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

3 AUTHORS:

Cina Foroutan-Nejad
Masaryk University
29 PUBLICATIONS   243 CITATIONS

SEE PROFILE

Shant Shahbazian
Shahid Beheshti University
52 PUBLICATIONS   563 CITATIONS

SEE PROFILE

Radek Marek
Masaryk University
126 PUBLICATIONS   1,728 CITATIONS

SEE PROFILE

Toward a consistent interpretation of the QTAIM: Tortuous link between chemical bonds, interactions and bond/line paths

Cina Foroutan-Nejad[1], Shant Shahbazian[2*], Radek Marek[1,3]

1. National Center for Biomolecular Research, Faculty of Science, Masaryk University, Kamenice 5/A4, CZ–62500 Brno, Czech Republic; Tel: 776 535 233.

2. Faculty of Chemistry, Shahid Beheshti University, G. C. , Evin, Tehran, Iran, 19839, P.O. Box 19395-4716.

3. CEITEC – Central European Institute of Technology, Masaryk University, Kamenice 5/A4, CZ–62500 Brno, Czech Republic

* Correspondence should be addressed to chemist_shant@yahoo.com

Abstract

Currently, bonding analysis of molecules based on the Quantum Theory of Atoms in Molecules (QTAIM) is popular; however, "misinterpretations" of the QTAIM analysis are also very frequent. In this contribution the chemical relevance of the bond path as one of the key topological entities emerging from the QTAIM's topological analysis of the one-electron density is reconsidered. The role of nuclear vibrations on the topological analysis is investigated demonstrating that the bond paths are not indicators of chemical bonds. Also, it is argued that the detection of the bond paths is not necessary for the "interaction" to be present between two atoms in a molecule. The conceptual disentanglement of chemical bonds/interactions from the bonds paths, which are alternatively termed "line paths" in this contribution, dismisses many superficial inconsistencies. Such inconsistencies emerge from the presence/absence of the line paths in places of a molecule where chemical intuition or alternative bonding analysis does not support the presence/absence of a chemical bond. Moreover, computational QTAIM studies have been preformed on some "problematic" molecules, which were considered previously by other authors, and the role of nuclear vibrations on presence/absence of the line paths is studied demonstrating that a bonding pattern consistent with other theoretical schemes appears after a careful QTAIM analysis and a novel "interpretation" of data is performed.

Keywords: Quantum theory of atoms in molecules; bond paths; chemical bond

Stating the problem

Advanced theories in physics and chemistry are usually composed of two aspects: a mathematical structure/formalism disclosing the basic entities of the theory and their mathematical relationships, and an "interpretative" recipe of basic entities of the theory. The latter discloses the qualitative meaning of the basic entities and their relation to other known entities within and beyond the theory. The connection between the mathematical formalism of a theory and its interpretation is always subtle. This is best illustrated in the case of the quantum mechanics. Although, almost all physicists agree on its formalism, after ninety years from its emergence, large numbers of interpretations have been flourished that each introduces a new "meaning" for the "mathematical symbols/entities" of the theory [1]. The quantum mechanics is the best example demonstrating the fact that generally, formalism does not in itself impose an interpretation. In other words, formalism may be compatible/coexist with a number of interpretations. In contrast to this relative autonomy of formalism and interpretation, an acceptable interpretation of a theory must be "self-consistent", free from "contradictions". A proposed meaning for an entity cannot lead to conclusions that challenge the meaning of other entities of a theory.

The Quantum Theory of Atoms in Molecules (QTAIM) [2-4] is also composed of a mathematical formalism and a "chemical interpretation" that introduces the glue linking the formalism and chemical concepts previously defined in the chemical discourse. The ignorance of making a distinction between the formalism and the interpretation has been one of the matters behind the most misunderstandings and controversies around the

QTAIM and its chemical applications. Indeed, this difference has not always been clearly stressed and disclosed in the original literature of the QTAIM. The methodology of recognizing chemical bonds within the context of the QTAIM is one of such "interpretative" problems, which is scrutinized in this report. Particularly, the premise of equivalence between chemical bonds and the bond paths (BPs) (vide infra) is one of these "misinterpretations" that is criticized in detail.

In view of these interpretative problems, the ingredients of a recently proposed interpretation [5] are discussed and scrutinized in this report in a more detail. First, it is demonstrated that the detection of the BPs between two atoms in a molecule, emerging from natural alignment of the gradient vector field of the one-electron density of a molecule [2-4], is neither necessary nor sufficient condition for the presence of a chemical bond between those atoms. Accordingly, the conceptual "disentanglement" of chemical bonds and bond paths not only resolves many misinterpretations regarding the applications of the QTAIM, but also reveals a clear need for a fresh viewpoint regarding the nature of interactions of atoms in molecules (AIMs) as is discussed in subsequent sections. It is important to emphasize that this disentanglement has been somehow mentioned previously, though sometimes just implicitly, by some researchers in various contexts (there is an extensive literature on this subject but for some discussions see [6-12]). However, in contrast to the previous discussions, our line of reasoning in this paper is solely based on the formalism of the orthodox QTAIM itself. What is particularly emphasized is the fact that the assumed equivalence between chemical bonds and BPs does not lead to a legitimate ingredient of a consistent interpretation of the QTAIM formalism. The relation of BPs to weak interactions between AIMs, usually termed non-

bonded interactions, are also addressed briefly with an emphasis on the point that like in the case of chemical bonds, BPs do not directly recognize interacting AIMs. Therefore, it is argued that energetic criterion is needed for a transparent description of the nature of weakly interacting AIMs. Rather than claiming for "the" final interpretation, one may hope that the proposed "reinterpretation" in this paper, paves the way towards "a" consistent interpretation.

The paper is organized as follows: in the subsequent section it is argued, solely based on the fabric of the topological analysis, that a number of molecular graphs (MGs) are associated with given local minimum structures. Thus, the tacit assumption that there is a one-to-one relation between each molecule in local minimum and its MG, derived at the equilibrium geometry, is not generally compatible with the formalism of the QTAIM. The implications of this observation on the chemical interpretation of the QTAIM are emphasized. In the next section, computational examples are considered demonstrating the importance of the molecular vibrations in materializing molecules with Multiple-MGs (M-MGs) status. It is demonstrated that in several molecules certain BPs appear and disappear during molecular vibrations. Also, it is shown that not all AIMs with significant interactions are linked with BPs. Finally, in the last two sections it is argued that the connection between chemical bonds and the concepts introduced within the context of QTAIM is not straightforward, calling for new theoretical tools yet to be invented or developed further. It is important to emphasize there is an extensive literature on the chemical applications of the QTAIM and just a handful of them are cited in the reference list that are of primary importance to the purpose of this report.

Molecular graphs and bond paths: Dynamic versus static viewpoint and its chemical implications

The distribution of electron density of a molecule parametrically depends on the nuclear geometry, thus the result of the relevant topological analysis of the gradient of the one-electron density also depends on the chosen geometry [2-4]. The theoretical framework of the topological analysis dictates that "continuous" changes of the geometrical parameters are accomplished with sudden, "discontinuous", appearance/disappearance of the critical points (CPs) accompanying the variations of MGs. Accordingly, in a systematic topological analysis of water molecule at various geometries (in its electronic ground state), as a classic example, one observes various distinct MGs and concomitant BPs (see subsection 3.2.1 in [2]). Even in simple diatomics, systematic survey of various inter-nuclear distances reveals a general pattern that upon contraction of inter-nuclear distances, non-nuclear attractors always emerge demonstrating that to each diatomic, two (sometime even more) MGs are associated [13,14]. Such usually small inter-nuclear distances and concomitant MGs are typically accessible only upon using extreme hydrostatic pressures confirming unambiguously the "dynamic" nature of MGs in diatomics, i.e. appearance/disappearance of non-nuclear attractors [15]. These observations tacitly imply that molecular vibrations may also trigger geometrical variations, upon contraction/extension of inter-nuclear distances, yielding novel MGs distinct from that of the equilibrium geometry.

In contrast to these observations and their implications, most computational QTAIM studies are usually restricted to the equilibrium geometries implicitly assuming that the amplitudes of the nuclear vibrations do not usually suffice to vary the MGs

observed at these geometries. Accordingly, attributing a single MG, just computed at the equilibrium geometry, to each local-minimum structure is commonplace. Notwithstanding, there is no reason to believe that this assumption is universally valid and in the subsequent section specific examples are given demonstrating the contrary. Based on the theory of molecular vibrations [16], every local minimum is "surrounded" by a set of accessible non-equilibrium geometries and their topological analysis may reveal more than a single MG. As the nuclear vibrational dynamics may alter the MG of the equilibrium geometry, yielding novel MGs at some non-equilibrium geometries, one is faced with a "dynamic" viewpoint of MGs against the usual "static" single MG viewpoint. However, before proceeding to the case studies describing real examples it is legitimate to discuss chemical implications of the presence of such M-MGs molecules.

Let's assume that there are two or more MGs each associated with a subset of accessible geometries; for such molecule, the MG of the equilibrium geometry is just one accessible MG. Roughly speaking, this situation is similar to the case of resonance structures used to represent the electronic structure. However, in contrast to the resonance hybrid, no "mean"/hybrid MG is introduced within the context of the QTAIM and one is faced with M-MGs case. A question may naturally arise that what will happen to BPs of these M-MGs cases? Obviously, since MGs are different at various geometries, some BPs must disappear in some MGs while appearing in others. Coming back to the originally stated problem, assuming the equivalence of chemical bonds and BPs, an unpleasant situation is emerging upon the molecular vibrations: chemical bonds are appearing and disappearing without any "external" influences. This is in sharp contrast with the classic chemical discourse assuming that chemical bonds are formed and

disrupted in chemical reactions whereas nuclear vibrations and internal rotations are just part of the "internal" dynamics of a molecule. Clearly, insisting on the equivalence between chemical bonds and BPs does not lead to a "consistent" picture since one must propose quite unnaturally that nuclear vibrations are capable of triggering the formation or disruption of chemical bonds. Alternatively, one may propose that solely the MG of the equilibrium geometry have to be used for bonding analysis of a molecule which is completely unjustified as well. Particularly, ignoring the internal dynamics is not legitimate since recently the nuclear vibrational dynamics has been incorporated explicitly within the context of the newly developed multi-component QTAIM [17-22]. Thus, it is safe to conclude unequivocally that BPs are not chemical bonds [23]. The fact that BPs are usually observed between the AIMs that are chemically bonded does not invalidate this conclusion but it merely demonstrates that in most but not all cases chemically bonded AIMs are linked by BPs [24]. Accordingly, using the terminology used by Farrugia and coworkers [25], observing Chemical Bonds without "Chemical Bonding", namely, finding chemical bonds between AIMs that are not linked by BPs, is not genuinely surprising and certainly not against the basic formalism of the QTAIM. Indeed, the theory of electron localization/delocalization within/between AIMs clearly demonstrates that the AIMs, which are not linked by BPs, are also "communicating" (exchanging electrons) and in certain cases these communications are not damped regularly with the separation distance [26-38] (see particularly the case of the para carbon atomic basins in benzene [28,38]). The localization/delocalization indices are deduced from the second-order reduced density matrices, as the carriers of the two-electron correlation information [39,40]. So, there is no reason, at least not in the mathematical

fabric of the QTAIM, to believe that the "lower order" one-electron density function and its topological characteristics, e.g. BPs, are the only means to be used to deduce the nature of the interactions between AIMs [41]. Of course the reverse is also true and there are cases when two AIMs are linked by BPs, but are neither appreciably exchanging electrons nor participating in stabilizing electrostatic interactions - the neutral van der Waals complexes and hydrocarbon contacts in crystals provide excellent examples [42,43]. Therefore, using terms like "missed" or "expected" BPs, inferred from chemical intuition, are just portraying a misunderstanding regarding the role of BPs within the context of the QTAIM. More generally, one may conclude that the QTAIM has its own jargon, while emerging entities, e.g. BPs, have not generally a one-to-one relation with chemical concepts, e.g. chemical bonds, introduced within classic chemical discourse. Accordingly, one may go one step further and stress that MGs are also not chemical/molecular structures since BPs are not chemical bonds. Once again this conclusion does not oppose the fact that in many molecules MGs are topologically equivalent to the molecular structures [24] but it disapproves the notion of "universal" equivalence between MGs and the chemical structures. The variations of MGs upon nuclear vibrations demonstrate that no such universal claim is acceptable as it would imply that chemical structures are varied without external effects/forces just by nuclear vibrations.

Since the terminology related to the word "bond" may be a source of confusions in the QTAIM's interpretation, in the rest of this paper the word "line" is used instead, in agreement with the usage of the words "ring" and "cage", emphasizing the geometrical nature rather than the chemical relevance. Accordingly, bond critical points (BCPs) are

called "line critical points" (LCPs) while BPs are called "line paths" (LPs) (beyond equilibrium geometries, the phrase "atomic interaction lines" are used instead of BPs [2-4], however, in this report no distinction is being made between topological entities at equilibrium and non-equilibrium geometries thus, LPs are used regardless of the nature of given geometry). Furthermore, instead of the phrase "bonded atoms", denoting two AIMs sharing an inter-atomic surface, they are just called "neighbors" while the phrase "passionate neighbors" is used for AIMs with an inter-atomic surface appearing and disappearing during the nuclear vibrations [5].

Let's also briefly mention and discard immediately an alternative "chemical interpretation" of LPs, scattered in literature, which assumes the presence of LPs denotes that the corresponding AIMs are "interacting". At first glance, this is seemingly a weaker claim compared to the previous discussion since it replaces chemical bond between AIMs, icon of strong interaction, with interacting AIMs that do not need to be strongly affecting each other. Apart from all previously discussed obstacles, a new inconvenience emerges as in the theory of intermolecular forces, each of two atoms in a molecule/complex, regardless of their interatomic distance, are interacting at least through long-range London type forces [44]. Therefore, restricting the interaction of AIMs just to the neighbors is quite artificial and one may further declare that LPs are not denoting "interacting AIMs" though it is probable, but not inevitable, in general that each atom in a molecule interacts, be it stabilizing or destabilizing, more strongly with its neighbors rather than distant atoms. All in all, the mutual interactions of AIMs are inevitably tied to the energetic aspects of the analysis of chemical bonds that are discussed in the last two sections in more detail.

Multiple-MGs versus single-MG molecules

Tthe exotic $B_6C^{(-2)}$ has been demonstrated to be an interesting M-MGs example with extremely flat electron density between the peripheral borons and the central carbon basins [45-47]. In this molecule a large number of MGs are accessible even through the zero-point vibrations that are operative at the absolute zero temperature [46]. Although this single example of a topologically floppy molecule suffices to dismiss the universal validity of the single-MG paradigm, the peculiarity of this illusive species may obscure the main reasoning behind the M-MGs paradigm. However, examples considered in this section are typical molecules, which have been analyzed previously by other researchers, thus casting no doubt on the importance of M-MGs paradigm and its implications on the consistent interpretation of the QTAIM. For brevity, the details of all used computational levels (method/basis set), employed computational packages as well as related references are found in the Supporting information. However, the strategy used to prepare non-equilibrium geometries are disclosed in detail.

Every molecule experiences non-equilibrium geometries because of the eternal nuclear vibrations; in polyatomic molecules these vibrations are described by the normal modes [16]. In order to generate non-equilibrium geometries for our topological analysis, we surveyed the vibrational spectrum of each molecule seeking for large-amplitude and low-frequency normal modes with small force constants ($f < 0.7$ mDyn.Å^{-1}). Then, a set of "testing" non-equilibrium geometries were generated along each normal mode. Only those members of the testing set were used for topological analysis whose energy difference to the total energy of the equilibrium geometry was at most equal to the energy of the first excited vibrational state of the corresponding normal mode, which is

populated significantly at room temperature. The molecules revealing altered MGs at some of their non-equilibrium geometries, differing from that of the equilibrium geometry were classified as M-MGs. On the contrary, if nuclear vibrations did not alter MG of the equilibrium geometry, the molecule was classified as single-MG. However, for such cases the search was expanded seeking for higher energy non-equilibrium geometries containing novel MGs though they are not accessible at room temperature. In reality each nucleus has a complicated motion since it participates in all normal modes not just a single mode. As a supplementary step, to simulate this complicated dynamics and the perturbation induced by other modes, nuclear positions of the non-equilibrium geometries along the normal modes containing novel MGs were "randomly drifted". A handful of these non-equilibrium geometries that retain novel MGs but are energetically near to the equilibrium geometry, are used for the quantitative analysis in following discussion.

Trimethylenemethane Complexes

The bonding modes in a number of trimethylenemethane complexes ($[(CO)_3X$-TMM] (X = Fe, Ru, Os, Rh^+), $[\eta^6$-C_6H_6X-TMM] (X = Fe, Ru, Os), $[\eta^5$-C_5H_5X-TMM] (X = Co, Rh, Ir), and $[\eta^4$-C_4H_4X-TMM] (X = Ni, Pd, Pt)) have been considered in detail in recent years [25,48,49]. Particularly, Mousavi and Frenking have done a comprehensive analysis on the bonding of TMM and metal-hydrocarbon unit, based on the energy decomposition analysis (EDA), considering the Laplacian maps of the electron density as well as quantitative molecular orbital diagrams [48,49]. Their analysis demonstrates that the central metal atom in each complex is chemically bonded to both the "central" and "terminal" carbon atoms of the TMM unit and particularly the bonding interaction with

terminal carbon atoms was found to be significant. However, the authors did not find any LCPs and LPs linking the terminal carbon atoms and the central metal. Assuming abovementioned direct analogy between the chemical bond and LPs, Mousavi and Frenking seemingly confused by the "missing BPs" concluded: "This (missing BPs) clearly shows that AIMs analysis does not faithfully represent the strongest pairwise interactions between the atoms in a molecule" (Italics is from present authors). Some of these complexes had been reconsidered in a previous communication and it was shown that the so-called missing LPs are indeed observable in some accessible low-energy non-equilibrium geometries [5]. In this section some other complexes are scrutinized.

Figure 1 depicts MGs of $[\eta^6\text{-}C_6H_6\text{Fe-TMM}]$, $[\eta^5\text{-}C_5H_5\text{Co-TMM}]$, $[\eta^4\text{-}C_4H_4\text{Ni-}$TMM] complexes all computed employing BP86/Def2-TZVPP computational level, as used in the original paper [49], at the equilibrium geometries (for details of the equilibrium geometries see Figure 1 in [49] or Supporting information). Indeed, no LPs are observed between the metals and the terminal carbon atoms of TMM at the equilibrium geometries. Therefore, these complexes are fine examples containing two atoms involved in a chemical bond but not linked by LPs. However, considering the inter-atomic surfaces of the central carbon in Figure 1 (also check Figure 5 in [49]), it is evident that the atomic basins of the metal and the terminal carbon are quite near and just a "tiny volume" of the central carbon's basin penetrates in between them. Pursuing the reasoning advocated previously, some non-equilibrium geometries and their associated MGs were produced. The primary desire behind searching for non-equilibrium geometries was to obtain and analyze non-equilibrium geometries with a smaller metal-terminal carbon inter-nuclear distance. Figure 2 depicts displacement vectors of some

selected vibrational normal modes and Figure 3 shows the MGs of some selected non-equilibrium geometries while Table 1 lists the relevant information for the analysis (for details of the non-equilibrium geometries, see Supporting information).

In the case of $[\eta^6\text{-}C_6H_6\text{Fe-TMM}]$ complex, from a large set of considered non-equilibrium geometries, three have been selected as typical examples (denoted as A, B, and C) with a MG different from that of the equilibrium geometry. From Figure 3 and Table 1 one may conclude that there are non-equilibrium geometries, with energies quite similar to that of the equilibrium geometry, with MGs containing the abovementioned "missing" LPs between the iron and the terminal carbon atoms. At least three new MGs appear all indicating LPs between the iron and each of the terminal carbons. Thus, $[\eta^6\text{-}C_6H_6\text{Fe-TMM}]$ complex is an example of M-MGs case while the terminal carbons and the iron basins are examples of the passionate neighbors. The computed electronic delocalization index (δ) between the iron atom and the central as well as the terminal carbon atoms are relatively insensitive to the geometrical variations, Table 1. Interestingly, the delocalization of electrons is larger between the terminal carbons and the iron atom in comparison with that of the central carbon and the iron atom. Clearly, "abrupt" variations of MGs are chemically unimportant and the "continuity" reveals itself in the delocalization index as a "basin property" (vide infra).

The properties of $[\eta^5\text{-}C_5H_5\text{Co-TMM}]$ and $[\eta^4\text{-}C_4H_4\text{Ni-TMM}]$ complexes are analogous and as is evident from Figure 3 and Table 1 the same pattern emerges, namely the M-MGs molecules, which are not reiterated. All the considered complexes clearly demonstrate the dynamic nature of MGs.

[HS(CH)(CH₂)]

Another M-MGs molecule is $HS(CH)(CH_2)$, depicted in Figure 4, which has been considered previously by Stalke and coworkers as well as Jacobsen [50,51]. Both studies, based on the natural bond orbital method as well as the localized-orbital-locator and the kinetic energy density analysis, came to the conclusion that there are chemical bonds between each of the carbon atoms and the sulfur atom. However, Stalke and coworkers were unsuccessful in locating LPs between the carbon atom of the CH group (hereafter denoted as C1) and the sulfur atom, from the one-electron densities derived from various ab initio and density functional based methods. In contrast, Jacobsen was able to locate the LPs using BP86 density functional but LPs was absent from the MG at other considered computational levels. Particularly, at the CCSD/TZVP level, as the highest employed computational level, LPs were not detected. Jacobsen also noticed that the differences in the geometries of the derived equilibrium structures at each computational level are more important than the resulting one-electron densities. He stressed: "The fact that the presence of BCP is indeed related to differences in geometry, and not due to the particular computational approach, has been tested in a set of E/TZVP//CCSD/TZVP and E/TZVP//PBE/TZVP calculations, E = PBE, PB86, BLYP, B3LYP, B3PW91, CCSD. For all calculations that utilize the CCSD-geometry with a large S-C^1 inter-nuclear distance of 2.007 Å, no BCP between S and C^1 atoms could be located. Furthermore, all calculations based on the PBE-geometry with a short S-C^1 inter-nuclear distance of 1.916 Å predict the presence of an S-C^1 bond" [51] (the word "bond" has been used by Jacobsen as an alternative for the presence of a LCP). In their detailed QTAIM analysis Stalke and coworkers were able to demonstrate that a tiny volume of the basin of the carbon atom of the CH_2 unit (hereafter denoted as C2), which

is closer to the sulfur atom, penetrates in between the sulfur and the C1 carbon basin prohibiting the appearance of the "expected" LCP (See panel (b) of Figure 4 or Figure 4 in [50]).

For the equilibrium geometry, derived at the CCSD/TZVP computational level (for details of geometry, see [50,51] or Supporting information), in line with the previous studies, LPs were not detected between the sulfur and the C1 atoms whereas LPs were observed between the sulfur and the C2 basins. Upon considering some non-equilibrium geometries (denoted by A and B), a novel MG emerges that is also presented in the panel (d) in Figure 4. Inspection of Table 2 demonstrates that in line with Jacobsen's finding, this MG emerges only when the S-C1 inter-nuclear distance contracts considerably with respect to its reference value at the equilibrium geometry (> 0.07 Å). However, the resulting non-equilibrium geometries are still energetically close to the equilibrium geometry and quite accessible even at room temperature. Accordingly, the confusions raised in the original studies have been the result of the fact that $HS(CH)(CH_2)$ is another example of the M-MGs systems. On the other hand, the computed electron delocalization index between the sulfur and each of the carbons are not much different and relatively insensitive to the geometrical variations demonstrating the fact that chemically, the appearance/disappearance of LPs is of no significance.

[$Co_2(CO)_8$]

Various structural, spectroscopic, and inter-conversion aspects of cobalt carbonyls have been investigated extensively by various computational methods (for example, see [52,53] and references cited therein). However, deciphering the nature of cobalt-cobalt "interaction" in the case of $Co_2(CO)_8$ as a typical bimetallic example of this class of

metal-carbonyls, with a C_{2v} symmetry point group (see Figure 5), is not straightforward. In older literature, based on the 18-electron rule, a bond between the cobalt atoms was proposed. Nevertheless, the reorganization of the 18-electron rule introducing three-center two-electron bond (3c-2e), involving two metal atoms and a carbonyl, relegates the need for a "direct" Co-Co bond (for an authoritative review see [54] and references cited therein). Detailed experimental [55] and theoretical [56] studies on the electron density of this complex, including the density difference maps and topological analysis, are generally all in line with the absence of a chemical bond between the metal atoms. Even so, Hall and coworkers stressed that a "weak Co-Co interaction" seems to be survived in this complex [56]. More recent QTAIM-based studies are ambiguous, indicative of both direct [57] and indirect [6,58] bonding mode depending on the "interpretation" of the QTAIM data. Probably, one of the most accurate computational studies on this complex is the analysis of the domain averaged Fermi hole by Ponec and coworkers [59]. This study not only confirms the 3c-2e bonding mode, but also points to the absence of Co-Co covalent bonding at least if one invokes an electron pair as the indicator of covalent bond [59]. One may conclude that at the present state of knowledge there is a weak direct interaction between cobalt atoms that does not deserve to be termed a covalent bond [6,54,59].

According to Figure 5 and in line with all the previous studies [6,56,57], the equilibrium-geometry MG of this complex (for details of geometry, see Supporting information), computed at BP86/Def2-TZVP level, does not indicate the LPs connecting the cobalt basins. Instead, a ring critical point (RCP) emerges in the middle of the ring composed of the two metal atoms and the two carbon basins of the bridged carbonyls. To

check the role of nuclear vibrations, various non-equilibrium geometries were constructed varying in the Co-Co and Co-C(b) inter-nuclear distances as well as the Co-C(b)-Co angle ("b" denotes the bridged carbonyl's carbon). Selected geometries denoted as A, B, and C are considered (for details of geometries, see Supporting formation). In contrast to the previous examples considered in this work, the non-equilibrium geometries containing a LCP in between the cobalt basins are energetically quite distinct from the equilibrium geometry and are not accessible at room temperature, Table 3. Indeed, Figure 5 demonstrates that the basins of the bridged carbon atoms penetrate between the cobalt atoms prohibiting the formation of an inter-atomic surface between the two metal atoms. Table 3 reveals that just by either a large contraction of the Co-Co inter-nuclear distance (> 0.2 Å) or a large expansion of the Co-C(b) inter-nuclear distances (> 0.2 Å) or both, the LCP and its concomitant inter-atomic surface appear between the cobalt basins. Therefore, the cobalt atoms are neither neighbors nor passionate neighbors. Interestingly, the small variations of the Co-Co delocalization index, which is less than 0.1, demonstrates that upon appearance/disappearance of the LCP and concomitant geometrical changes the electron delocalization does not alter significantly. Clearly, the Co-Co electron delocalization index is large (~ 0.35), even at the equilibrium geometry, revealing the fact that there is a small but quite distinct interaction between these two atomic basins. The cobalt basins in $Co_2(CO)_8$ may serve as examples of cases where two basins have non-negligible interactions but the "expected" LP is "missing" between the interacting basins. This observation indeed confirms the previously stated theoretical assertion that the presence of LPs is not necessary for non-negligible interaction between atomic basins.

[(F₃C)F₂SiONMe₂]

The 1,3 geminal silicon-nitrogen interaction, usually called α-effect, is the subject of numerous theoretical and experimental investigations (see [60-65] and references cited therein). $(F_3C)F_2SiONMe_2$ is a proper model for this interaction that has been synthesized and extensively studied by Mitzel and coworkers using various aspects of its structural, energetic and electron density characteristics [61]. The electron diffraction analysis in a gas phase demonstrates that the molecule is composed of two distinguishable conformers, termed gauche and anti; here only the anti conformer is reconsidered, Figure 6. In older literature the α-effect had been described as originating in a dative bond between the silicon and the nitrogen atoms. Two comprehensive studies on $F_3SiONMe_2$ [60] and $(F_3C)F_2SiONMe_2$ [61] by Mitzel and coworkers based on details of electronic structure and one-electron density of these molecules ruled out the presence of dative bond between the nitrogen and the silicon atoms. Instead, the atomic charges of the silicon and nitrogen atoms, variation of atomic charges by changing the Si-O-N angle, the magnitude of electric dipole moment of the molecule, flatness of the potential energy surface upon variations of the Si-O-N angle, and certain qualitative features of the Laplacian maps of the one-electron density are all consistent with an electrostatic interaction (probably with some contribution from the dispersion interaction). One may conclude that although the geminal interaction probably does not deserve to be called a bond, at least in the Lewis type paradigm, its effect on various characteristics of the molecule casts no doubt that the interaction between the silicon and nitrogen atoms is non-negligible.

The anti conformer of $(F_3C)F_2SiONMe_2$ was optimized at the MP2/6-311++g(d,p) level (for details of the geometry, see Supporting information); panel (a) in Figure 6 depicts the MG of the equilibrium geometry. In line with a previous study [61], no LCP and associated LPs are observed between the Si and N basins. Panel (b) of Figure 6 demonstrates that the oxygen basin penetrates in between the Si and N basins preventing the formation of an inter-atomic surface. Like for the previous cases, various non-equilibrium geometries were constructed, however, geometries containing LPs, linking the Si and N basins are energetically high above the energy of the equilibrium geometry and, therefore, not accessible at room temperature. Table 4 contains the relevant computed data of selected non-equilibrium geometry (for details of the geometry, see Supporting formation). Accordingly, at current state of knowledge, $(F_3C)F_2SiONMe_2$ is better described as a single-MG molecule. The small values of the electron delocalization index for Si and N basins, at both the equilibrium and non-equilibrium geometries, demonstrate that marginal electron delocalization is taking place between the two basins. This is certainly consistent with the absence of a covalent Si-N bond. However, both the atomic charges of Si and N as well as the basin electric dipoles are large enough to be consistent with an electrostatic interaction between Si and N atoms. Particularly, at the equilibrium geometry the electric dipole of the N basin is the second largest atomic dipole (almost equal to the oxygen's dipole). All of these observations are indeed in line with predominant electrostatic nature of Si…N interaction and conforms to the picture of the α-effect as articulated previously [60-65]. This is another example demonstrating that LPs are not essential for two AIMs to be interacting. Even more, LPs cannot be used to "gauge" the strength of the interaction. While LPs are

observed between AIMs in many van der Waals complexes [42], just involved in very weak dispersion interactions (like the case of the helium dimer [5]), they are not observed in the case of the much stronger geminal interaction.

Chemical bonds and QTAIM: The combinatorial /synthetic approach

Based on what was discussed in the previous sections, it must be concluded that no "gold"/unique index of chemical bond is defined within the context of the QTAIM; indeed, the QTAIM is not "the" theory of chemical bond. Then, if the QTAIM is not the theory of chemical bond, how one must "discover" and classify chemical bonds with the toolbox of the QTAIM? In the rest of this section a general scheme is scrutinized briefly referring to previous appropriate references. However, before answering this question, it is instructive to briefly mention how a new bond is introduced in chemistry and then identified in molecules.

There is a tendency among theoretical chemists as well as historians of chemistry to simplify and incarnate the concept of chemical bond in the Lewis electron pair paradigm and its subsequent "quantization" by Pauling and others [66-77]. Though there is no question that the Lewis paradigm is an important ingredient in current chemical discourse, "non-Lewis" bonds, e.g. multi-center two-electron bonds [78-80], are also now a pivotal part of chemical discourse. Therefore, there is no general theoretical scheme that may claim to encompass the description of all known types of chemical bonds. Even more, new types of non-Lewis chemical bonds are discovered time to time particularly in the realm of "weak interactions" demonstrating temporary nature of current "bond type" classifications. The recently proposed dihydrogen bond is an example that helps us to comprehend the "real procedure" of introducing novel chemical bonds [81-85]. Detailed

reading of the original papers reveals the fact that no "single" criterion has been used to introduce the dihydrogen bond. But, the reasoning was based on geometrical (X-ray and Neutron diffraction data), spectroscopic (e.g. IR, NMR), thermochemical criteria (e.g. melting points, H-H interaction energies), theoretical analysis of the electronic structures (e.g. qualitative molecular orbital models, atomic charges) as well as considering reaction mechanisms and tracing relevant intermediates. Clearly, the dihydrogen bonds deserve to be named and introduced as independent "chemical phenomena" since their fingerprints are seen in all abovementioned properties. Based on the case of the dihydrogen bond as a typical example, one may conclude that the identification of a chemical bond is a delicate task that is performed by combination/synthesis of various chemical and physical properties. Assuming that a type of chemical bond is well-established, i.e. the list of relevant criteria to be checked for its presence is well-known, the aforementioned combinatorial/synthetic approach must be used to identify the relevant chemical bond in a new molecule. Of course there will be always "gray" examples, i.e. at the edge of bond/no-bond, that are hard to be categorized since they satisfy some criteria of the list but not others demonstrating the inherent ambiguity/fuzziness of the bond classifications. In fact, in a high "magnification", the concept of chemical bond has an intrinsic floppiness. The same combinatorial approach must be used when tracing chemical bonds within the context of the QTAIM while the gray examples also inevitably emerge. It is worth reemphasizing that this ambiguity points to the intrinsic floppiness of the concept of chemical bond rather than a deficiency of the QTAIM (probably it is a solace for chemists to know that biologists also encounter with the same kind of "classification obstacles" [86,87]).

The QTAIM analysis yields point, surface, and basin properties. The point properties include the amount of the one-electron and the property densities at LCPs, usually called topological indices [2-4] (in principle, any other type of CPs or even an arbitrary point in space can be used for "density sampling"). The surface properties similarly include surface integrals of the one-electron and the property densities over the inter-atomic surfaces [88-90]. Finally, the basin properties include volume integrals of the one-electron and the property densities over the atomic basins [2-4]. Although none of these properties uniquely determines the presence/absence of a chemical bond, the combinatorial approach must be used for the recognition and classification of chemical bonds. In this QTAIM-based combinatorial approach the list of criteria is composed of a set of QTAIM derived indices. Indeed, beyond Bader's classics on covalent and ionic bonds in general [2], and a dedicated study on transition metal-carbonyl bonds in particular [91], in the case of the dihydrogen [81-85], hydrogen and agostic bonds [92-94], Popelier has introduced and elaborated such combinatorial methodology [95-97]. Also, in the case of metal-metal bonds from transition-metal block the same methodology has been employed masterfully by Macchi and Sironi [6] (see also section 13 in [4]). In the combinatorial methodology, the QTAIM analysis yields a wealth of "raw properties" which can be used to construct correspondence rules [6]. Accordingly, a set of molecules with well-established target bond must be analyzed as a first step, seeking for correspondence between the bond and the QTAIM derived properties of the atomic basins involved in the bonding. Subsequently, the derived correspondence rules should be used to establish the presence/absence of a target bond in a larger set of molecules. There is no unique recipe guiding how to choose the primary set of typical molecules

containing a certain type of bond, or what type of the QTAIM indices should be used as proper criteria to decipher the bond, or how to tune the range of continuous indices determining the bond/no-bond boundary. Thus, such combinatorial approach does not yield the "final" set of correspondence rules so it is prone to revision and constant evolution. Particularly, since the gray examples are also conceivable within the QTAIM-based correspondence rules one must always be prepared to discover two AIMs that is hard to ascertain the presence/absence of a certain kind of chemical bond in between them. In other words, this observation points to the fact that the QTAIM does not make chemical bond classification procedure less fuzzy or more definite.

Based on all previous discussions on LCPs and LPs, the emphasis on the point and surface properties in such a list of criteria does not seem to be legitimate. Such emphasis dismisses, unreasonably, the possibility of considering the presence of bonds between atomic basins that are not neighbors. Consequently, in designing correspondence rules, the presence of LPs as a necessary and/or sufficient criterion for a certain kind of chemical bond must be eliminated and the emphasis has to be shifted toward the basin properties as well as general qualitative features of various property densities at the region of bonding (for a transparent discussion on the use of the Laplacian of one-electron density, as a typical density, in recognizing various types of bonds, see [98]). Atomic electron population (atomic charge) [2-4], atomic polarization dipole and higher order multipoles [2-4], atomic polarizability [2,4], atomic energies [2,99], localization and delocalization indices [2,26-38], and the source function [100-104] are just examples of proper basin properties that have been utilized in previous high-quality QTAIM analyses.

Prospects beyond the orthodox QTAIM: The nature of AIMs interactions

Inherent in all previous discussions on various types of chemical bonding was the strength of the interactions of AIMs, for example covalent bonds are typical strong interactions whereas the dihydrogen bonds are examples of weakly interacting AIMs. Since each atom in a molecule always interacts with all other atoms of the system [44], the key point in using the QTAIM analysis is not distinguishing the interacting and non-interacting AIMs, but "gauging" the strength and nature of interactions. Currently, gauging the interactions of neighbors is done "indirectly", i.e. without direct evaluation of the interaction energy. This is done by considering topological indices at LCPs and/or surface integrals over inter-atomic surfaces or more generally, through combinatorial strategy, employing various basin properties thus encompassing the case of the interaction of non-neighbors. Such indirect approach may trigger controversies on the true nature of interacting AIMs, of which the case of the "H-H bonding controversy" is a vivid but not exclusive example [105-114]. Such controversies clearly point to the fact that a "direct" gauging approach attributing interaction energy to each pair of AIMs is a missing ingredient within the formalism of the QTAIM. The Interacting Quantum Atoms (IQA) methodology, developed by Pendás and coworkers [115-125], is a proper example of such a direct approach that is used currently in parallel with the QTAIM analysis [126-129]. However, in long term the QTAIM needs its own direct gauging approach to answer delicate questions regarding the nature of interactions of AIMs that are currently debated usually without clear cut conclusions [130-171]. One may hope that upon introduction of direct gauging, a truly consistent and comprehensive chemical

interpretation will emerge relegating most of the current ongoing controversies around the QTAIM.

Acknowledgments

References

[1]   A. Whitaker, in Einstein, Bohr and the Quantum Dilemma, Cambridge University press, Cambridge, **1996**.

[2]   R. F. W. Bader, in Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, **1990**.

[3]   P. L. A. Popelier, in Atoms in Molecules an Introduction, Pearson, London, **2000**.

[4]   C. F. Matta, R. J. Boyd, in Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design, Wiley-VCH, Weinheim, **2007**.

[5]   S. Shahbazian, **2013**, arxiv.org/abs/1306.6350.

[6]   P. Macchi, A. Sironi, Coord. Chem. Rev. **2003**, 238-239, 383.

[7]   A. Krapp, G. Frenking, Chem. Eur. J. **2007**, 13, 8256.

[8]   A. Martín Pendás, E. Francisco, M. A. Blanco, C. Gatti, Chem. Eur. J. **2007**, 13, 9362.

[9]   R. Ponec, C. Gatti, Inorg. Chem. **2009**, 48, 11024.

[10]   L. J. Farrugia, H. M. Senn, J. Phys. Chem. A **2010**, 114, 13418.

[11]   M. García-Revilla, P. L. A. Popelier, E. Francisco, A. Martín Pendás, J. Chem. Theory Comput. **2011**, 7, 1704.

[12]   M. García-Revilla, E. Francisco, P. L. A. Popelier, A. Martín Pendás, ChemPhysChem **2013**, 14, 1211.

[13]   A. Martín Pendás, M. A. Blanco, A. Costales, P. M. Sánchez, V. Luaña, Phys. Rev. Lett. **1999**, 83: 1930.

[14]   A. Costales, M. A. Blanco, A. Martín Pendás, P. M. Sánchez, V. Luaña, J. Phys. Chem. A **2004**, 108, 2794.

[15]   P. M. Sánchez, A. Martín Pendás, V. Luaña, Phys. Rev. B, **2001**, 63, 125103.

[16]   I. N. Levine in Molecular Spectroscopy, Wiley-Interscience publication, New York, **1975**.

[17]   M. Goli, S. Shahbazian, Theor. Chem. Acc. **2011**, 129, 235.

[18]   M. Goli, S. Shahbazian, Theor. Chem. Acc. **2012**, 131, 1208.

[19]   M. Goli, S. Shahbazian, Theor. Chem. Acc. **2013**, 132, 1362.

[20]   M. Goli, S. Shahbazian, Theor. Chem. Acc. **2013**, 132, 1365.

[21]   M. Goli, S. Shahbazian, Theor. Chem. Acc. **2013**, 132, 1410.

[22]   S. Shahbazian, Found. Chem. **2013**, 15, 287.

[23]   R. F. W. Bader, J. Phys. Chem. A **2009**, 113, 10391.

[24]   R. F. W. Bader, J. Phys. Chem. A **2010**, 114, 7431.

[25]   L. J. Farrugia, C. Evans, M. Tegel, J. Phys. Chem. A **2006**, 110, 7952.

[26]   R. F. W. Bader, M. E. Stephens, Chem. Phys. Lett. **1974**, 26, 445.

[27]   R. F. W. Bader, M. E. Stephens, J. Am. Chem. Soc. **1975**, 97, 7391.

[28]   R. F. W. Bader, A. Streitwieser, A. Neuhaus, K. E. Laidig, P. Speers, J. Am. Chem. Soc. **1996**, 118, 4959.

[29]   R. F. W. Bader, S. Johnson, T.-H. Tang, P. L. A. Popelier, J. Phys. Chem. **1996**, 100, 15398.

[30]   R. J. Gillespie, D. Bayles, J. Platts, G. L. Heard, R. F. W. Bader, J. Phys. Chem. A **1998**, 102, 3407.

[31]   X. Fradera, M. Austen, R. F. W. Bader, J. Phys. Chem. A **1999**, 103, 304.

[32]   R. F. W. Bader, G. L. Heard, J. Chem. Phys. **1999**, 111, 8789.

[33]   J. M. Molina, J. A. Dobado, G. L. Heard, R. F. W. Bader, M. R. Sundberg, Theor. Chem. Acc. **2001**, 105, 365

[34]   C. F. Matta, J. Hernández-Trujillo, R. F. W. Bader, J. Phys. Chem. A **2002**, 106, 7369.

[35]   J. Poater, M. Solá, M Duran, X. Fradera, Theor. Chem. Acc. **2002**, 107, 362.

[36]   X. Fradera, J. Poater, S. Simon, M. Duran, M. Solá, Theor. Chem. Acc. **2002**, 108, 214.

[37]   C. F. Matta, J. Hernández-Trujillo, J. Phys. Chem. A **2003**, 107, 7496.

[38]   J. Poater, X. Fradera, M. Duran, M. Solà, Chem. Eur. J. **2003**, 9, 400

[39]   R. G. Parr, W. Yang, in Density-Functional Theory of atoms and Molecules, Oxford University Press, New York, **1989**.

[40]   R. McWeeny in Methods of Molecular Quantum Mechanics, Second Ed. Academic Press, London, **1989**.

[41]   S. Shahbazian, Found. Chem. **2013**, 15, 327.

[42]   R. G. A. Bone, R. F. W. Bader, J. Phys. Chem. **1996**, 100, 10892.

[43]   J. D. Dunitz, A. Gavezzotti, Chem. Soc. Rev. **2009**, 38, 2622.

[44]   A. J. Stone, The Theory of Intermolecular Forces, Oxford University Press, Oxford, **1996**.

[45]   C. Foroutan-Nejad, G. H. Shafiee, A. Sadjadi, S. Shahbazian, Can. J. Chem. **2006**, 84, 771.

[46]   S. Shahbazian, A. Sadjadi J. Mol. Struct: Theochem **2007**, 822, 116.

[47]   S. Shahbazian, S. Alizadeh, J. Phys. Chem. A **2008**, 112, 10365.

[48]   M. Mousavi, G. Frenking, J. Organomet. Chem. **2013**, 748, 2.

[49]   M. Mousavi, G. Frenking, Organometallics **2013**, 32, 1743.

[50]   J. Henn, D. Leusser, D. Stalke, J. Comput. Chem. **2007**, 28, 2317.

[51]   H. Jacobsen, J. Comput. Chem. **2009**, 30, 1093.

[52]   J. P. Kenny, R. B. King, H. F. Schaefer III, Inorg. Chem. **2001**, 40, 900.

[53]   G. Aullón, S. Alvarez, Eur. J. Inorg. Chem. **2001**, 3031

[54]   J. G. Green, M. L. H. Green, P. Gerard, Chem. Commun. **2012**, 48, 11481.

[55]   P. C. Leung, P. Coppens, Acta. Cryst. B **1983**, 39, 535.

[56]   A. A. Low, K. L. Kunze, P. J. MacDougall, M. B. Hall, Inorg. Chem. **1991**, 30, 1079.

[57]   M. Finger, J. Reinhold, Inorg. Chem. **2003**, 42, 8128.

[58]   P. Macchi, L. Garlaschelli, S. Martinengo, A. Sironi, J. Am. Chem. Soc. **1999**, 121, 10428.

[59]   R. Ponec, G. Lendvay, J Chaves, J. Comput. Chem. **2008**, 29, 1387.

[60]   N. W. Mitzel, U. Losehand, A. Wu, D. Cremer, D. W. H. Rankin, J. Am. Chem. Soc. **2000**, 122, 4471.

[61]   N. W. Mitzel, K. Vojinović, R. Fröhlich, T. Foerster, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin, J. Am. Chem. Soc. **2005**, 127, 13705.

[62]   T. Foerster, D. A. Wann, D. W. H. Rankin, Dalton Trans. **2008**, 5999.

[63]   M. Woski, R. J. F. Berger, N. W. Mitzel Dalton Trans. **2008**, 5652.

[64]   N. W. Mitzel, K. Vojinović, T. Foerster, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin, Chem. Eur. J. **2008**, 11, 5114.

[65]   M. Hagemann, R. J. F. Berger, S. A. Hayes, H.-G. Stammler, N. W. Mitzel, Chem. Eur. J. **2008**, 14, 11027.

[66]   B. T. Sutcliffe, Int. J. Quantum Chem. **1996**, 58, 645.

[67]   R. Hoffmann, J. Mol. Struct; Theochem, **1998**, 424, 1.

[68]   B. S. Park, Br. J. Hist. Sci. **1999**, 32, 21.

[69]   B. S. Park, Stud. Hist. Phil. Mod. Phys. **2000**, 31, 451.

[70]   W. H. E. Schwarz, Theor. Chem. Acc. **2001,** 105, 271.

[71]   S. Shahbazian, M. Zahedi, Found. Chem. **2006**, 8, 37.

[72]   S. Shahbazian, M. Zahedi, Found. Chem. **2007**, 9, 85.

[73]   G. Frenking, A. Krapp, J. Comp. Chem. **2007**, 28, 15.

[74]   S. Shaik, J. Comp. Chem. **2007**, 28, 51.

[75]   A. Simões, J. Comp. Chem. **2007**, 28, 62.

[76]   R. J. Gillespie, E. A. Robinson, J. Comp. Chem. **2007**, 28, 87.

[77]   M. L. Harris, Stud. Hist. Phil. Sci. **2008**, 39, 78.

[78]   D. Y. Zubarev, B. B. Averkiev, H.-J. Zhai, L.-S. Wang, A. I. Boldyrev, Phys. Chem. Chem. Phys. **2008**, 10, 257.

[79]   D. Y. Zubarev, A. I. Boldyrev, Phys. Chem. Chem. Phys. **2008**, 10, 5207.

[80]   D. Y. Zubarev, A. I. Boldyrev, J. Org. Chem. **2008**, 73, 9251.

[81]   T. B. Richardson, S. deGala, R. H. Crabtree, P. E. M. Siegbahn, J. Am. Chem. Soc. **1995**, 117, 12875.

[82]   R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, T. F. Koetzle, Acc. Chem. Res. **1996**, 29, 348.

[83]   R. H. Crabtree, Science **1998**, 282, 2000.

[84]   R. Custelcea, J. E. Jackson, Chem. Rev. **2001**, 101, 1963.

[85]   V. I. Bakhmutov, in Dihydrogen Bonds: Principles, Experiments and Applications, Wiley-Interscience, New Jersey, **2008**.

[86]   M. W. Ho, J. Theor. Bio. **1990**, 147, 43.

[87]   W. Kunz, in Do Species Exist? Principles of Taxonomic Classification, Wiley-Blackwell, Weinheim, **2012**.

[88]   R. F. W. Bader, T.-T. Tang, Y. Tal, F. W. Biegler-König, J. Am. Chem. Soc. **1982**, 104, 946.

[89]   D. Cremer, E. Kraka, Croat. Chem. Acta. **1984**, 57, 1259.

[90]   R. F. W. Bader, K. B. Wiberg, in Density Matrices and Density Functionals, (Eds: R. Erdahl, V. H. Smith), Reidel Publishing Company, Holland, **1987**, pp. 677-692.

[91]   F. Cortés-Guzmán, R. F. W. Bader, Coord. Chem. Rev. **2005**, 249, 633.

[92]   G. A. Jeffrey, W. Saenger, in Hydrogen Bonding in Biological Structures, Springer-Verlag, Berlin, **1991**.

[93]   G. Gilli, P. Gilli in The Nature of the Hydrogen Bonding: Outline of a Comprehensive Hydrogen Bond Theory, Oxford University Press, Oxford, **2001**.

[94]   M. Brookhart, M. L. H. Green, G. Parkin, Proc. Nat. Acad. Sci. **2007**, 104, 6908.

[95]   U. Koch, P. L. A. Popelier, J. Phys. Chem. **1995**, 99, 9747.

[96]   P. L. A. Popelier, J. Phys. Chem. **1998**, 102, 1873.

[97]   P. L. A. Popelier, G. Logothetis, J. Organometal. Chem. **1998**, 555, 101.

[98]   R. J. Gillespie, P. L. A. Popelier, in Chemical Bonding and Molecular Geometry, Oxford University Press, Oxford, **2001**.

[99]   I. S. Bushmarinov, K. A. Lyssenko, M. Y. Antipin, Russ. Chem. Rev. **2009**, 78, 283.

[100]   R. F. W. Bader, C. Gatti, Chem. Phys. Lett. **1998**, 287, 233.

[101]   C. Gatti, F. Cargnoni, L. Bertini, J. Comput. Chem. **2003**, 24, 422.

[102]   C. Gatti, L. Bertini, Acta. Crst. A **2004**, 60, 438.

[103]   L. J. Farrugia, P. Macchi, J. Phys. Chem. A **2009**, 113, 10058.

[104]   C. Gatti, Struct. Bond. **2012**, 147, 193.

[105]   C. F. Matta, J. Hernández-Trujillo, T.-H. Tang, R. F. W. Bader, Chem. Eur. J. **2003**, 9, 1940.

[106]   J. Poater, M. Solá, F. M. Bickelhaupt, Chem. Eur. J. **2006**, 12, 2889.

[107]   R. F. W. Bader, Chem. Eur. J. **2006**, 12, 2896.

[108]   J. Poater, M. Solá, F. M. Bickelhaupt, Chem. Eur. J. **2006**, 12, 2902.

[109]   C. F. Matta, in Hydrogen Bonding-New Insights, (Eds: S. Grabowski) Springer **2006**, pp. 337-375.

[110]   J. Poater, R. Visser, M. Solá, F. M. Bickelhaupt, J. Org. Chem. **2007**, 72, 1134.

[111]   J. Hernández-Trujillo, C. F. Matta, Struct. Chem. **2007**, 18, 849.

[112] J. Poater, F. M. Bickelhaupt, M. Solà, J. Phys. Chem. A **2007**, 111, 5063.

[113]   J. Poater, J. J. Dannenberg, M. Solá, F. M. Bickelhaupt, Int. J. Chem. Model. **2008**, 1, 63.

[114]   J. Poater, M. Solá, F. M. Bickelhaupt, Int. J. Chem. Model. **2010**, 2, 181.

[115]   A. Martin Pendás, M. A. Blanco, E. Francisco, J. Chem. Phys. **2004**, 120, 4581.

[116]   M. A. Blanco, A. Martin Pendás, E. Francisco, J. Chem. Theory Comput. **2005**, 1, 1096.

[117]   A. Martin Pendás, E. Francisco, M. A. Blanco, J. Comput. Chem. **2005**, 26, 344.

[118]   S. F. Vyboishchikov, P. Salvador, M. Duran, J. Chem. Phys. **2005**, 122, 244110.

[119]   E. Francisco, A. Martin Pendás, M. A. Blanco, J. Chem. Theor. Comput. **2006**, 2, 90.

[120]   A. Martin Pendás, E. Francisco E, M. A. Blanco, J. Phys. Chem. A **2006**, 110, 12864.

[121]   A. Martin Pendás, M. A. Blanco, E. Francisco, J. Chem. Phys. **2006**, 125, 184112.

[122]   A. Martin Pendás, M. A. Blanco, E. Francisco, J. Comput. Chem. **2007**, 28, 161.

[123]   A. Martin Pendás, M. A. Blanco, E. Francisco, J. Comput. Chem. **2009**, 30, 98.

[124]   M. García-Revilla, E. Francisco, A Costales, A. Martin Pendás, J. Phys. Chem. A **2011**, 116, 1237.

[125]   V. Tognetti, L. Joubert, J. Chem. Phys. **2013**, 138, 024102.

[126]   P. I. Demýanov, P. M. Polestshuk, Chem. Eur. J. **2012**, 18, 4982.

[127]   P. I. Demýanov, P. M. Polestshuk, Chem. Eur. J. **2013**, 19, 10945.

[128]   J. Dillen, Int. J. Quantum Chem. **2013**, 113, 2143.

[129]   I. Cukrowski, J. H. de Lange, M. Mitoraj, J. Phys. Chem. A **2014**, 118, 623.

[130]   J. Cioslowski, S. T. Mixon, W. D. Edwards, J. Am. Chem. Soc. **1991**, 113, 1083.

[131]   J. Cioslowski, S. T. Mixon, J. Am. Chem. Soc. **1992**, 114, 4382.

[132]   J. Cioslowski, S. T. Mixon, Can. J. Chem. **1992**, 70, 443.

[133]   J. D. Dunitz, A. Gavezzotti, Acc. Chem. Res. **1999**, 32, 677.

[134]   K. N. Robertson, O. Knop, T. S. Cameron, Can. J. Chem. **2003**, 81, 727.

[135]   F. Cortés-Guzmán, J. Hernández-Trujillo, G. Cuevas J. Phys. Chem. A **2003**, 107, 9253.

[136]   A. Haaland, D. J. Shorokhov, N. V. Tverdova, Chem. Eur. J. **2004**, 10, 4416.

[137]   C.-C. Wang, T.-H. Tang, L.-C. Wu, Y. Wang, Acta. Cryst. A **2004**, 60, 488.

[138]   I. V. Glukhov, M. Y. Antipin, K. A. Lyssenko, Eur. J. Inorg. Chem. **2004**, 1379.

[139]   M. Montejo, A. Navarro, G. J. Kearley, J. Vázquez, J. J. López-González, J. Am. Chem. Soc. **2004**, 126, 15087.

[140]   C. F. Matta, N. Castillo, R. J. Boyd, J. Phys. Chem. A **2005**, 109, 3669.

[141]   J. D. Dunitz, A. Gavezzotti, Angew. Chem. Int. Ed. **2005**, 44, 1766.

[142]   D. J. Wolstenholme, T. S. Cameron, J. Phys. Chem. A **2006**, 110, 8970.

[143]   R. Parthasarathi, V. Subramanian, N. Sathyamurthy, J. Phys. Chem. A **2006**, 110, 3349.

[144]   L. Pacios, Struct. Chem. **2007**, 18, 785.

[145]   M. Palusiak, S. Grabowski, Struct. Chem. **2007**, 18, 859.

[146]   D. J. Wolstenholme, C. F. Matta, T. S. Cameron, J. Phys. Chem. A **2007**, 111, 8803.

[147]   T. Strenalyuk, A. Haaland, Chem. Eur. J. **2008**, 14, 10223.

[148]   M. v. Hopffgarten, G. Frenking, Chem. Eur. J. **2008**, 14, 10227.

[149]   S. Grimme, C. Mück-Lichtenfeld, G. Erker, G. Kehr, H. Wang, H. Beckers, H. Willner, Angew. Chem. Int. Ed. **2009**, 48, 2592.

[150]   E. Cerpa, A. Krapp, R. Flores-Moreno, K. J. Donald, G. Merino, Chem. Eur. J. **2009**, 15, 1985.

[151]   S.-G. Wang, Y.-X. Qiu, W. H. E. Schwarz, Chem. Eur. J. **2009**, 15, 6032.

[152]   S.-G. Wang, Y.-X. Qiu, W. H. E. Schwarz, Chem. Eur. J. **2010**, 16, 9107.

[153]   I. Cukrowski, C. F. Matta, Chem. Phys. Lett. **2010**, 499, 66.

[154]   H. Jacobsen, Dalton Trans. **2010**, 39, 5426.

[155]   I. Cukrowski, K. Govender, M. P. Mitoraj, M. Srebro, J. Phys. Chem. A **2011** 115, 12746.

[156]   J. Echeverría, G. Aullón, D. Danovich, S. Shaik, S. Alvarez, Nat. Chem. **2011**, 3, 323.

[157]   G. V. Baryshnikov, B. F. Minaev, V. A. Minaeva, J. Struct. Chem. **2011**, 52, 1051.

[158]   E. Orgaz, A. Aburto, Int. J. Quantum Chem. **2012**, 112, 3490.

[159]   R. D. Hancock, I. V. Nikolayenko, J. Phys. Chem. A **2012**, 116, 8572.

[160]   W. H. E. Schwarz, H. Schmidbaur, Chem. Eur. J. **2012**, 18, 4470.

[161]   Y. Mo, J. Phys. Chem. A **2012**, 116, 5240.

[162]   D. Danovich, S. Shaik, F. Neese, J. Echeverría, G. Aullón, S. Alvarez, J. Chem. Theory Comput. **2013**, 9, 1977.

[163] A. V. Vashchenko, T. N. Borodina, J. Struct. Chem. **2013**, 54, 479.

[164] J. R. Lane, J. Contreras-Garvia, J.-P. Piquemal, B. J. Miller, H. G. Kjaergaard J.
Chem. Theory Comput. **2013**, 9, 3263.

[165] M. Jabloński, J. Phys. Chem. A **2013**, 116, 5240.

[166] M. Jabloński, M. Palusiak, Chem. Phys. **2013**, 415, 207.

[167] O. A. Syzgantseva, V. Tognetti, L. Joubert L, J. Phys. Chem. A **2013**, 117, 8969.

[168] R. J. Kalescky, E. Kraka, D. Cremer, J. Phys. Chem. A **2014**, 118, 223.

[169] D. S. Sabirov, Comput. Theor. Chem. **2014**, 1030, 81.

[170] N. K. V. Monteiro, C. L. Firme, J. Phys. Chem. A **2014**, 118, 1730.

[171] D.-X. Zhao, Z.-Z. Yang, J. Compute. Chem. **2014**, doi: 10.1002/jcc.23570.

Figure captions:

Figure 1- A two-dimensional view of the basin of the central carbon (red region) of the TMM unit in (a) [η^6-C$_6$H$_6$Fe-TMM], (b) [η^5-C$_5$H$_5$Co-TMM] and (c) [η^4-C$_4$H$_4$Ni-TMM] complexes. Both the contours (blue curves) as well as the gradient paths (red curves) of the electron density are depicted in a plane containing the nuclei of the central carbon of TMM, the metal and one of the terminal carbons of the TMM. The LCPs are shown as green dots whereas LPs are depicted as black lines. The ring and cage CPs are eliminated for clarity.

Figure 2- Selected low frequency and low force constant normal modes of (a) [η^6-C$_6$H$_6$Fe-TMM], (b) [η^5-C$_5$H$_5$Co-TMM], and (c) [η^4-C$_4$H$_4$Ni-TMM] complexes; during corresponding vibrations the inter-nuclear metal-terminal carbon distances decreases.

Figure 3- The MGs of some selected non-equilibrium geometries (denoted by M-A, M-B, and M-C, M= Fe, Co, Ni) of η^6-C$_6$H$_6$Fe-TMM], [η^5-C$_5$H$_5$Co-TMM], [η^4-C$_4$H$_4$Ni-TMM] complexes (for details of geometries, see Supporting information). The LCPs are shown with green dots, red dots are used for RCPs, and LPs are depicted as black lines. The cage CPs are eliminated for clarity.

Figure 4- (a) The MG of the equilibrium geometry, (b) the basin of the C2 carbon (red region), (c) a selected low frequency/force constant normal mode, and (d) the MGs of two selected non-equilibrium geometries (denoted as A and B) of HS(CH)(CH$_2$) molecule. The green dots in panels (a), (b), and (d) are LCPs and the red dot in (d) is a RCP. The black lines in panels (a), (b), and (d) are LPs. In panel (b) the contours (blue curves) as well as the gradient paths (red curves) of the electron density are depicted in a plane containing the nuclei of the carbons and the sulfur atom.

Figure 5-(a) The MG of the equilibrium geometry, (b) the MGs of the three selected non-equilibrium geometries (denoted as A, B and C), (c) the inter-atomic surfaces separating

cobalt atoms and the bridged carbon basins in $Co_2(CO)_8$ molecule. The green dots in panels (a), (b), and (c) are LCPs and RCPs are denoted by red dots. The black lines in panels (a), (b), and (c) are LPs. In panel (c) the greens surfaces are the inter-atomic surfaces.

Figure 6-(a) The MG of the equilibrium geometry, (b) the basins of the silicon (orange region), nitrogen (blue region), and oxygen (red region) atoms at the equilibrium geometry, (c) the basins of the silicon (orange region), nitrogen (blue region), and oxygen (red region) atoms at the selected non-equilibrium geometry of $(F_3C)F_2SiONMe_2$ molecule. The green dots in panels (b) and (c) are LCPs and RCPs are denoted by red dots. The black lines are LPs. In panels (b) and (c) the contours (blue loops) of the electron density are depicted in a plane containing the nuclei of the silicon, nitrogen, and oxygen atoms.

Table 1 - Some geometrical parameters (inter-nuclear distance are given in Angstroms) as well as relative energies (kcal.mol^{-1}) and the electron delocalization index (δ) computed at both the equilibrium (denoted by Opt suffix) and selected non-equilibrium geometries of $[\eta^6\text{-}C_6H_6Fe\text{-}TMM]$, $[\eta^5\text{-}C_5H_5Co\text{-}TMM]$, $[\eta^4\text{-}C_4H_4Ni\text{-}TMM]$ complexes.[*]

	Fe-C(t)	Fe-C(c)-C(t)	ΔE[**]	δ(Fe-C(c))	δ(Fe-C(t))[***]
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)	ΔE[**]	δ(Co-C(c))	δ(Co-C(t))[***]
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)	ΔE[**]	δ(Ni-C(c))	δ(Ni-C(t))[***]
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

[*] c and t are used for the central and the terminal carbons, respectively.

[**] Relative to the energy of the equilibrium geometry.

[***] This is the terminal carbon atom that its inter-nuclear distance is varied according to the first column. The delocalization index of the remaining terminal carbons with iron is practically equal to that observed at the equilibrium geometry.
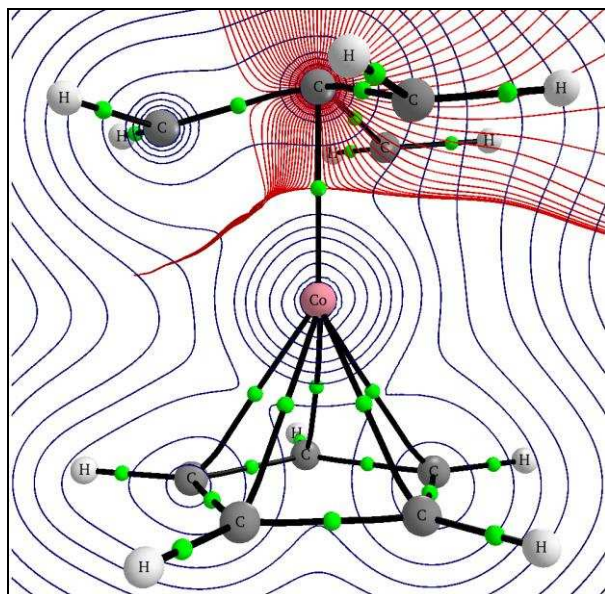
Table 2- Some geometrical parameters (inter-nuclear distance are given in Angstroms) as well as relative energies (kcal.mol^{-1}) and the electron delocalization index (δ) computed at both the equilibrium (denoted as Opt) and selected non-equilibrium geometries of HS(CH)(CH$_2$).

	S-C1	S-C2-C1	ΔE^{*}	δ(S-C1)	δ(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

*Relative to the energy of the equilibrium geometry.

Table 3- Some geometrical parameters (inter-nuclear distance are given in Angstroms) as well as relative energies (kcal.mol^{-1}) and the electron delocalization index (δ) computed at both the equilibrium (denoted as Opt) and some selected non-equilibrium geometries of $Co_2(CO)_8$.

	Co-Co	Co-C	Co-C-Co	ΔE^{**}	δ (Co-Co)	δ (Co-C(b))*
Opt	2.55	1.96	81.3	0	0.36	0.69
A	2.55	2.17	72.0	21.0	0.43	0.56
B	2.47	2.11	71.7	14.2	0.44	0.60
C	2.35	1.93	75.0	4.5	0.46	0.71

*"b" is an abbreviation for the carbon atom of the bridged carbonyl.
**Relative to the energy of the equilibrium geometry.

Table 4- Some geometrical parameters (inter-nuclear distance are given in Angstroms), relative energies (kcal.mol^{-1}), the electron delocalization index (δ), atomic charges and the magnitude of total basin dipole moments computed at both the equilibrium (denoted as Opt) and one selected non-equilibrium geometry of $(F_3C)FSiONMe_2$.

	Si-N	Si-O-N	ΔE^*	δ (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

*Relative to the energy of the equilibrium geometry. This is the lowest energy discovered non-equilibrium geometry that yet contains a LCP between Si and N atoms.

(a)

(b)

(c)

Figure-1

$\upsilon = 387$ cm^{-1}
f = 0.52 mDyn.Å^{-1}

(a)

$\upsilon = 367$ cm^{-1}
f = 0.53 mDyn.Å^{-1}

(b)

$\upsilon = 300$ cm^{-1}
f = 0.31 mDyn.Å^{-1}

(c)
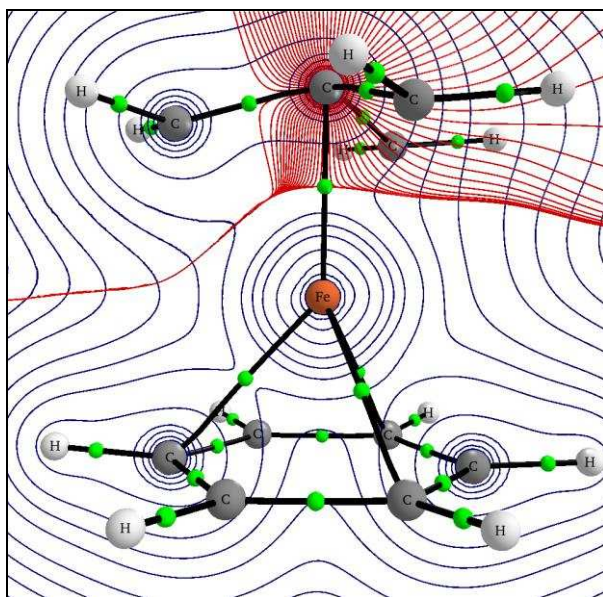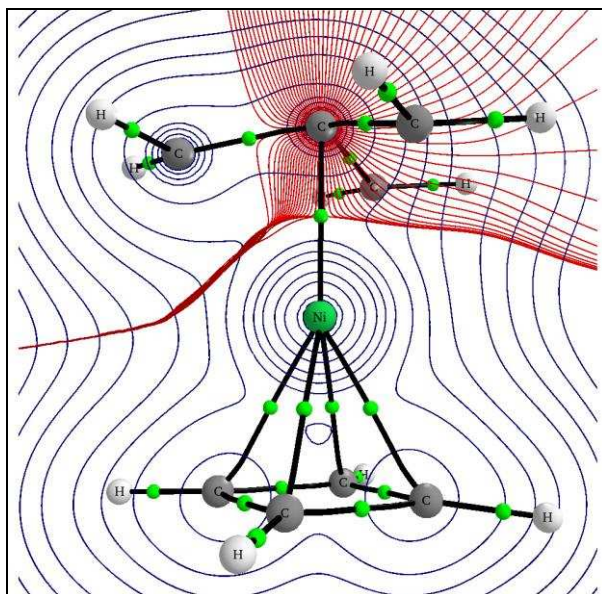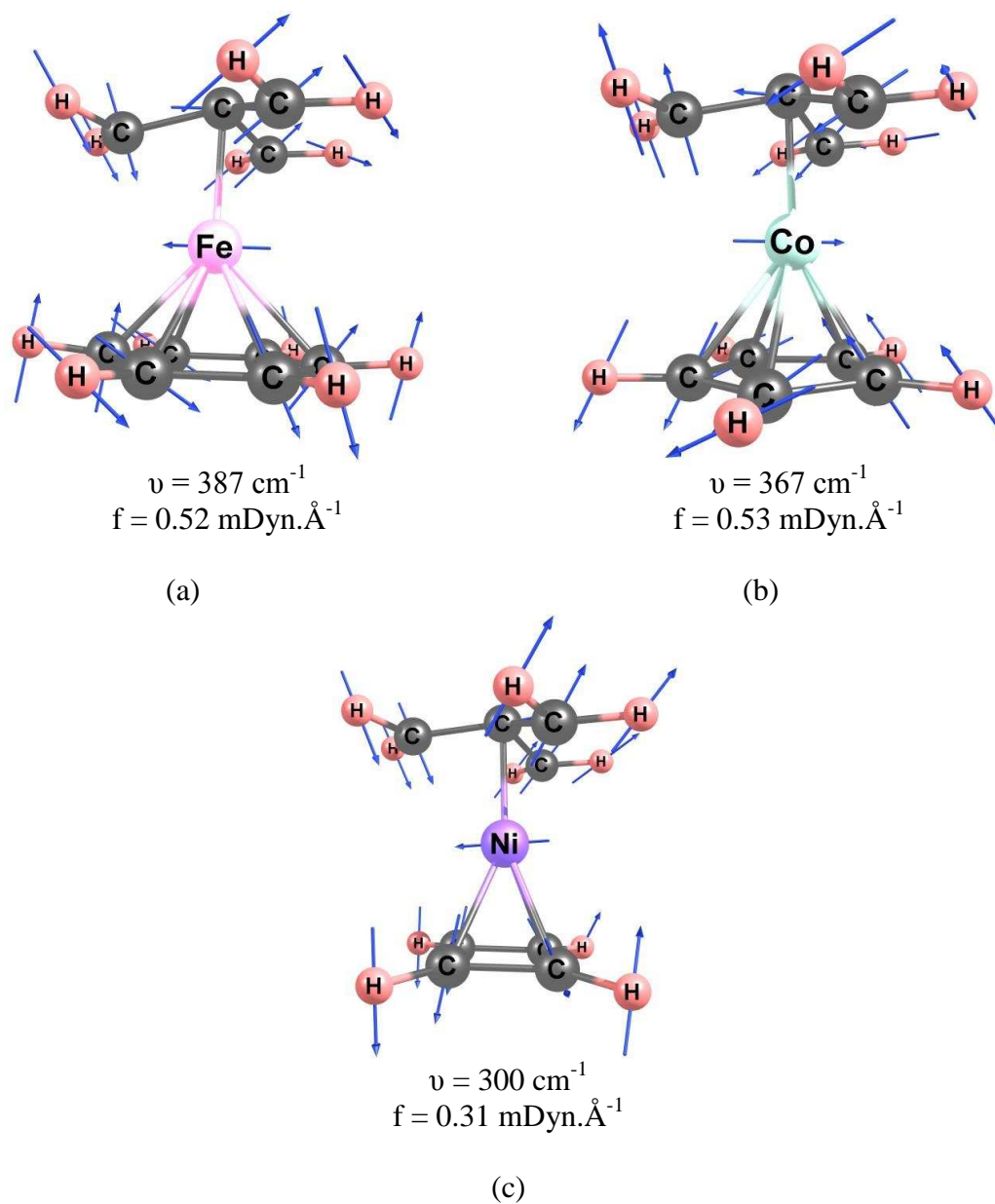
Figure-2

Fe: A

Fe: B, C

Co: A

Co: B, C

Ni: A   Ni: B, C

Figure-3

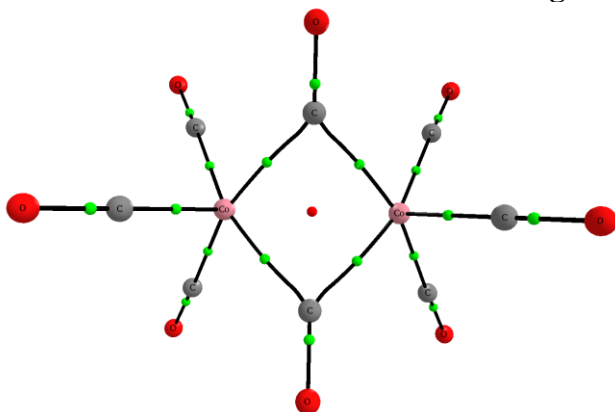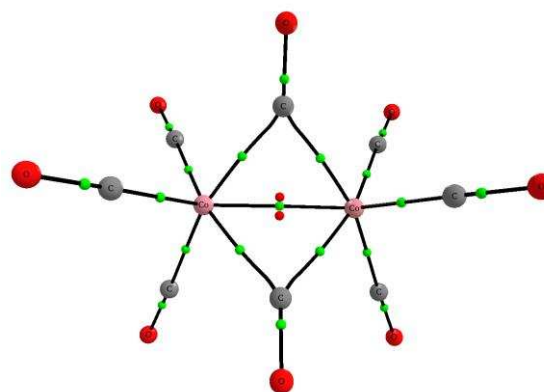(a)   (b)

$\upsilon = 360$ cm^{-1}
$f = 0.63$ mDyn.Å^{-1}
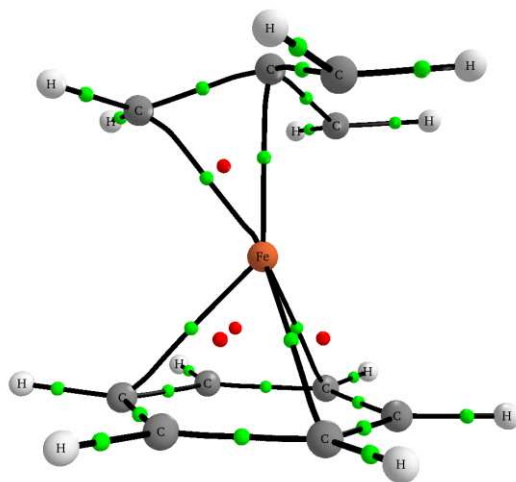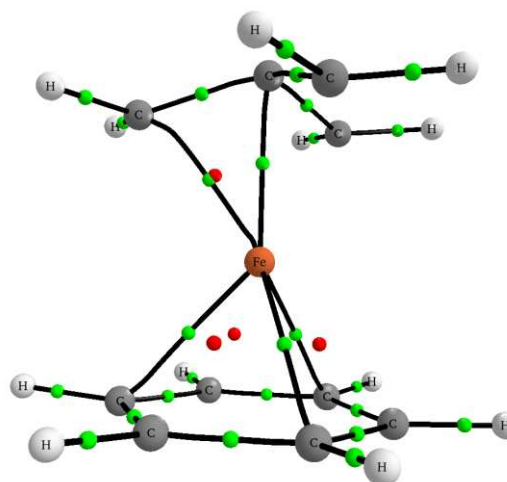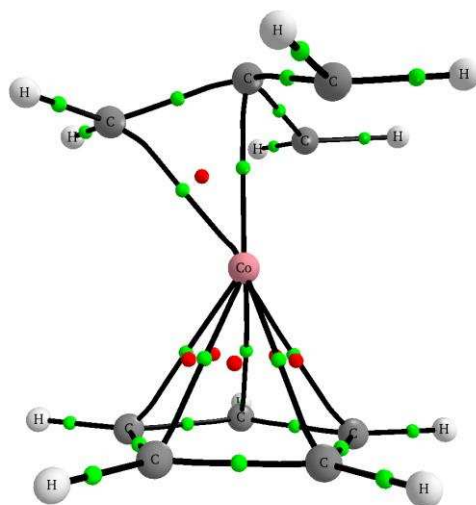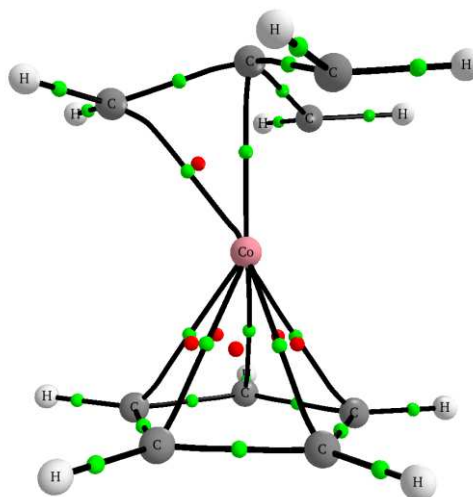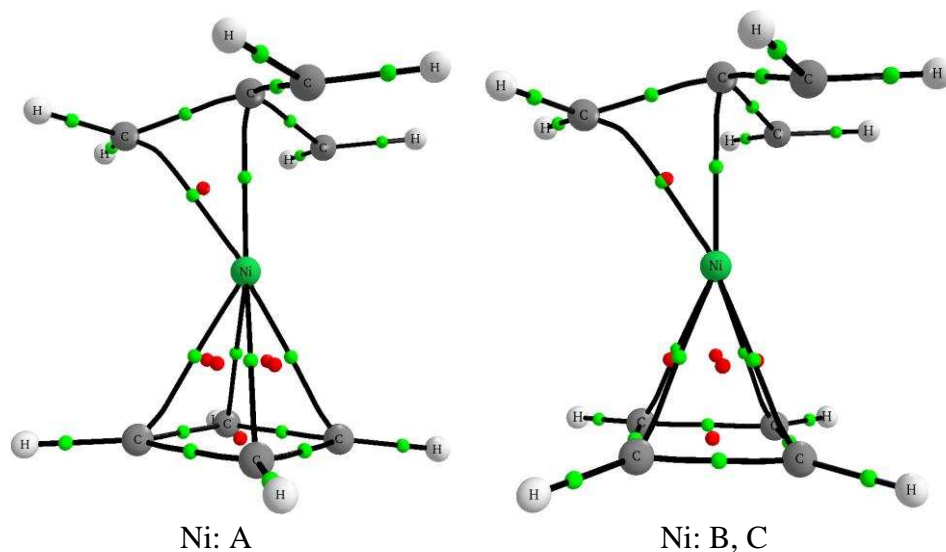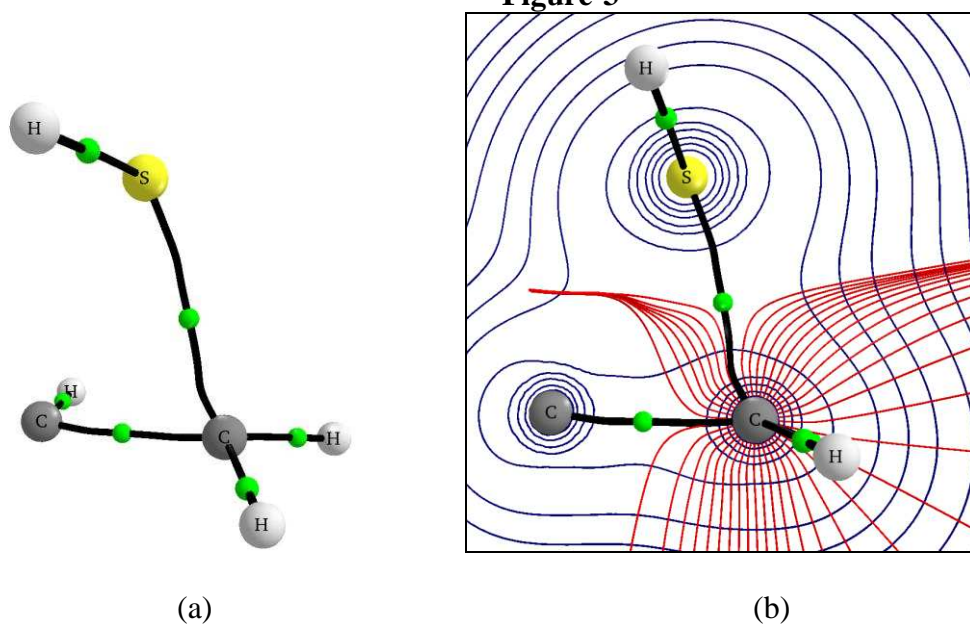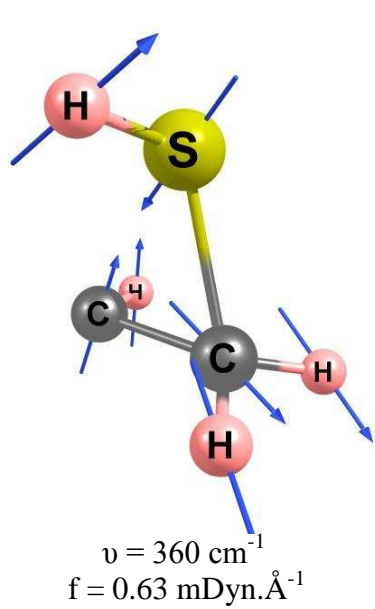
(c)
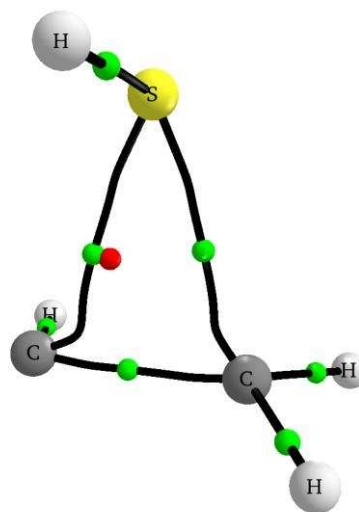
A and B

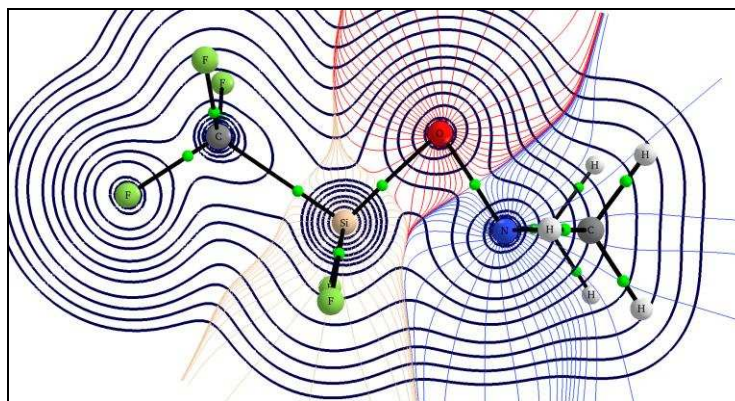(d)

Figure-4

(a)
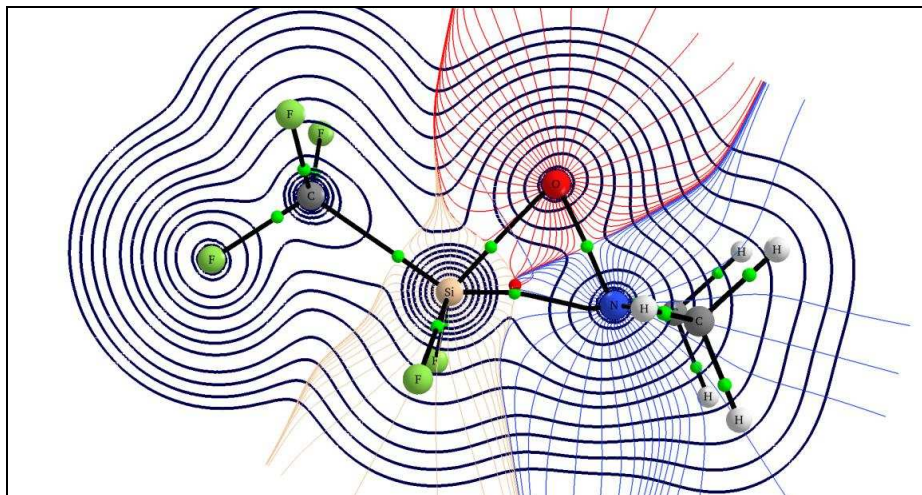

A, B, C

(b)
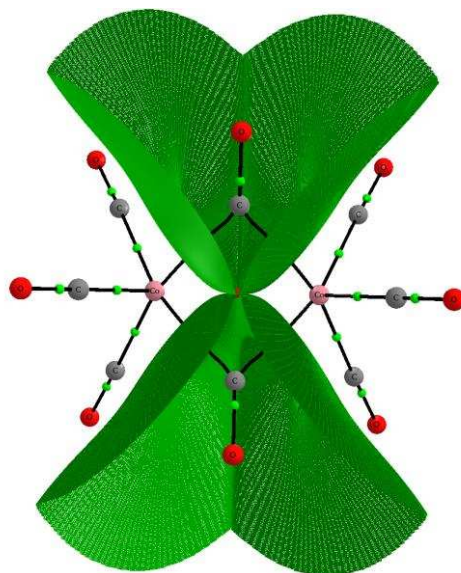
(c)

Figure-5
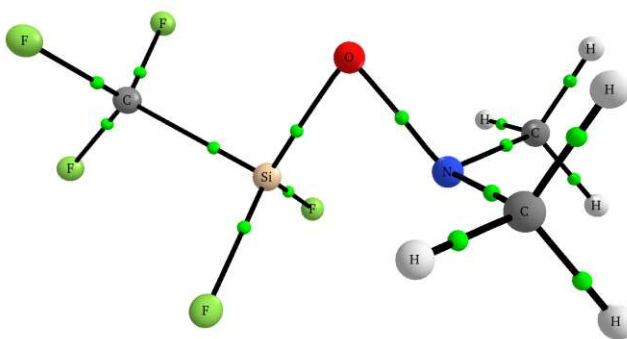
(a)

(b)

(c)

Figure-6

Table of contents

Careful "reinterpretation" of the Quantum Theory of Atoms in Molecules 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 so circumventing conceptual obstacles.