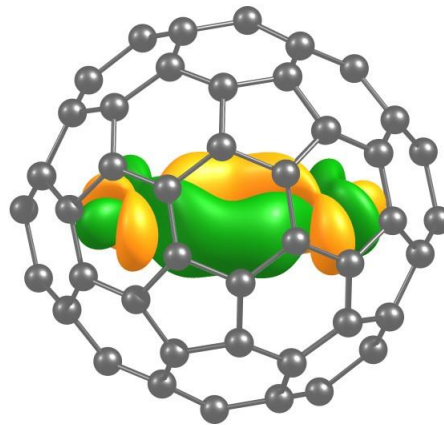
HOMO - 1



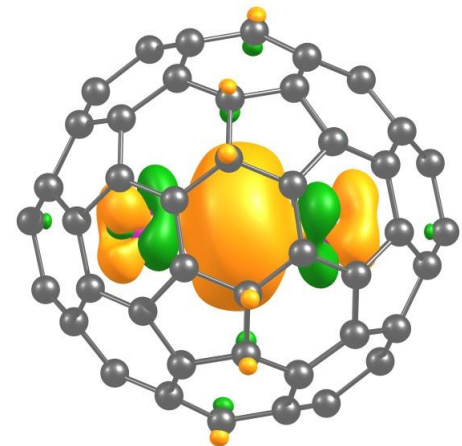
HOMO - 2



HOMO - 3

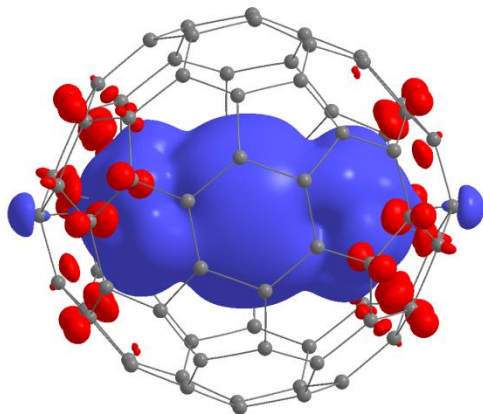


HOMO - 4

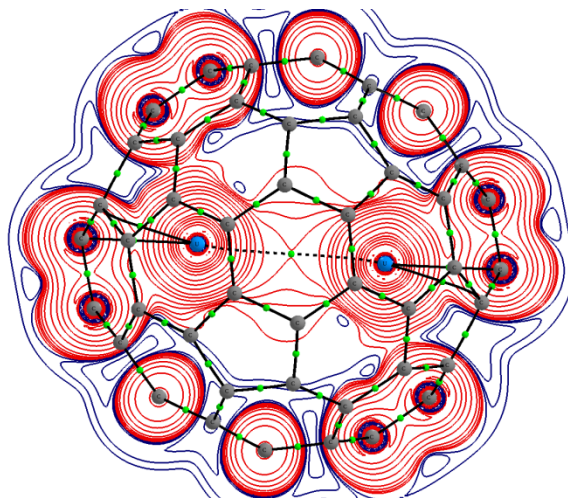


HOMO - 5

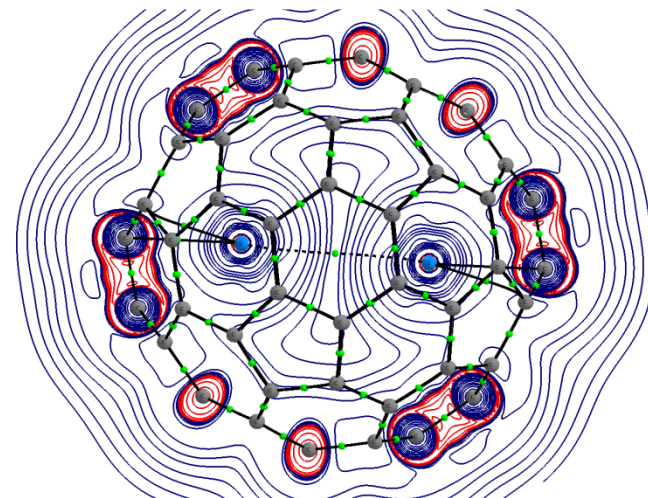
Electron Density Analysis



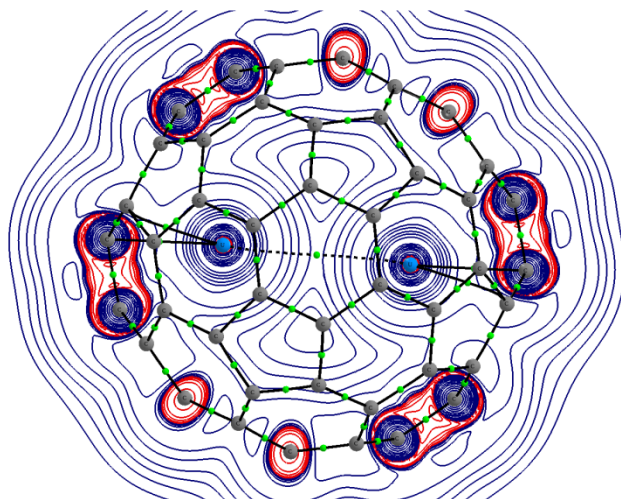
$\rho_\alpha - \rho_\beta$



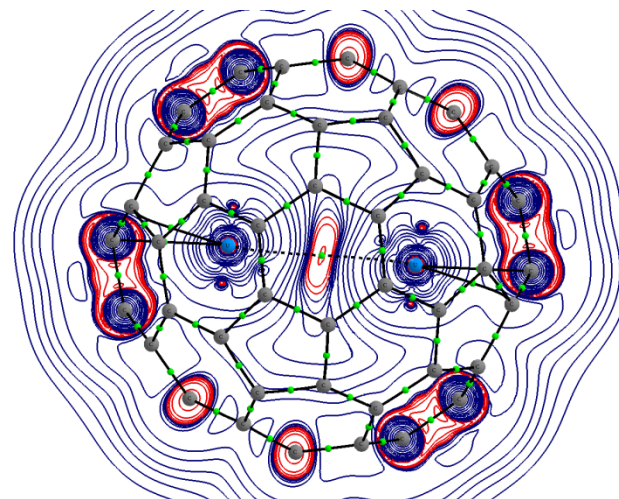
Energy Density, $H(r)$



$\nabla^2\rho$



$\nabla^2\rho_\beta$



$\nabla^2\rho_\alpha$

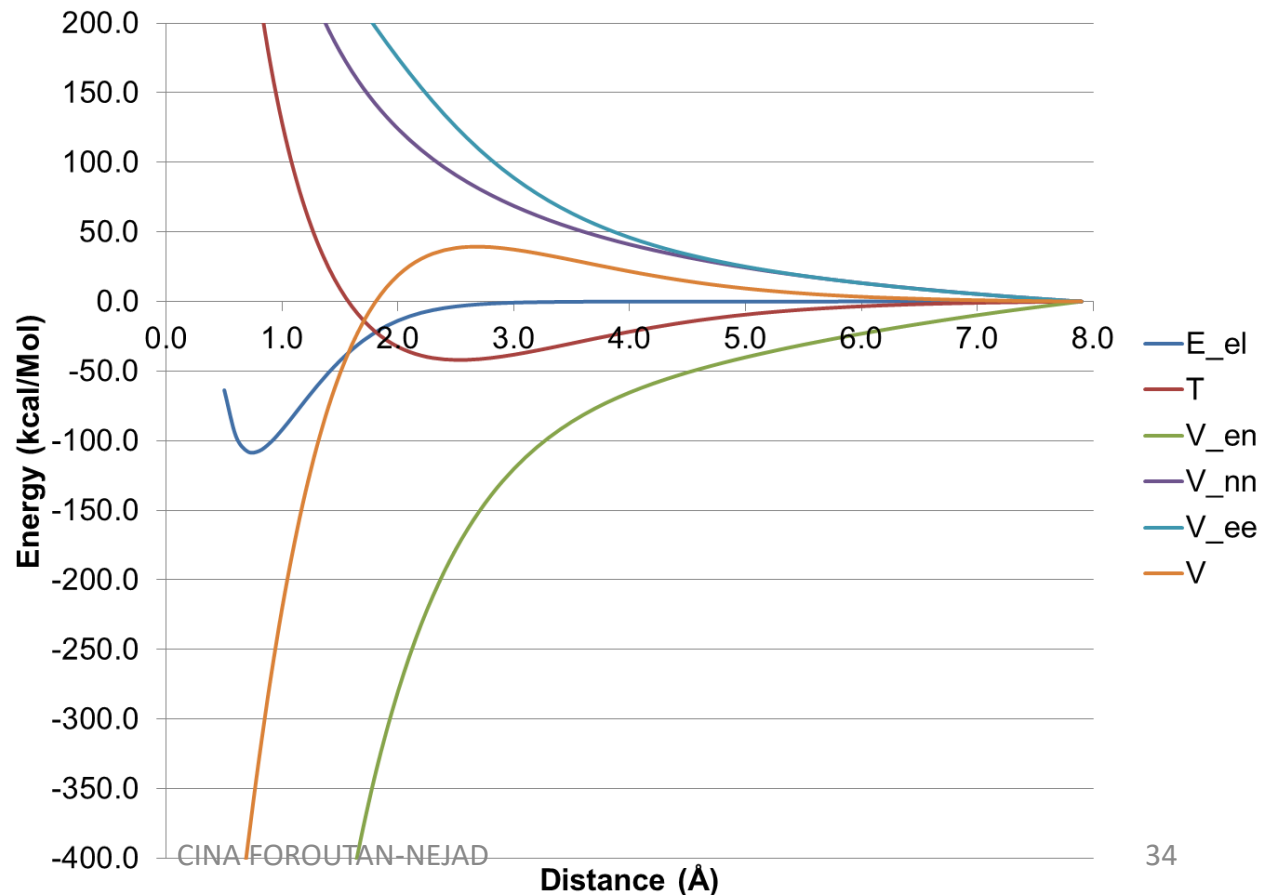
Don't Forget Comparison & DI

- Selected model system free U_2 molecule
- U_2 is known to have a quintuple bond
- DI (U_2): 5.02
- DI $U_2@C_{80}$: 1.01
- DI is consistent with a single bond or two single-electron bonds also confirms MO analysis results

$U_2@C_{80}$ are Bonded

Background: Chemical Bond

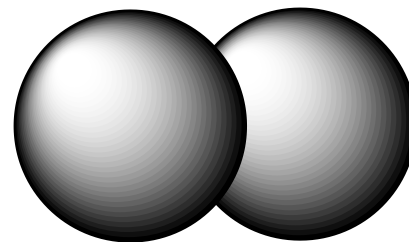
Unlike ionic bonds, which are formed by attraction between ions, formation of covalent bonds does not have an electrostatic driving force.^[1]



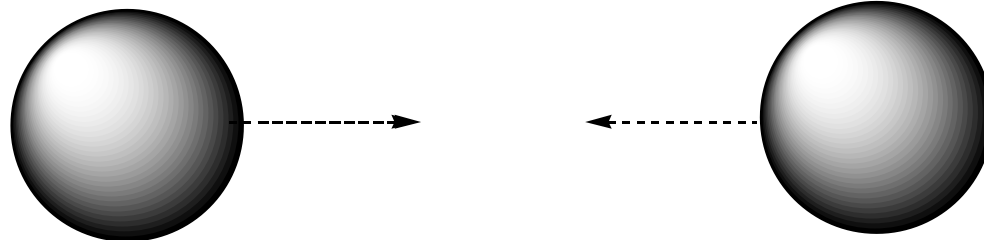
[1] J. C. Slater, J. Chem. Phys., 1933, 1, 687.

Different Views On Covalency

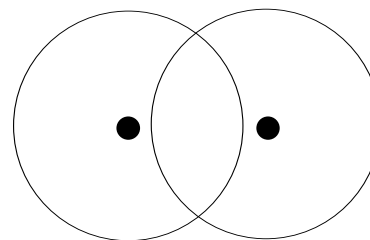
1. Morokuma-Zeigler-Rauk



2. Bader



3. Ruedenberg



Bond Order from IUPAC Definition to QTAIM

- **What is a covalent bond order?**
- According to the IUPAC definition the bond order is defined as the *total* orbital overlap population between a pair of atoms. In QTAIM, this quantity is called *delocalization index*, $\delta(A,B)$, and can be calculated between any pair of atoms like A and B in a molecule or a supramolecular complex.

$$\delta(A, B) = -2cov(n_A, n_B) = -2[\langle n_A n_B \rangle - \langle n_A \rangle \langle n_B \rangle]$$

$$\delta(A, B) = - \sum_{i,j} S_{i,j}(A) S_{i,j}(B)$$

Towards a Physically Meaningful Energy Decomposition Scheme

No matter **how you select molecular fragments**, a physically meaningful energy decomposition scheme (EDS) must have certain properties.

- Should recover binding energy in terms of **physical** terms, i.e., kinetic and potential energy components, with least number of **arbitrary** energy components such as “polarization”, “orbital interaction”, etc. (**Occam’s Razor**).
- Must enable user to recover **chemically relevant** data.

Interacting Quantum Atoms Energy Decomposition Scheme

- IQA analysis can be performed employing overlapping (fuzzy atoms) or non-overlapping (QTAIM) molecular subspaces.
- IQA analysis in QTAIM atomic space has unique advantages. Non-overlapping atoms permits defining “chemically meaningful fragments” and studying inter-fragment interactions.
- QTAIM atoms satisfy atomic virial theorem.

IQA Energy Decomposition Scheme

- It has been demonstrated that QTAIM fragments need the least promotion energy^[9], also satisfying Li and Parr partitioning model, among various partitioning methods.^[10]
- For any atomic space one can define self-interaction energy as the following:

$$E_{self}(\Omega) = T(\Omega_A) + V_{en}(\Omega_A) + V_{ee}(\Omega_A)$$

- Similarly interatomic interaction energy can be broken to the following components:

$$\begin{aligned} E_{inter}(\Omega_A, \Omega_B) &= V_{nn}(\Omega_A, \Omega_B) + V_{XC_ee}(\Omega_A, \Omega_B) + V_{coulomb_ee}(\Omega_A, \Omega_B) + \\ &\quad V_{en}(\Omega_A, \Omega_B) + V_{ne}(\Omega_A, \Omega_B) \\ &= V_{EI} + V_{XC} \end{aligned}$$

[9] L. Li and R. G. Parr, J. Chem. Phys. 1986, 84, 1704.

[10] A. M. Pendas, M. A. Blanco and E. Francisco, J. Comput. Chem. 2007, 28, 161.

IQA Energy Decomposition Scheme

- IQA recovers the binding energy components in terms of physically meaningful terms as the following:

$$E_{Bind} = V_{El} + V_{XC} + E_{Pr}$$

- V_{El} and V_{XC} represent contribution of all classical and exchange-correlation energy components, respectively.
- The promotion energy, E_{Pr} , is the sum of all factors that change the energy of an atomic sub-space, including kinetic energy, electron-electron repulsion, and electron-nucleus attraction.
- In IQA analysis the kinetic energy has no interatomic component and nuclear-nuclear repulsion clearly has no atomic component.

How Electron Delocalization Lowers Energy of a molecule?

- This old question can be quantitatively answered in the context of IQA. The electron delocalization and exchange correlation energy component can be linked together by a first order approximation.

$$\delta(\Omega_A, \Omega_B) = -2 \int_{\Omega_A} \int_{\Omega_B} [\rho_2^{AB}(\mathbf{r}_1, \mathbf{r}_2) - \rho_A(\mathbf{r}_1)\rho_B(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2$$

$$V_{XC}(\Omega_A, \Omega_B) = \int_{\Omega_A} \int_{\Omega_B} [\rho_2^{AB}(\mathbf{r}_1, \mathbf{r}_2) - \rho_A(\mathbf{r}_1)\rho_B(\mathbf{r}_2)] r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\frac{\delta(\Omega_A, \Omega_B)}{R_{AB}} = m V_{XC}(\Omega_A, \Omega_B)$$



Thank you for your
attention!

Now it is time for
question!