Jyväskylä Summer School on Charge Density August 2007

Topological Analysis of Electron Density

Louis J Farrugia

UNIVERSITY
of
GLASGOW

West
CHEM

What is topological analysis ?

A method of obtaining chemically significant information from the electron density ρ (rho)

ρ is a quantum-mechanical *observable*, and may also be obtained from experiment

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

“It seems to me that experimental study of the scattered radiation, in particular from light atoms, should get more attention, since in this way it should be possible to determine the arrangement of the electrons in the atoms.”

P. Debye, *Ann. Phys.* (1915) **48**, 809.

Why analyse the charge density ?

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

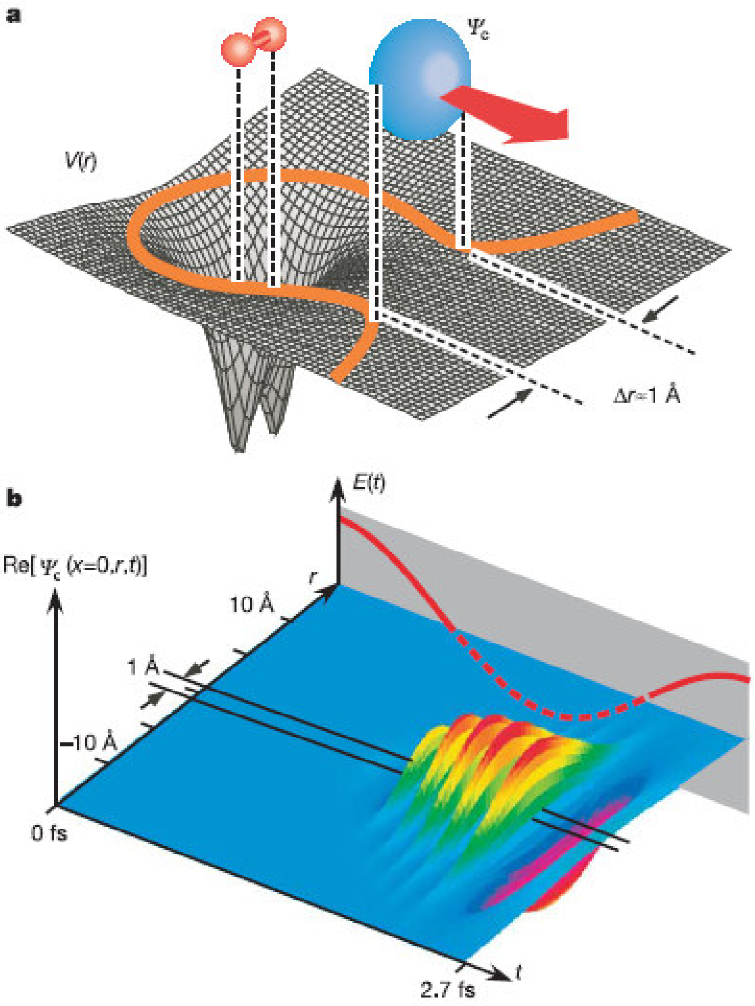
$$H\Psi = E\Psi$$

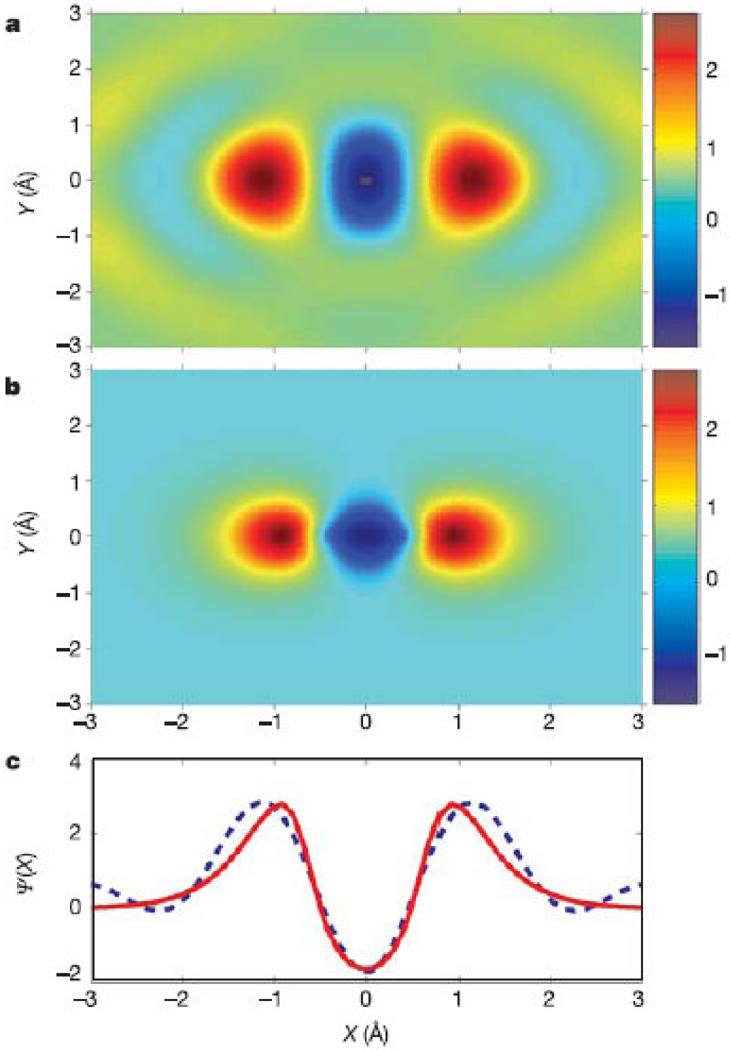
The Hohenberg-Kohn theorem confirmed that the density, $\rho(\mathbf{r})$, is the fundamental property that characterises the ground state of a system - once $\rho(\mathbf{r})$ is known, the energy of the system is uniquely defined, and from there a diverse range of molecular properties can, in principle,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

Thus a knowledge of $\rho(\mathbf{r})$ opens the door to understanding of all the key challenges of chemistry. *ρ is a quantum-mechanical observable*.

P. Hohenberg, W. Kohn *Phys. Rev.* **1964**, *136*, B864.

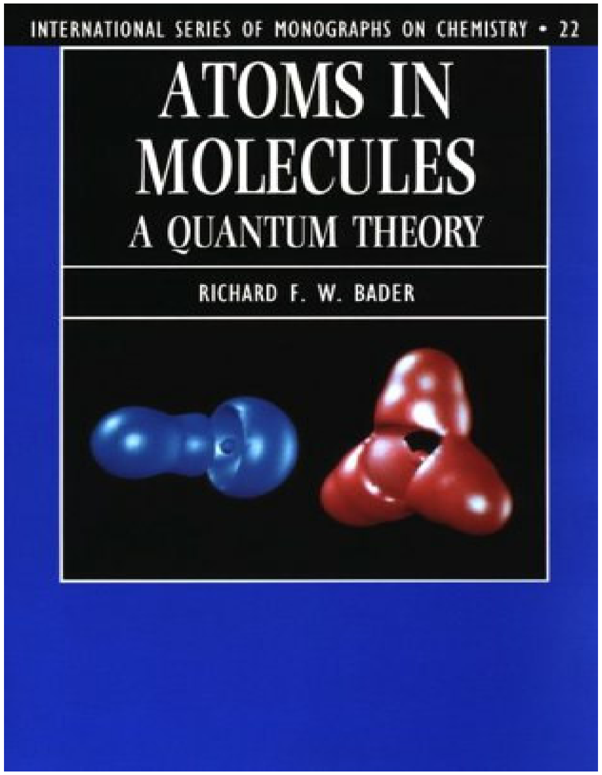
Can we ever observe orbitals ?





Simply not ever possible - see E. Scerri (2000) *J. Chem. Ed.* **77**, 1492.
However ?? - see J. Itani *et al* (2004) *Nature* **432,** 867

What is topological analysis ?



INTERNATIONAL SERIES OF MONOGRAPHS ON CHEMISTRY • 22

ATOMS IN
MOLECULES
A QUANTUM THEORY

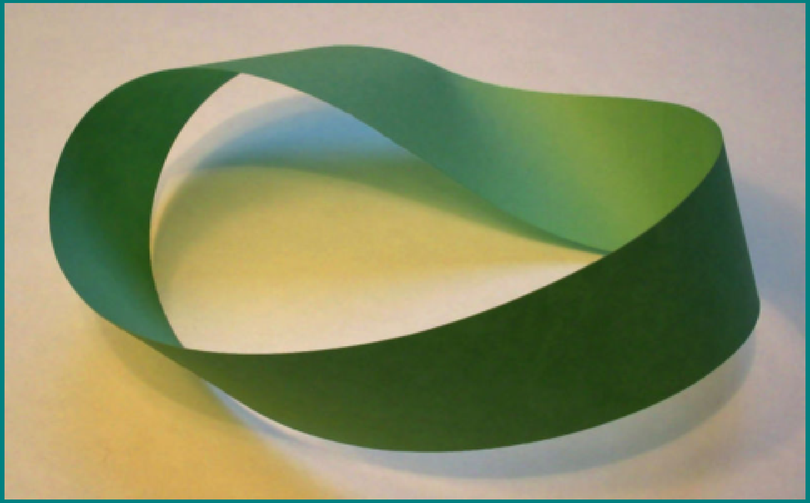
RICHARD F. W. BADER

R. F. W. Bader *Atoms in Molecules : A quantum theory*, OUP 1990

P. L. A. Popelier *Atoms in Molecules : An Introduction*, Pearson, 2000.
R. J. Gillespie & P. L. A. Popelier *Chemical Bonding and Molecular Geometry*, OUP, 2001.

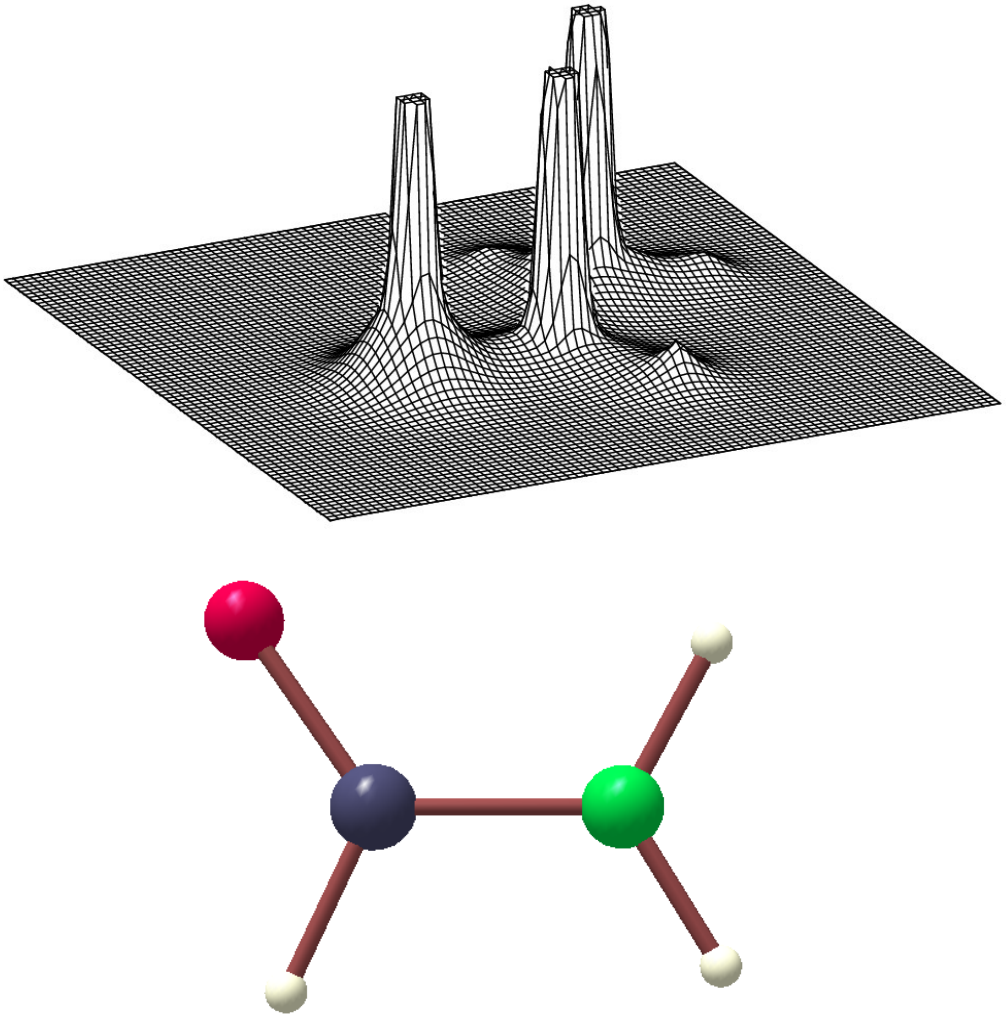
What is topological analysis ?

Topology is a branch of mathematics involving the study of the nature of space. The theorems are used extensively in subjects like geography



In chemical topology, we are concerned with the properties of *scalar fields*, like the (continuous) real function $\rho(\mathbf{r})$. These properties are displayed in global terms in the *gradient vector field* of $\rho(\mathbf{r})$. An analysis of the topology of $\rho(\mathbf{r})$ leads directly to the chemical concepts of *atoms*, *molecules*, *structures* & *bonds*.

Representation of the total charge density



A representation of the total charge density $\rho(\mathbf{r})$ in the plane of the formamide molecule H_2N-CHO.

This is a typical picture of $\rho(\mathbf{r})$, 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.

The Hessian matrix and Laplacian

A quantitative way to analyse the topology of ρ is to consider the first derivative (gradient) $\nabla(\rho)$. At certain points, called *critical points*, this gradient vanishes. The characteristic of these points is determined by the second derivative $\nabla^2(\rho)$, and the so-called Hessian of ρ. The Hessian is the (3×3) symmetric matrix of partial second derivatives

$$\begin{array}{ccc} \partial^2\rho/\partial x^2 & \partial^2\rho/\partial x\,\partial y & \partial^2\rho/\partial x\,\partial z \\ \partial^2\rho/\partial y\,\partial x & \partial^2\rho/\partial y^2 & \partial^2\rho/\partial y\,\partial z \\ \partial^2\rho/\partial z\,\partial x & \partial^2\rho/\partial z\,\partial y & \partial^2\rho/\partial z^2 \end{array}$$

By diagonalisation of this matrix, we set the off-diagonal terms to zero, and obtain the three *principal axes of curvature*. These principal axes will correspond to symmetry axes, if the critical point lies on a symmetry element. The sum of the diagonal terms is called the Laplacian of ρ, $\nabla^2(\rho)$, and is of fundamental importance.

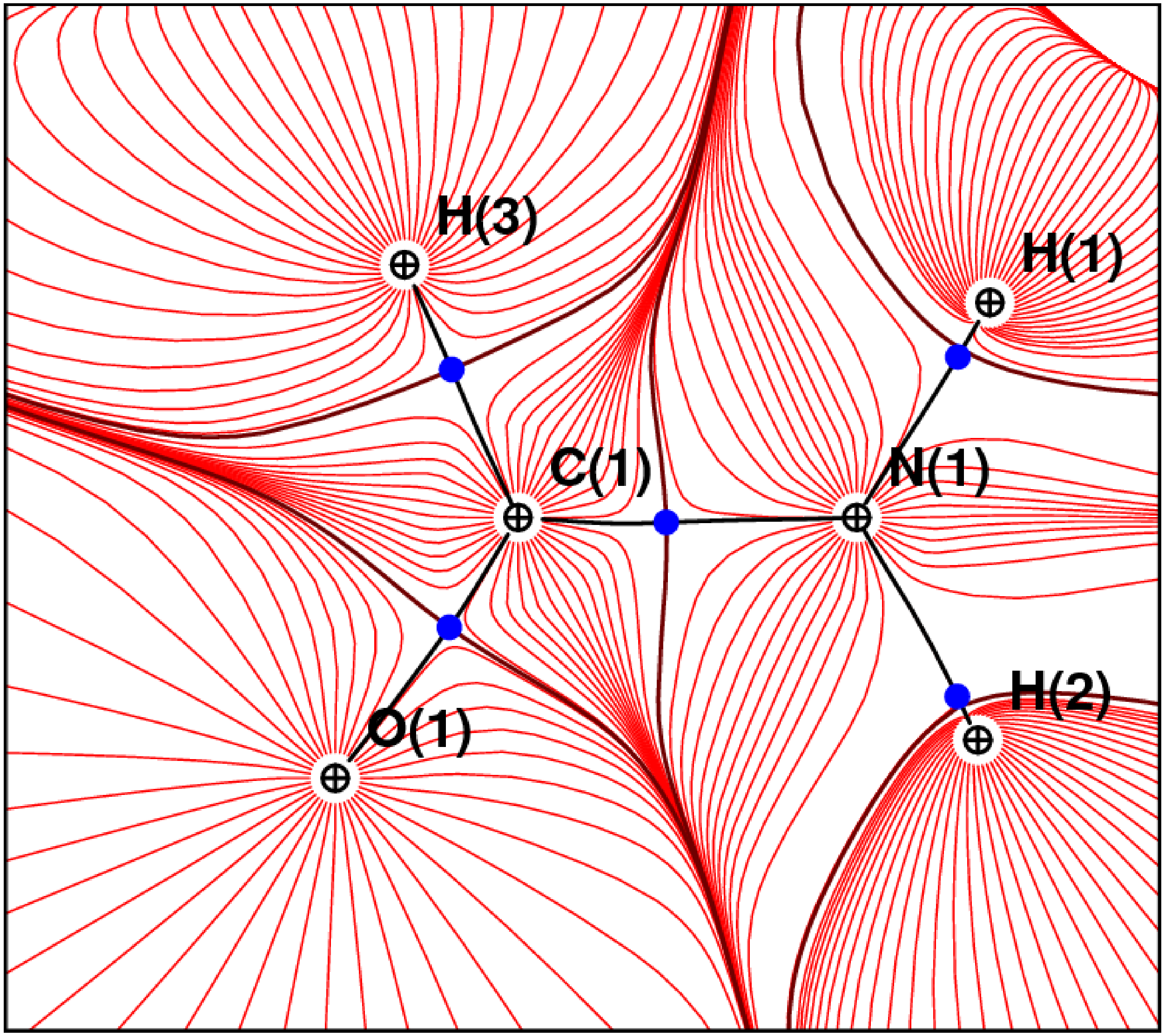
$$\nabla^2(\rho) = \partial^2\rho/\partial x^2 + \partial^2\rho/\partial y^2 + \partial^2\rho/\partial z^2$$

Critical point definitions

At a critical point, the eigenvalues of the Hessian are all real and are generally non-zero. The *rank* of the critical point is defined as the number of non-zero eigenvalues, while the *signature* is defined as the algebraic sum of the signs of the eigenvalues. These two characteristics are used to label a critical point (*rank*,*signature*). For topologically stable critical points, the *rank* is always 3. The four possibilities are then

(3,-3)	All curvatures –ve, a local maximum
(3,-1)	Two curvatures are –ve and one is +ve ρ is a maximum in a plane and a minimum perpendicular to this plane – a bond cp
(3,+1)	Two curvatures are +ve and one is -ve ρ is a minimum in a plane and a maximum perpendicular to this plane - a ring cp
3,+3)	All curvatures +ve, a local minimum – a cage cp

The gradient vector field

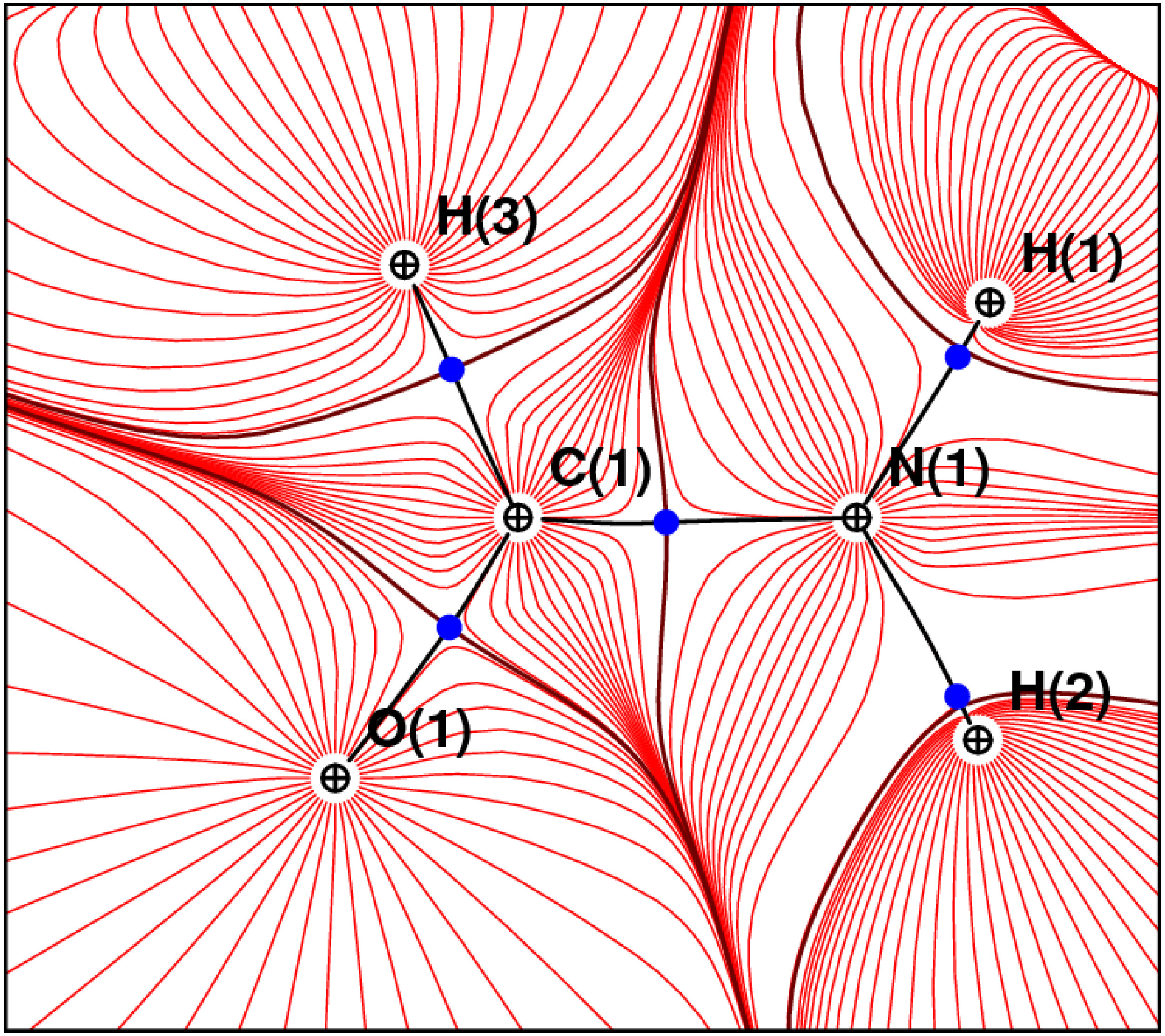


This is a representation of the gradient vector field of ρ in the molecular plane of formamide

The red paths trace the direction of maximum gradient of ρ in leaving the nucleus. For a molecule in the gas phase, the trajectories will generally terminate at infinity.

In special cases however they will terminate at another nucleus – these special trajectories are known as *bond paths*

The gradient vector field



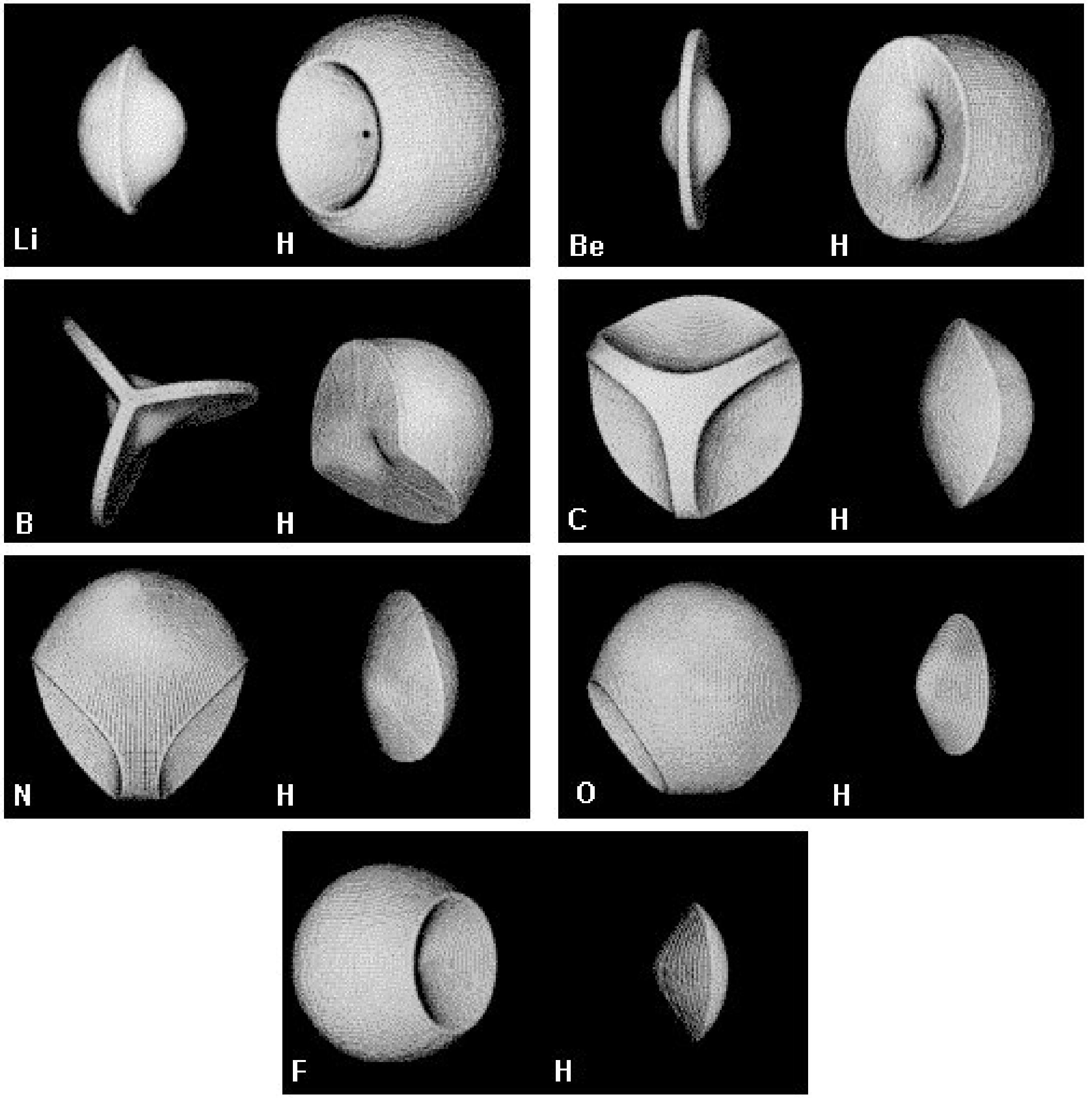
These special paths are associated with the another topological object, the bond critical point (shown in blue)

Two other trajectories leave the critical point and terminate at infinity. These are part of a family of trajectories defining the *zero flux surface*.

$$\nabla\rho(\mathbf{r})\bullet\mathbf{n}(\mathbf{r}) = 0$$

The scalar product of $\nabla\rho(\mathbf{r})$ with $\mathbf{n}(\mathbf{r})$ the vector normal to the surface. This surface encloses each atom and defines a sub-space – the quantum topological definition of an *atom in a molecule*.

The topological atom

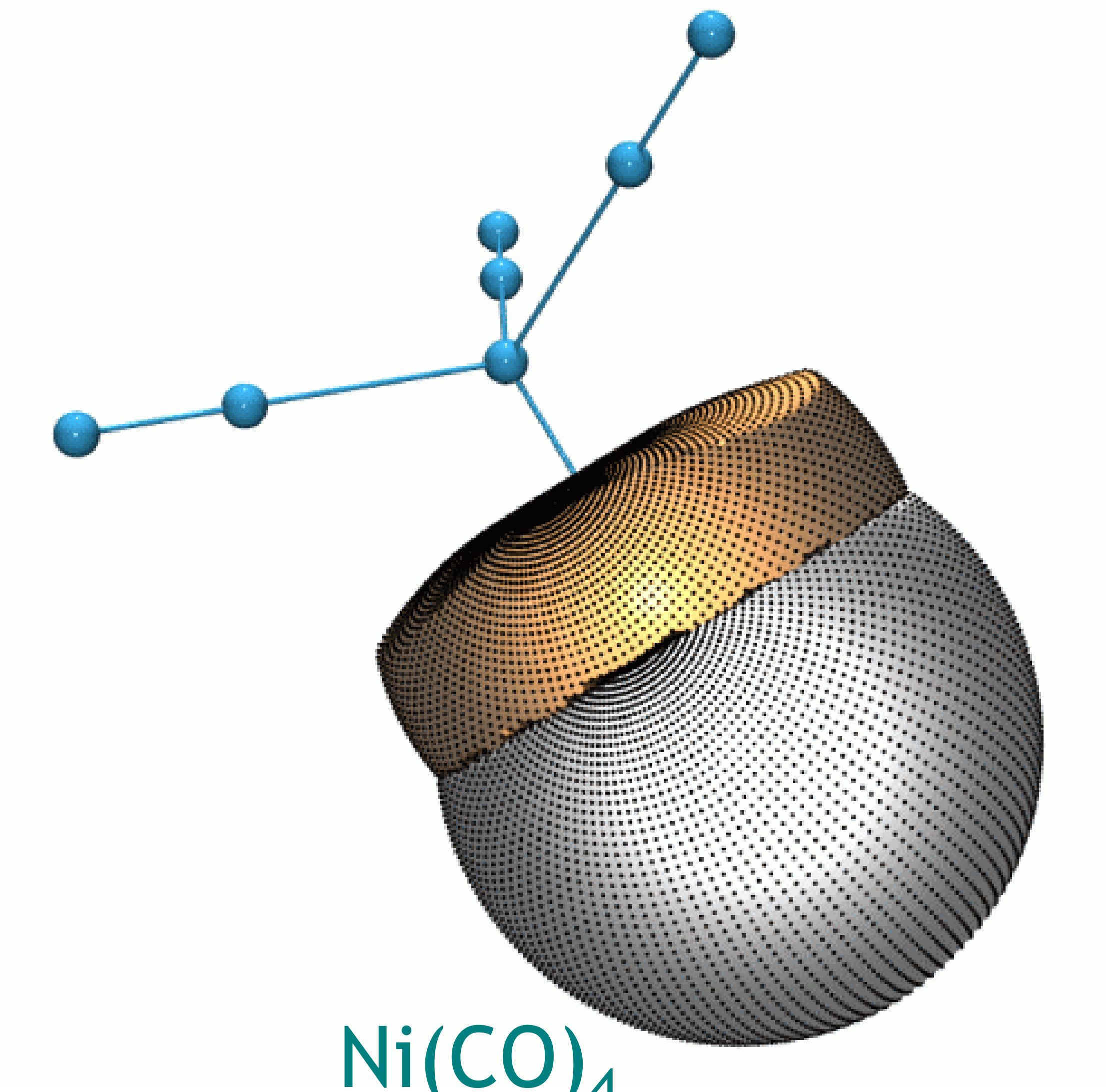


These interatomic surfaces result in a unique way of partitioning 3D-space in molecules into *atomic basins*.

The topological atoms are quite transferable and additive, but do not look very much like the balls and spheres of molecular models !!!

The simple binary hydrides of the second period elements show that the relative volumes of space associated with each element is determined by their relative electro-negativities. Surfaces are truncated at 0.001 au.

The topological atom



$Ni(CO)_4$

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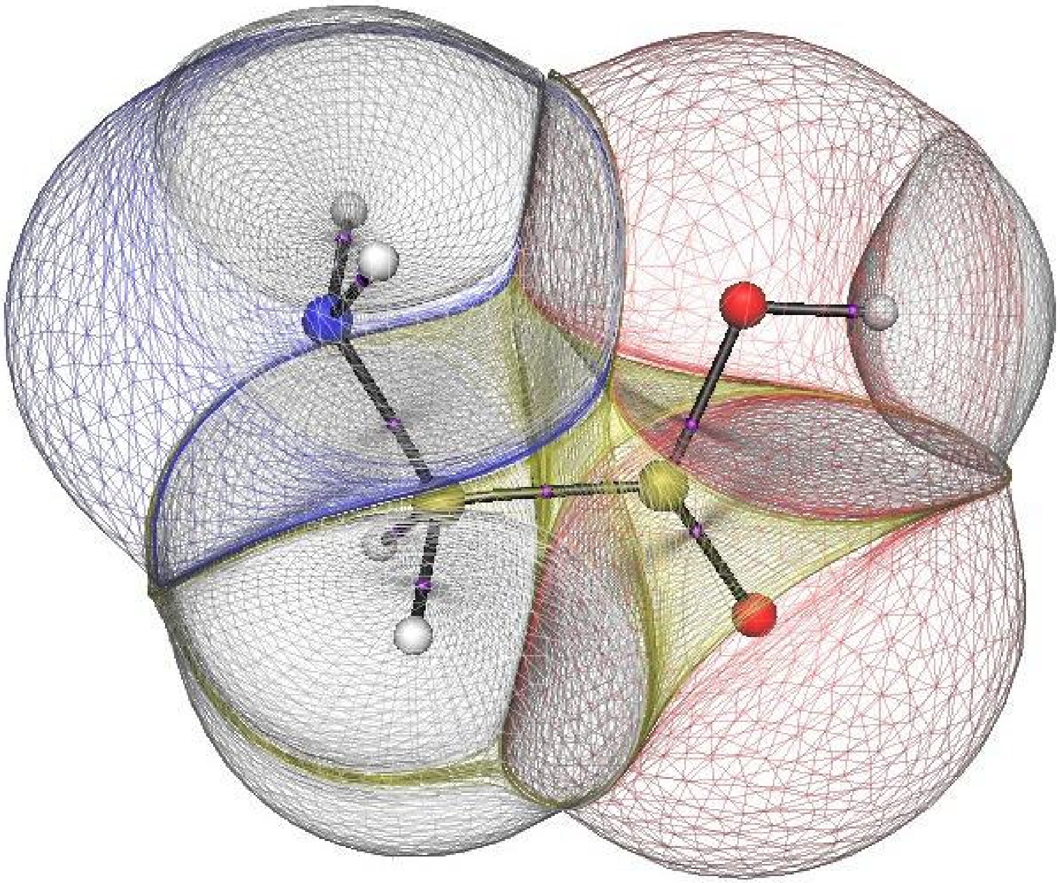
WinXD program – XD2006 T. Koritsanszky et al (2006)

The topological atom



glycine

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The simple binary hydrides of the second period elements show that the relative volumes of space associated with each element is determined by their relative electro-negativities. Surfaces are truncated at 0.001 au.

Morphy98 program P. L. A. Popelier et al (1998)

The topological atom

The partitioning in real space of molecules into atoms by using these interatomic surfaces is a fundamental, quantum mechanically rigorous, method. It allows properties to be calculated for proper open systems, where exchange, e.g. with charge may occur between atoms. The properties calculated by integration within these boundaries, O(Ω), are chararacteristic of that atom in its chemical environment. Such integrated properties include

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 Vol(Ω) – 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.

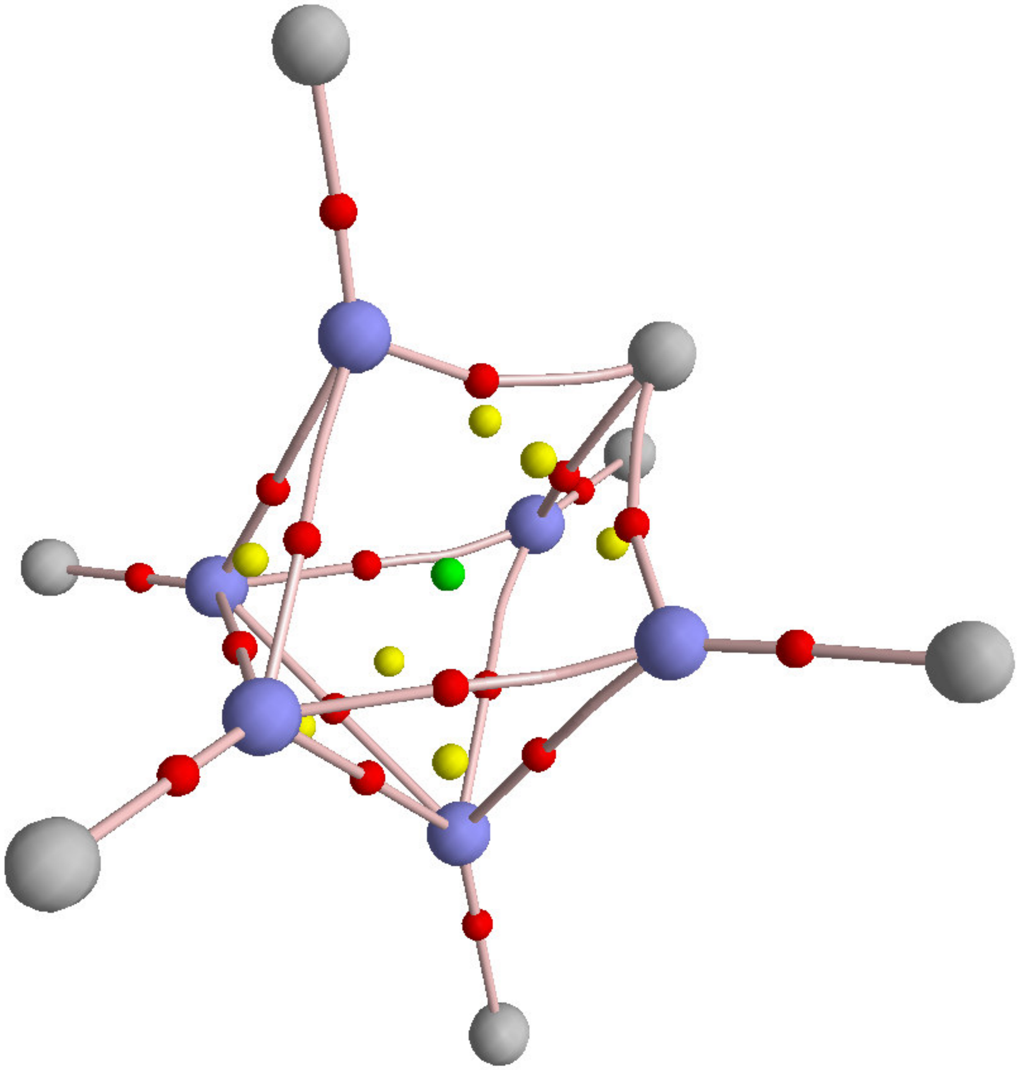
3. Atomic Laplacian $L(\Omega)$ - this property should vanish, and the actual magnitude is used as a gauge for the accuracy of integration.

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 $Q(\Omega)$ polarisations.

R. F. W. Bader & C. Matta (2004) *J. Phys. Chem. A* **108**, 8385.

The molecular graph



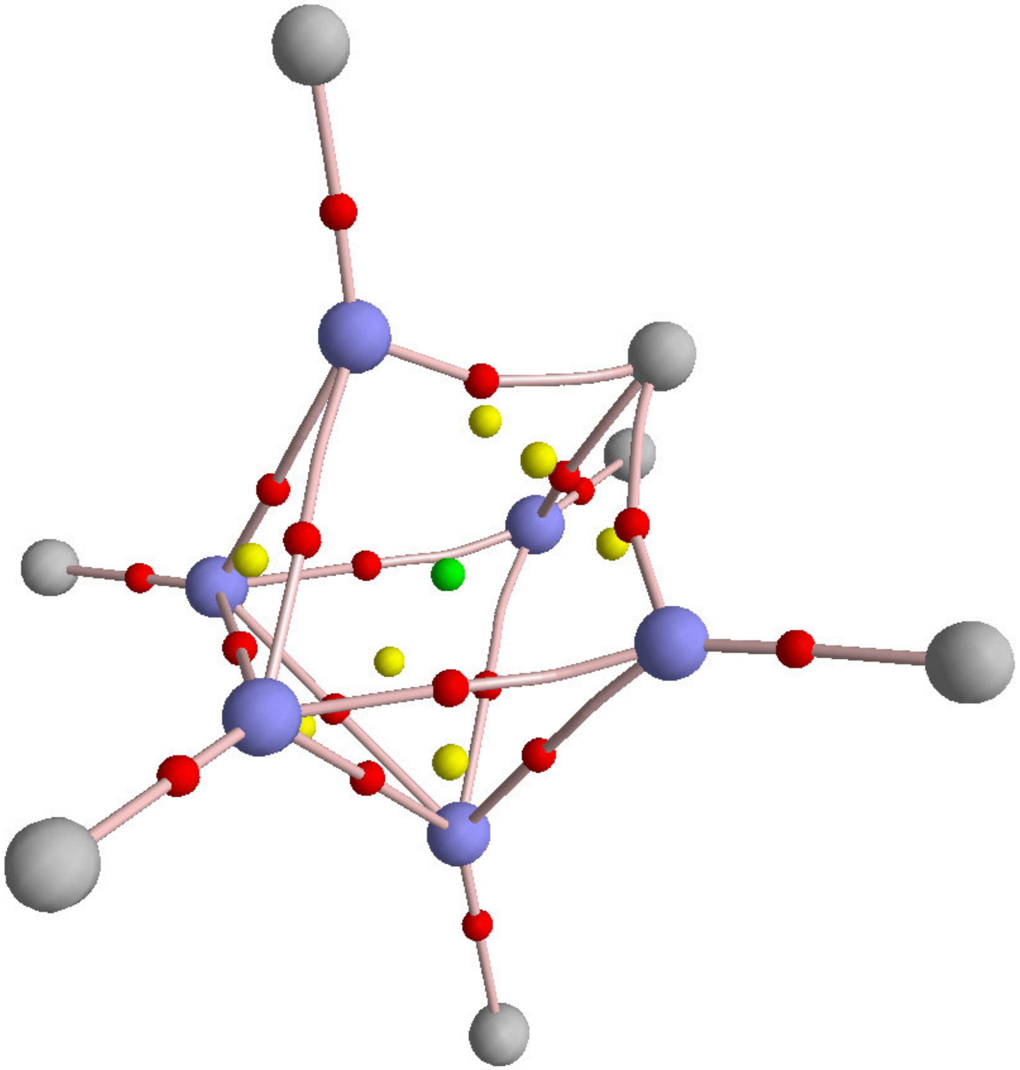
Of especial importance, in terms of chemistry, is the ability to *unambiguously* define a chemical structure from a topological analysis.

Shown here is the QTAIM definition of the structure of the $[B_6H_7]^-$ monoanion. The bcp's are shown in red, the (3,+1) ring cp's in yellow and the (3,+3) cage cp in green

The bond paths link atoms via their associated bcp's, and indicate their is *no direct chemical bonding* along the B-B vectors which are triply bridged by the H atom.

DFT/B3LYP optimised structure of $[B_6H_7]^-$, 6-311G** basis

The Poincaré-Hopf rule



The mathematical connections between the topological objects leads to a simple way of checking whether the obtained topology is self-consistent.

This is the Poincaré-Hopf rule for determining the completeness if the topological space

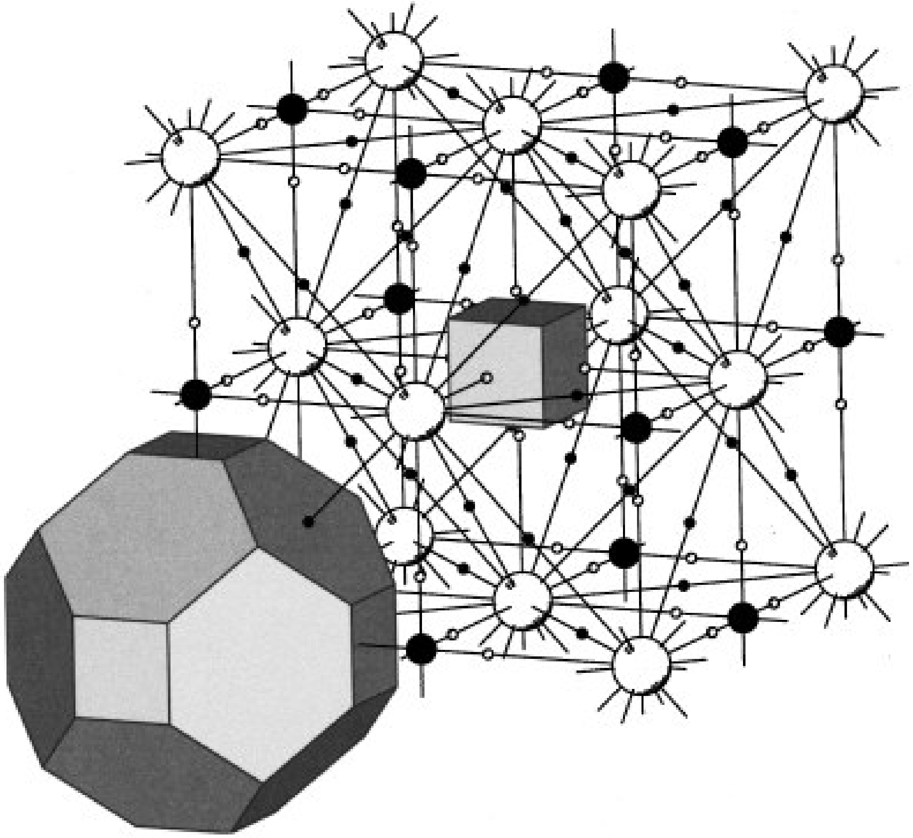
$n - b + r - c = 1$

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

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

DFT/B3LYP optimised structure of $[B_6H_7]^-$, 6-311G** basis

The topology in a crystal



The Poincaré-Hopf rule only applies for molecules in the gas phase.

For periodic crystals, the topology is governed by the Morse relationship

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

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

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

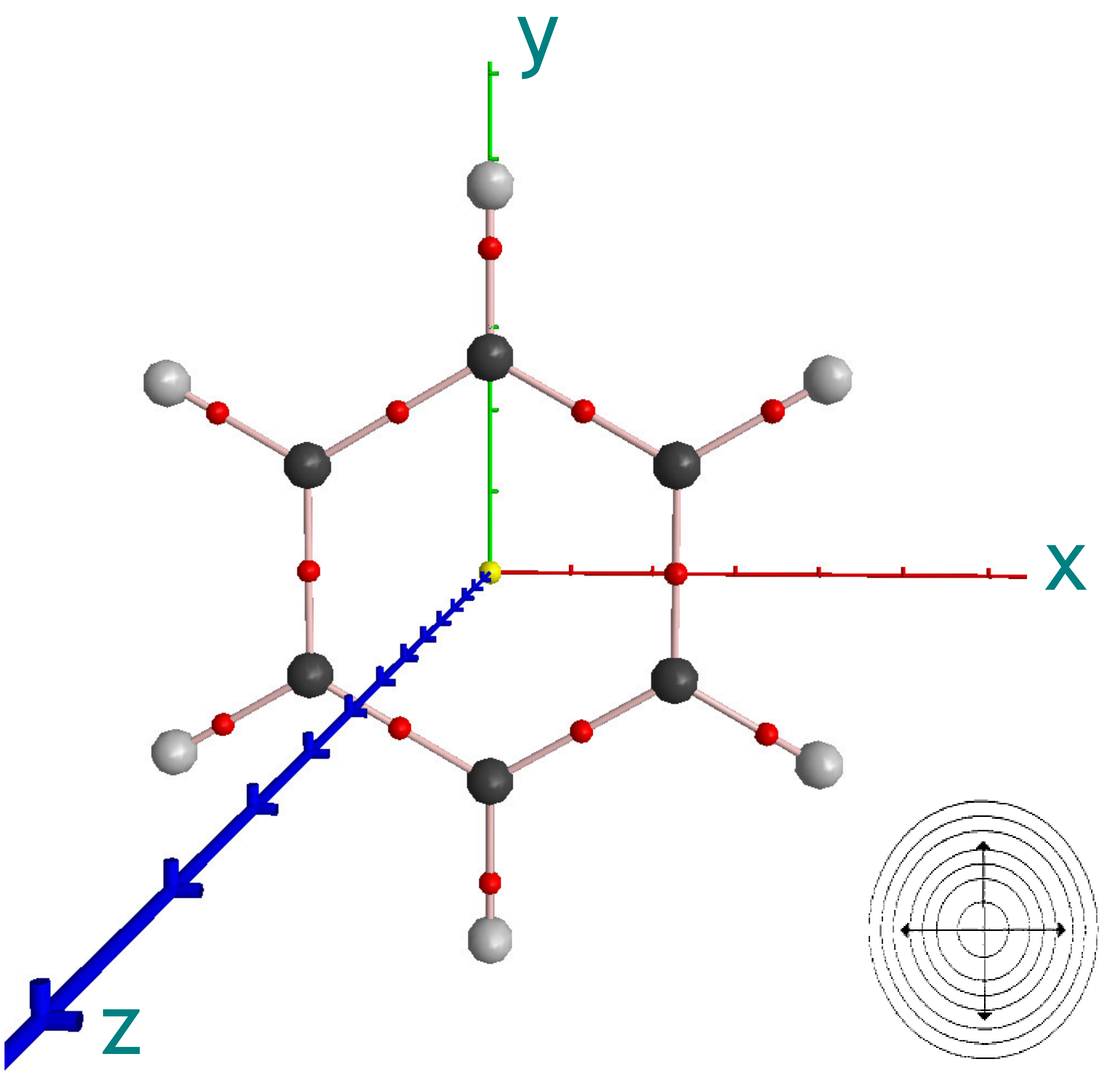
In crystals :

- the atomic basins are finite
- all types of critical points are present
- crystallographic symmetry mandates cp's

Atomic polyhedra of $Li^{+}I^{-}$ space group *F*m-3m

M. Pendás, A. Costales & V. Luaña (1997) *Phys. Rev. B.* **55**, 4275
C. Gatti (2005) *Z. Kristallogr.* **220**, 399.

The ellipticity at the bond critical point



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

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

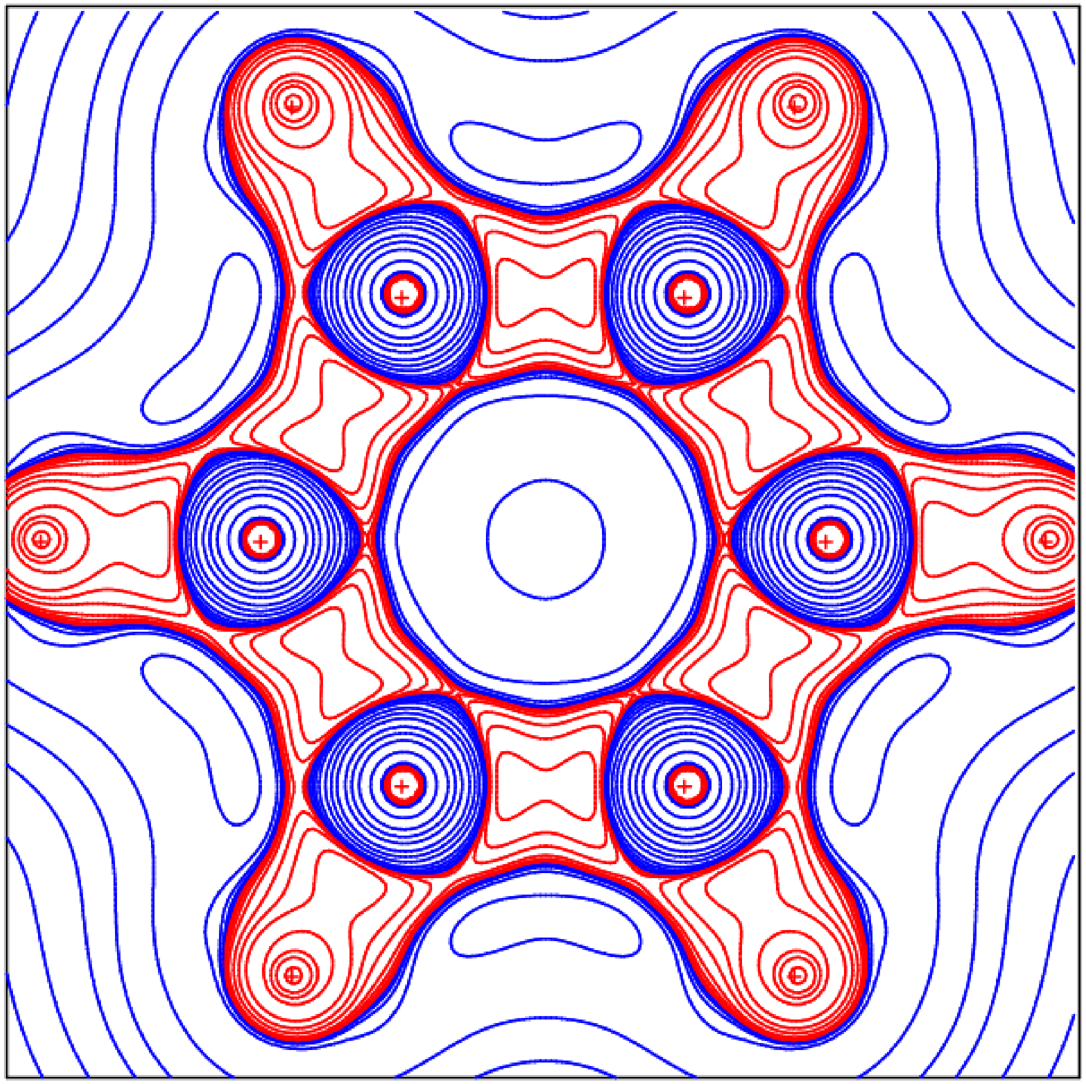
Rho(r)	1.901
Lap(r)	-23.379
Eigenvalues	
λ_1	-18.033
λ_2	-17.728
λ_3	12.382
ε	0.017 (cylindrical)

Units in Å

R.F.W. Bader *et al* (1983) *J. Am. Chem. Soc.* **105**, 5061

DFT/B3LYP optimised structure of benzene , 6-311G** basis

The Laplacian of the charge density



The Laplacian of rho, $\nabla^2(\rho)$, provides a measure of the *local* charge concentration or depletion.

+ve values mean local charge depletion (blue)

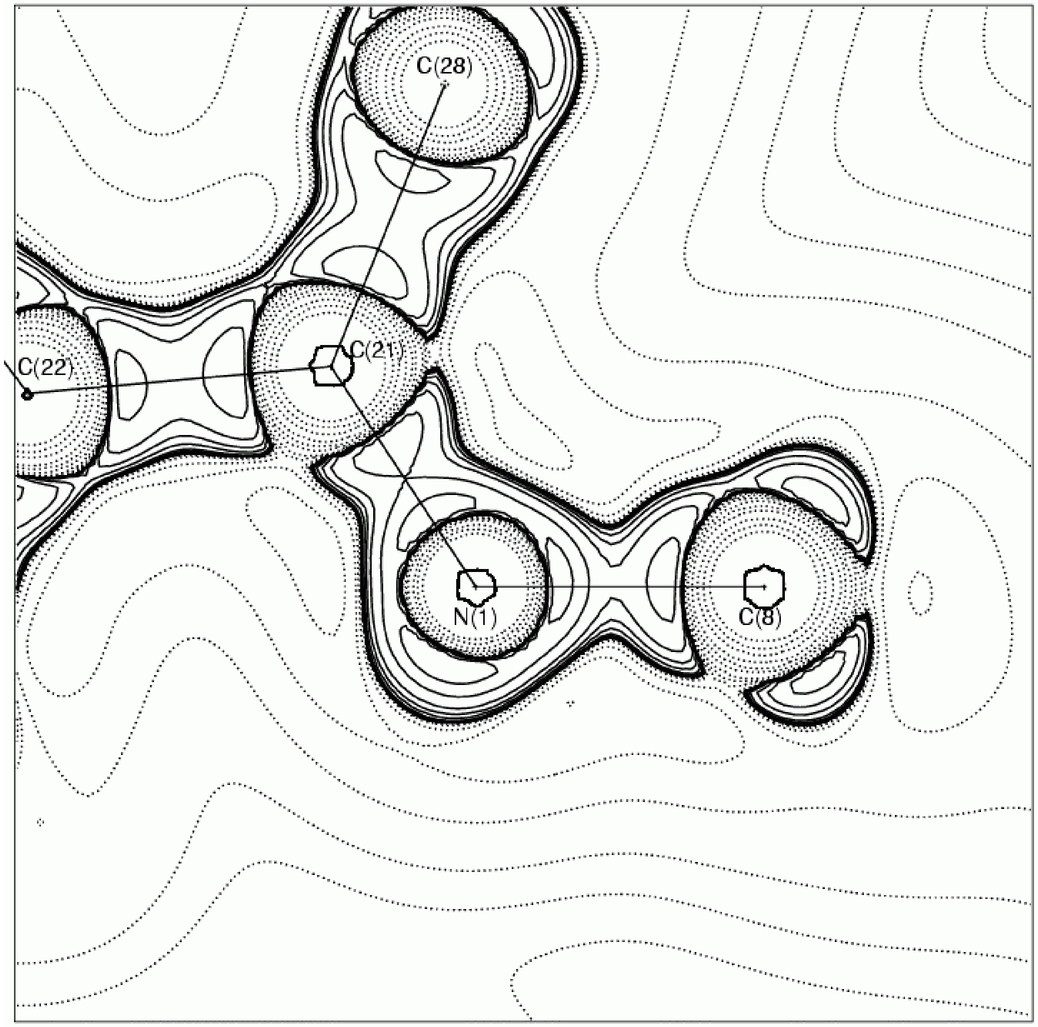
-ve values mean local charge concentration (red)

Often maps of $-\nabla^2(\rho)$, sometimes also called *L*, are drawn, where the +ve contours imply charge concentrations !

Local charge concentration does not imply a maximum.

DFT/B3LYP optimised structure of benzene , 6-311G** basis

The Laplacian of the charge density



Experimental Laplacian in plane of $R_2C{=}NR'$ group

The Laplacian of rho, $\nabla^2(\rho)$, provides a measure of the *local* charge concentration or depletion.

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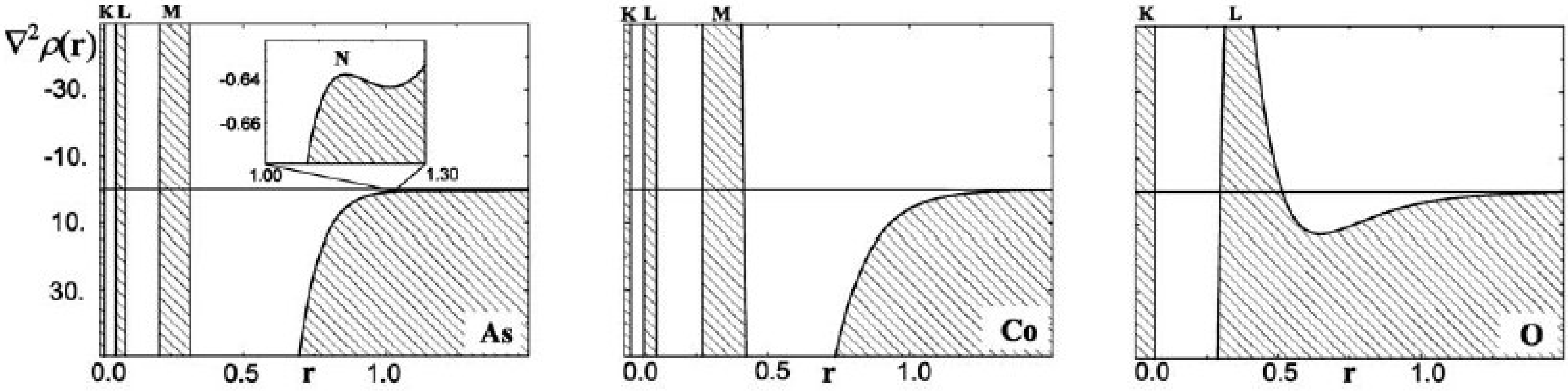
Local charge concentration does not imply a maximum.

The Laplacian of the charge density



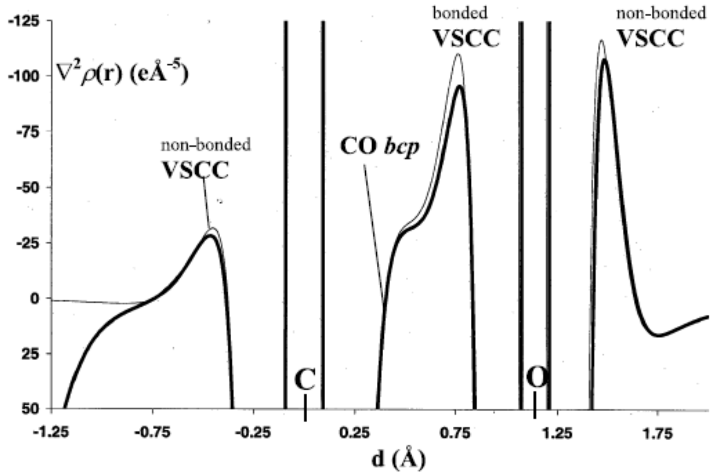


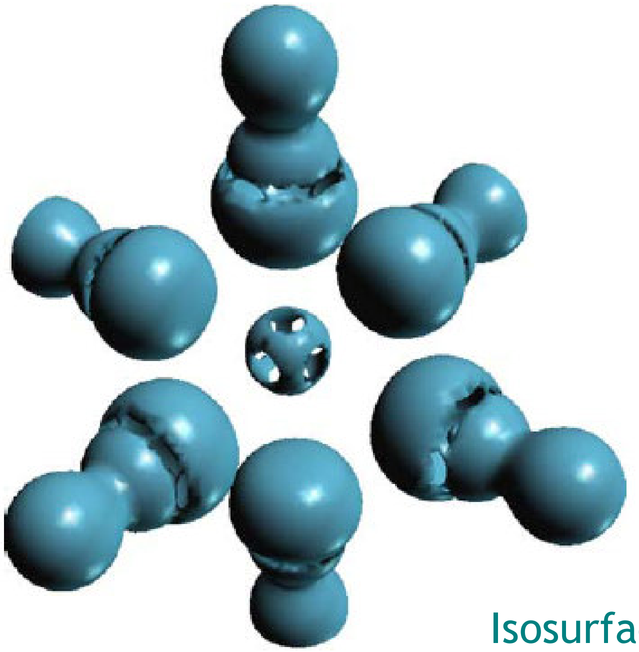
Fig. 2. Profile of the $-\nabla^2\rho(\mathbf{r})$ distribution along the C–O bond path in isolated CO molecule and in $Cr(CO)_6$ (bold line). The two curves are centred on C. Note the small differences along the C–O bond and at the non-bonded VSCC of the carbon atom. The depletion occurring in the $Cr(CO)_6$ molecule is due to the interaction with Cr atom. Units as in Fig. 1.

The Laplacian $\nabla^2(\rho)$ recovers the shell structure of atoms - with the general exception of the transition metals, where the N shell effects are not observed (4*s* density is too diffuse ?) .

The Laplacian allows us to trace the effects of chemical bonding in the total charge density

P. Macchi & A. Sironi (2003) *Coord. Chem. Rev.* **238-239**, 383

The Laplacian of the charge density



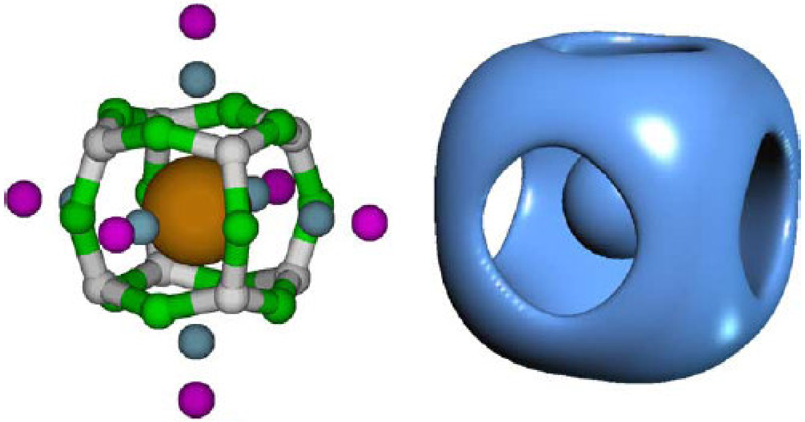
The topology of the Laplacian $\nabla^2(\rho)$, provides a rationalisation for chemical reactivity and formation of complexes.

In this example, the areas of charge depletion on the metal atom are matched by areas of charge concentrations on the carbonyl ligands – the “lock and key” mechanism.

Isosurface at *L* = 0 (encloses charge concentrations)

$Cr(CO)_6$

Atomic graph of Cr atom, i.e. the “net” of critical points in $L(\mathbf{r})$ in the valence shell charge concentration - VSCC



F. Cortes-Guzman & R.F.W. Bader (2005) *Coord. Chem. Rev.* **249**, 633

Topological characterisation of chemical bonds

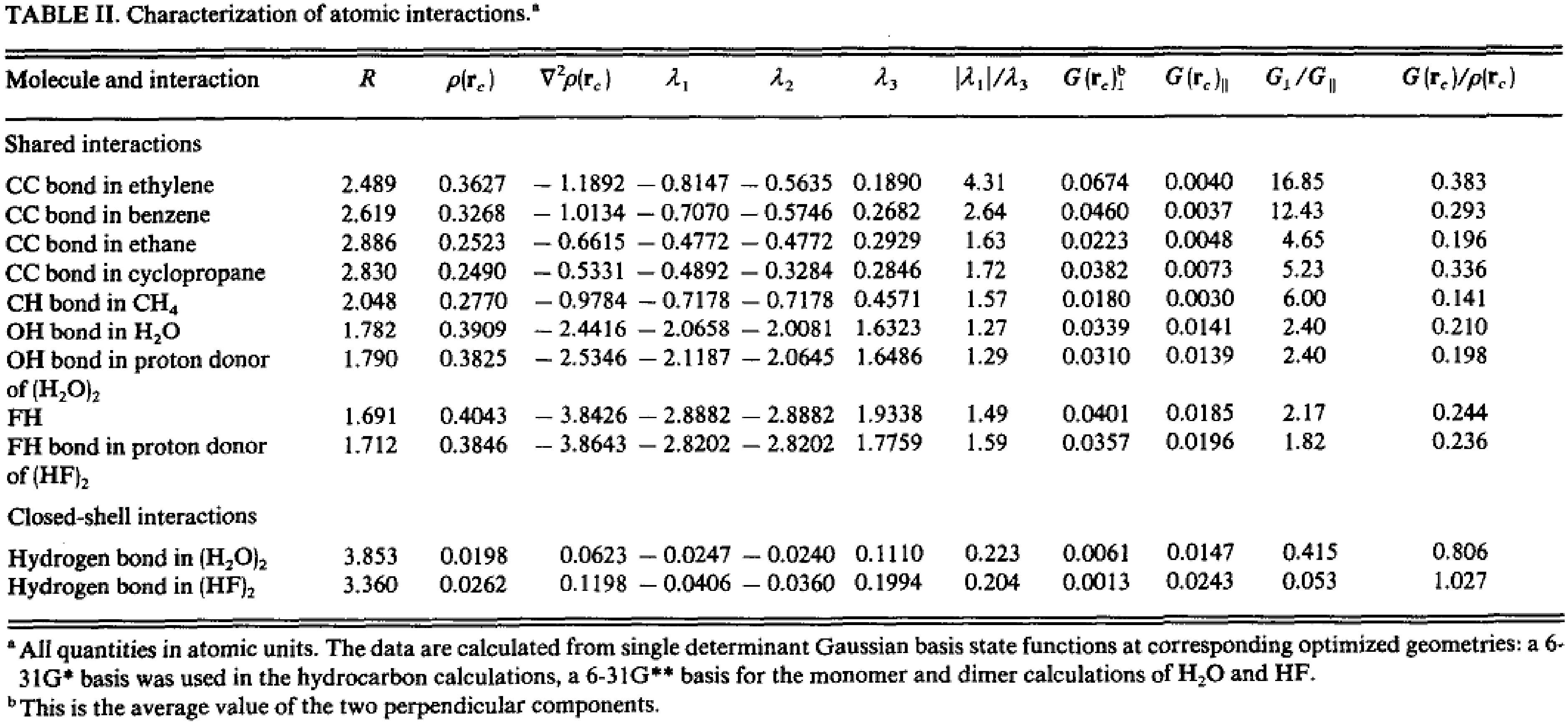


TABLE II. Characterization of atomic interactions.[a]

Molecule and interaction	R	$\rho(\mathbf{r}_c)$	$\nabla^2\rho(\mathbf{r}_c)$	λ_1	λ_2	λ_3	$\lvert\lambda_1\rvert/\lambda_3$	$G(\mathbf{r}_c)_\perp^b$	$G(\mathbf{r}_c)_\parallel$	$G_\perp/G_\parallel$	$G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$
Shared interactions											
CC bond in ethylene	2.489	0.3627	−1.1892	−0.8147	−0.5635	0.1890	4.31	0.0674	0.0040	16.85	0.383
CC bond in benzene	2.619	0.3268	−1.0134	−0.7070	−0.5746	0.2682	2.64	0.0460	0.0037	12.43	0.293
CC bond in ethane	2.886	0.2523	−0.6615	−0.4772	−0.4772	0.2929	1.63	0.0223	0.0048	4.65	0.196
CC bond in cyclopropane	2.830	0.2490	−0.5331	−0.4892	−0.3284	0.2846	1.72	0.0382	0.0073	5.23	0.336
CH bond in CH_4	2.048	0.2770	−0.9784	−0.7178	−0.7178	0.4571	1.57	0.0180	0.0030	6.00	0.141
OH bond in H_2O	1.782	0.3909	−2.4416	−2.0658	−2.0081	1.6323	1.27	0.0339	0.0141	2.40	0.210
OH bond in proton donor of $(H_2O)_2$	1.790	0.3825	−2.5346	−2.1187	−2.0645	1.6486	1.29	0.0310	0.0139	2.40	0.198
FH	1.691	0.4043	−3.8426	−2.8882	−2.8882	1.9338	1.49	0.0401	0.0185	2.17	0.244
FH bond in proton donor of $(HF)_2$	1.712	0.3846	−3.8643	−2.8202	−2.8202	1.7759	1.59	0.0357	0.0196	1.82	0.236
Closed-shell interactions											
Hydrogen bond in $(H_2O)_2$	3.853	0.0198	0.0623	−0.0247	−0.0240	0.1110	0.223	0.0061	0.0147	0.415	0.806
Hydrogen bond in $(HF)_2$	3.360	0.0262	0.1198	−0.0406	−0.0360	0.1994	0.204	0.0013	0.0243	0.053	1.027

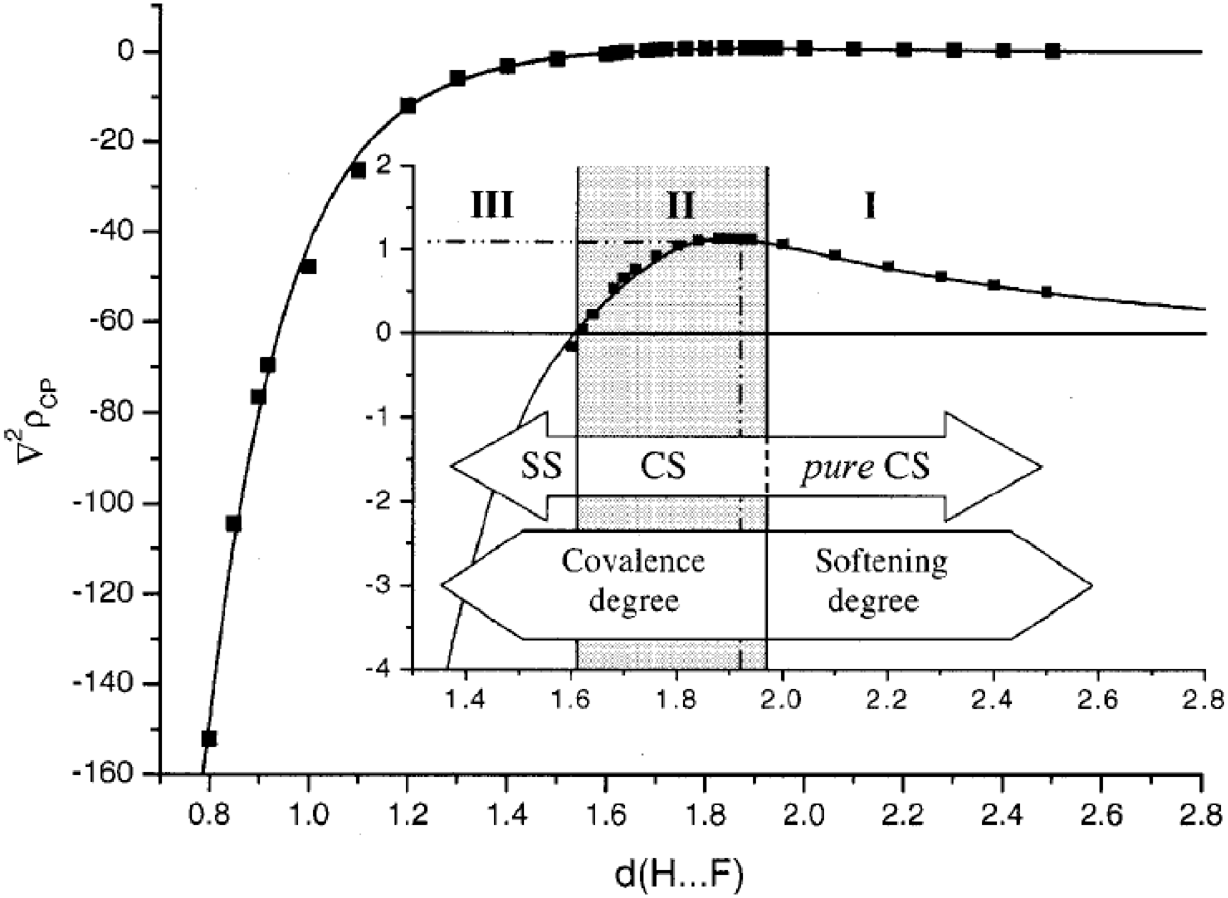
[a] All quantities in atomic units. The data are calculated from single determinant Gaussian basis state functions at corresponding optimized geometries: a 6-31G* basis was used in the hydrocarbon calculations, a 6-31G** basis for the monomer and dimer calculations of H_2O and HF.

[b] This is the average value of the two perpendicular components.

Empirical bond order *n* = exp[*A*(ρ_{bcp}) - *B*], where *A*,*B* are empirical constants
bond-length – e.d. relationships : see also A. Alkorta et al (1998) *Struct. Chem.* **9**, 243 and Tsirelson *et al* (2007) *Acta Cryst* **B63**, 142

R.F.W. Bader & H. Essén (1984) *J. Phys. Chem.* **80**, 1943
D. Cremer & E. Kraka (1984) *Angew, Chemie* **23**, 67

Topological characterisation of chemical bonds



Study on X-H...F-Y interactions- uses the $|V_{bcp}|/G_{bcp}$ indicator
Defines two boundaries I where $|V_{bcp}|/G_{bcp} = 1$ and II where $\nabla^2(\rho) = 0$

E. Espinosa, I Alkorta, J. Elguerdo & E. Molins (2002) *J. Chem.Phys* **117**, 5529

Topological characterisation of chemical bonds

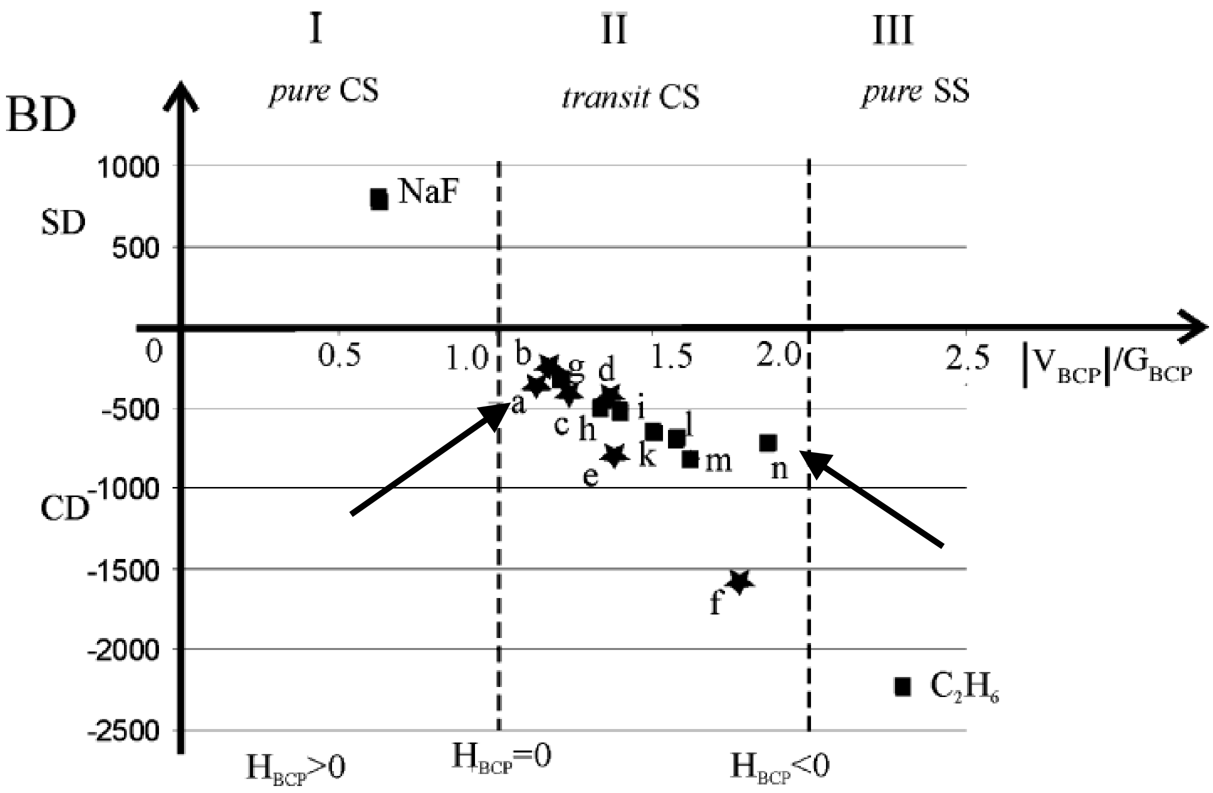


Fig. 2. A square and a star represent, respectively, theoretical and experimental data of the bond degree parameter ($BD = H_{BCP}/\rho_{BCP}$, where the units of H are kJ/mol per atomic unit volume and units of ρ are e. Å^{-3}) as a function of $|V_{BCP}|/G_{BCP}$. Data for the following complexes are reported: (a,n) $Mn_2(CO)_{10}$ [9]; (b,g) $Co_2(CO)_7AsPh_3$ [6]; (c) $Co_4(CO)_{11}PPh_3$ [7]; (d) $Mn_2(CO)_{10}$ [1,2]; (e) $Co_2(CO)_7(C_4H_2O_2)$ [4]; (f) $Co_2(CO)_7(C_4H_2O_2)$ [3]; (h,i,k,l) Ni–In, Ni–Ga, Ni–Ni and Ni–Ni, respectively, in [CpNi{μ-In(SiMe$_3$)$_3$}$_2$NiCp] and [CpNi{μ-GaIn(SiMe$_3$)$_3$}$_2$NiCp] [12]; (m) $(H_2N)TiCo(CO)_3(CO, PH_3)$ [11].

Characterisation of transition metal-metal bonds - $\nabla^2(\rho) < 0$, $H_{bcp} \sim 0$

G. Gervasio, R. Bianchi & D. Marabello (2004) *Chem. Phys. Lett.* 387, 481

Topological characterisation of chemical bonds

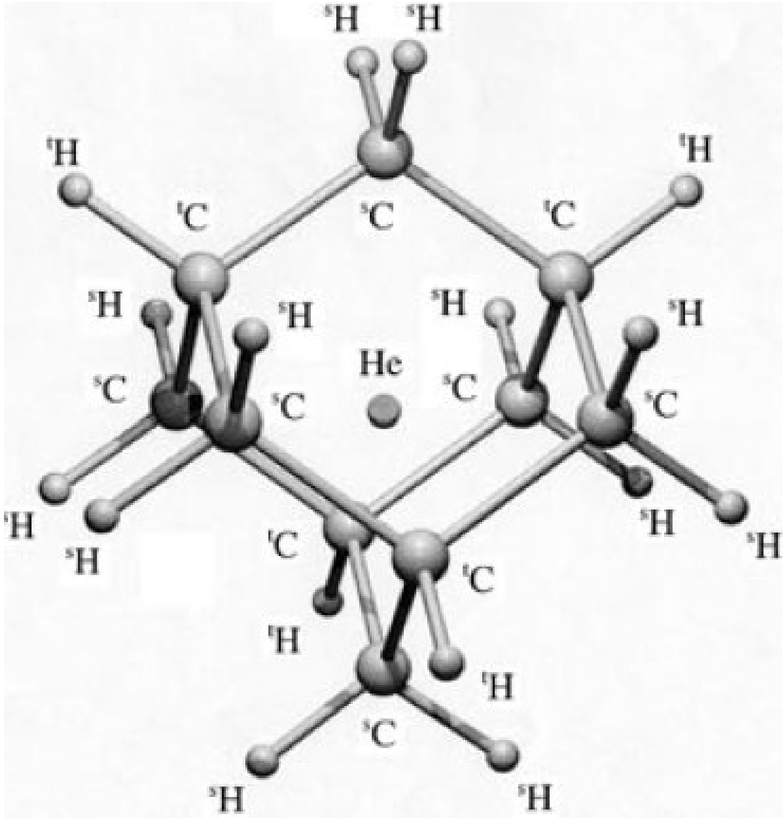
It is important to emphasise that bond paths CANNOT be simply equated with chemical bonds.

"The adoption of the theory of atoms in molecules requires the replacement of the model of structure that imparts an existence to a bond separate from the atoms it links - the ball and stick model or its orbital equivalents of atomic and overlap contributions - with the concept of *bonding* between atoms; two atoms are bonded if they share an interatomic surface and are consequently linked by a bond path."

Topological characterisation of cp's in regions of low e.d. (e.g. in ionic crystals and for transition metal bonds) becomes problematical and even controversial.

R. F. W Bader "A Bond Path – A Universal Indicator of Bonded Interactions" (1998) *J. Phys. Chem. A.* **102**, 7314-7323

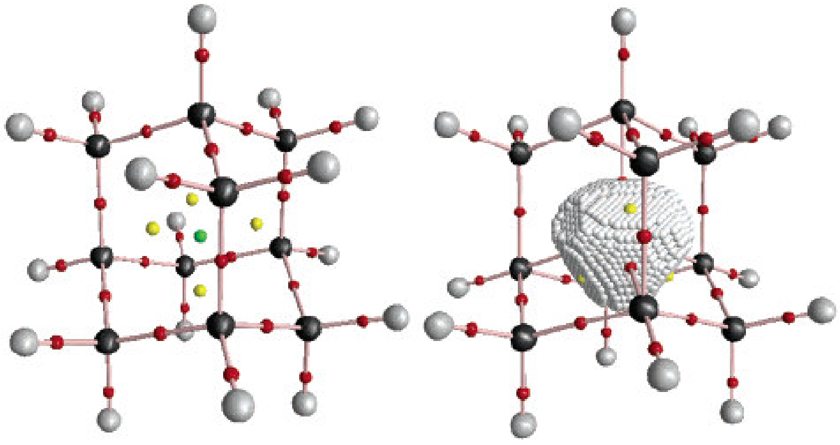
Topological characterisation of chemical bonds



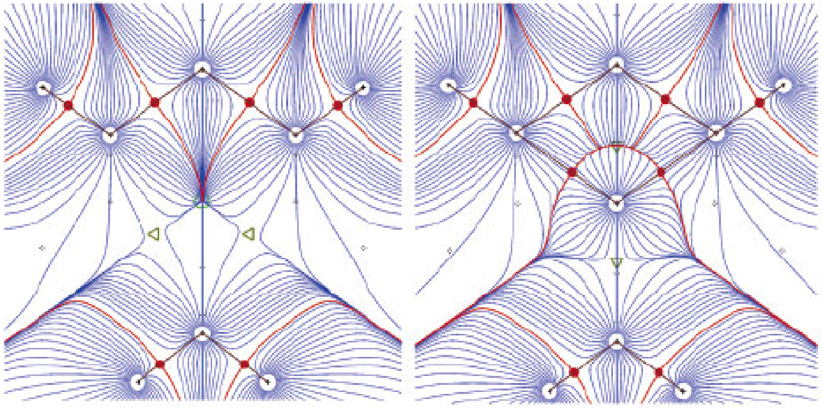
> “Even though the He atom in the inclusion complex He@*adamantane* is connected to the four tertiary C atoms through atomic interaction lines with (3,-1) critical points, the He···^{t}C interactions are in fact strongly *antibonding*. This means that the conjecture that an AIL between two atoms in an equilibrium structure implies the presence of a chemical bond between them is *not valid*.”

A. Haaland *et al* “Topological Analysis of Electron Densities: Is the Presence of an Atomic Interaction Line in an Equilibrium Geometry a Sufficient Condition for the Existence of a Chemical Bond?” (2004) *Chem. Eur J.* **10**, 4416-4421

Topological characterisation of chemical bonds



(a) adamantane (b) He@adam

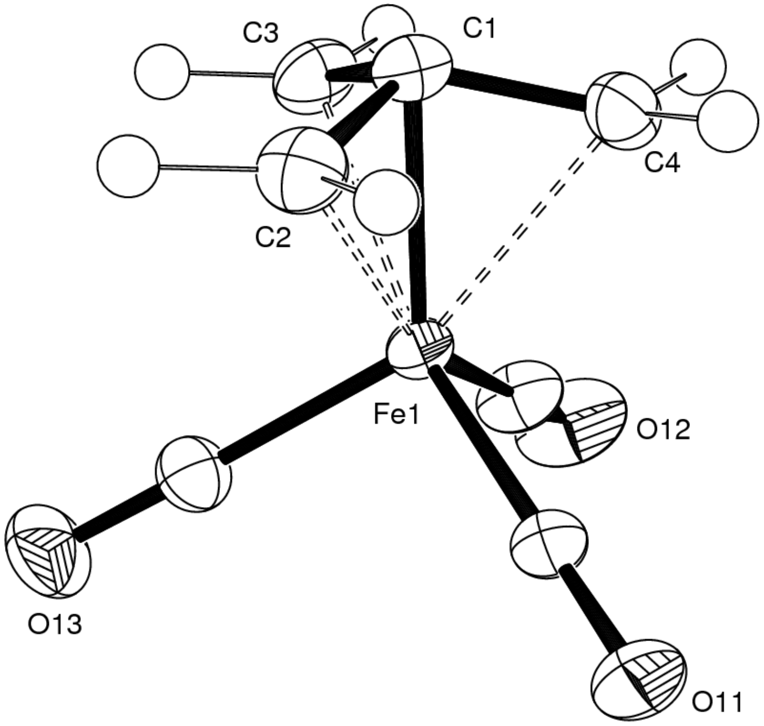


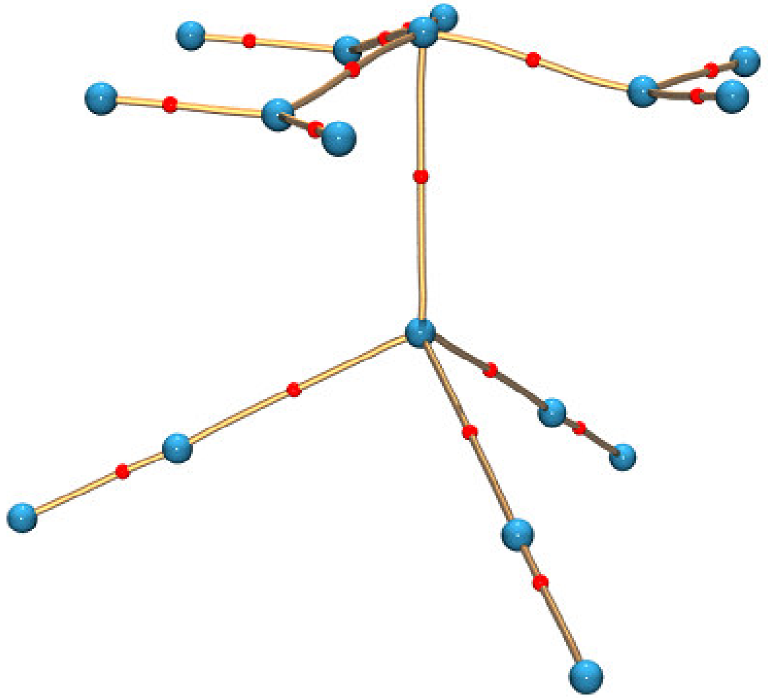
(c) adamantane (d)He@adam

“The presence of … atoms linked by a bond path implies not only the absence of repulsive Feynman forces on the nuclei but also the presence of attractive Ehrenfest forces acting across the interatomic surface shared by the bonded atoms.”

R. F. W Bader & D. E. Fang “Properties of Atoms in Molecules: Caged Atoms and the Ehrenfest Force” (2005) *J. Chem. Theory Comput* **1**, 403-414

Topological characterisation of chemical bonds





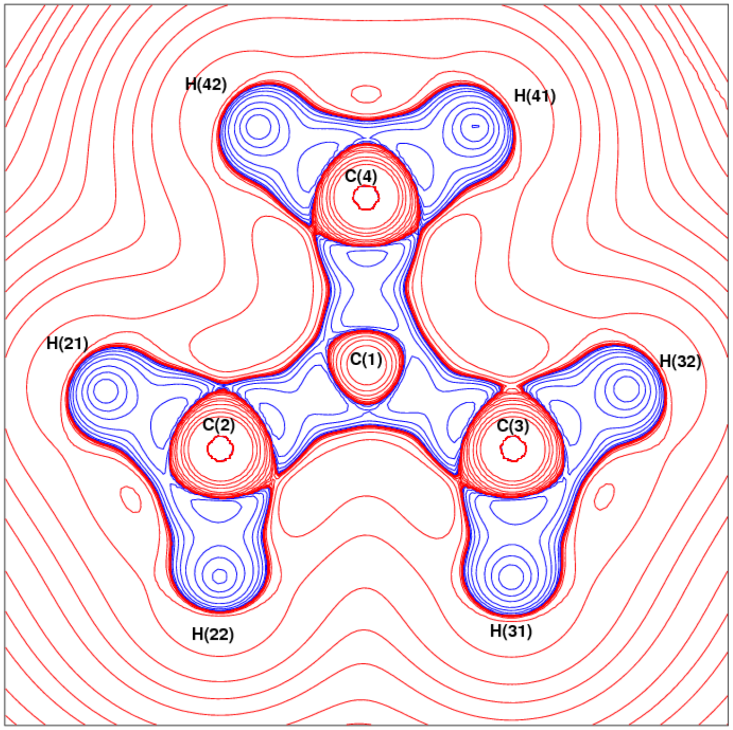
Fe(1)-C(1) = 1.9449(2) C(1)-C(2)=1.4294(3)
Fe(1)-C(2) = 2.1237(2) C(1)-C(3)=1.4288(3)
Fe(1)-C(3) = 2.1326(3) C(1)-C(4)=1.4304(3)
Fe(1)-C(4) = 2.1343(3)
av Fe-C(O) = 1.7983(3)

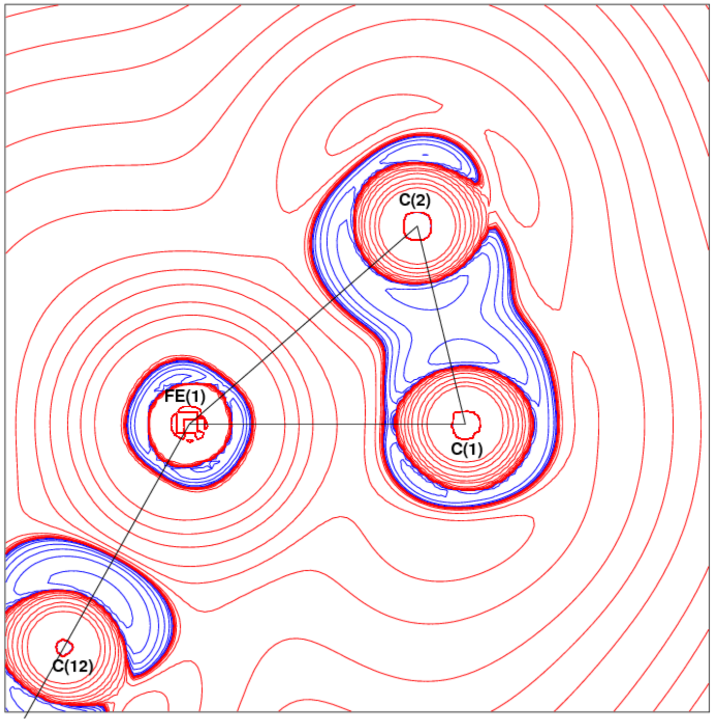
No bond path observed between Fe-C_β

Independent of level of theory
Independent of multipole model

C. Evans, L. J. Farrugia, M, Tegel (2006) *J. Phys Chem A* **110**, 7952-7961

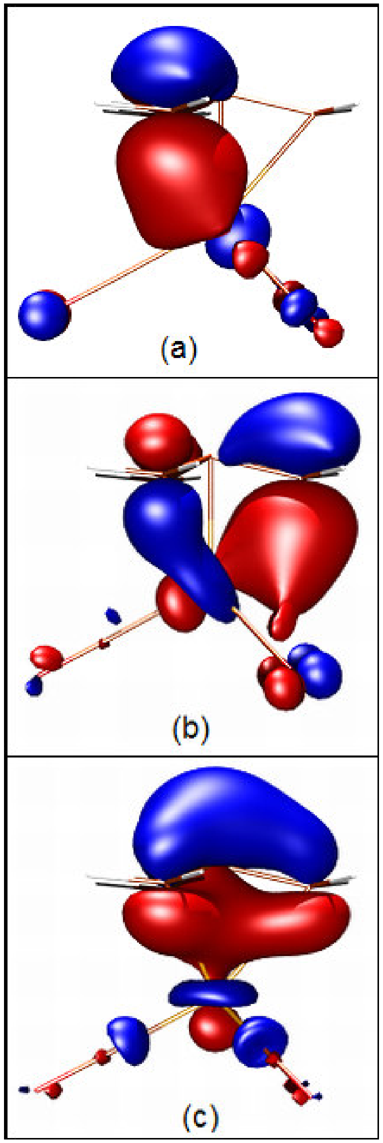
Topological characterisation of chemical bonds





C. Evans, L. J. Farrugia, M, Tegel (2006) *J. Phys Chem A* **110**, 7952-7961

Topological characterisation of chemical bonds



A normal mode analysis of the vibrational spectrum indicates that the ν(Fe-TMM) stretch has a large force constant of 3.7 mdyn/Å. Conclude that a model with a single bond from Fe to C_α is inadequate, and that significant π-interactions with the C-C bonds occurs.

DH Finseth et al (1976) *J Phys Chem* **80**, 1248-1261

The NMR barrier to rotation of the TMM ligand is generally found to be quite high, again indicative of significant Fe π-interactions

MD Jones & RDW Kemmitt (1987) *Adv Organomet Chem* **27**, 279-309

An MO analysis of the DFT wavefunction agrees with the qualitative Hoffmann EHMO scheme. The frontier orbitals primarily responsible for the Fe-TMM bonding (15*e* and 16a_1) imply significant Fe-C_β interactions.

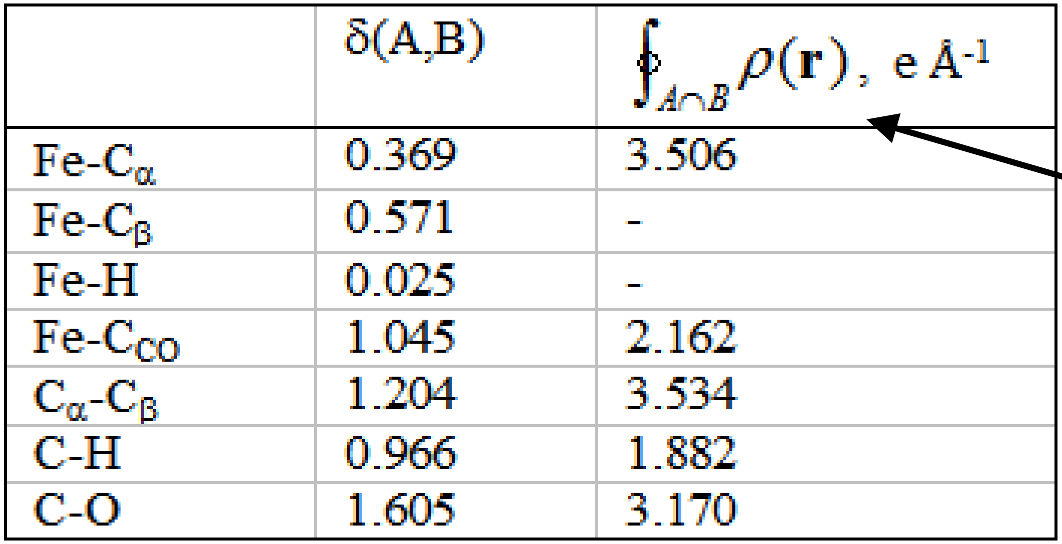
R. Hoffmann (1977) *J. Am. Chem. Soc.* **99**, 7546-7557.

C. Evans, L. J. Farrugia, M, Tegel (2006) *J. Phys Chem A* **110**, 7952-7961

Topological characterisation of chemical bonds

Delocalisation indices from DFT wavefunction

Delocalisation indices provide a measure of the total Fermi correlation shared between atoms, *i.e.* number of shared pairs.



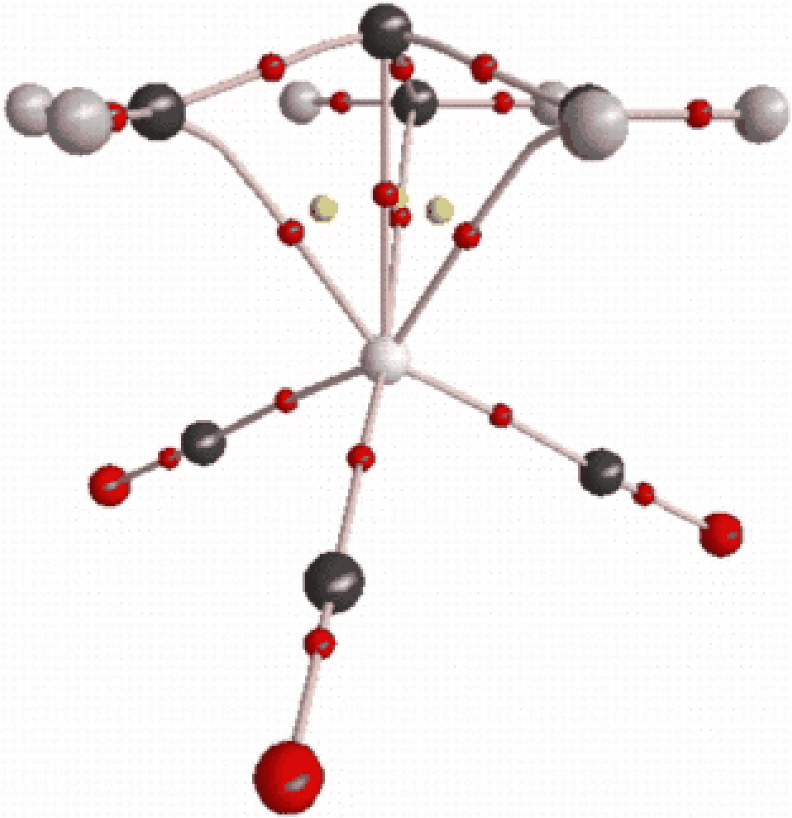
	δ(A,B)	$\oint_{A\cap B}\rho(\mathbf{r})$, e Å^{-1}
Fe-C_α	0.369	3.506
Fe-C_β	0.571	-
Fe-H	0.025	-
Fe-C_{CO}	1.045	2.162
C_α-C_β	1.204	3.534
C-H	0.966	1.882
C-O	1.605	3.170

Integrated charge over the common interatomic surfaces of A and B

Σ δ(Fe-C) = 2.082 ≡ ~ 2 pairs of e^- shared between ring and Fe

R.F.W. Bader & M. E. Stephens (1975) *J. Am. Chem Soc*. **97**, 7391-7399
X. Fradera et al (1999) *J. Phys. Chem. A* **103**, 304-314

Topological characterisation of chemical bonds



$\rho(r)$ eÅ^{-3}
bcp 0.662
rcp 0.655

	δ(A,B) - equil	δ(A,B) – 72 °
Fe-C_α	0.369	0.351
Fe-C_β	0.571	0.609
Fe-C_{CO}	1.045	1.026
C_α-C_β	1.204	1.191
C-H	0.966	0.959
C-O	1.605	1.600

The average MDA of C_β in the direction of Fe is 0.12 Å, from thermal parameters at 100K