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Do the Structural Changes Defined by the Electron Density Topology Necessarily Affect the Picture of the Bonding?

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The analysis of domain averaged Fermi holes (DAFH) was applied to the elucidation of the nature of the bonding interactions in supported metal carbonyls, where multicenter bonding of the bridging ligands and direct metal−metal bonds are considered as possible alternatives. The main focus is directed on the detailed scrutiny of the possible impact of the changes in the topology of electron density induced by the systematic variation of the geometry of the studied carbonyls on the picture of the bonding provided by the visual description in terms of DAFH analysis. It has been shown that irrespective of the dramatic changes in the topology of electron density exemplified by the existence and/or the lack of direct metal−metal bond path, the DAFH picture of the bonding remains practically unaffected and in all cases consistently suggests that the bonding of the bridging ligands exhibits the typical features of delocalized 3c-2e bonding.

Introduction

There is probably no other concept that contributed to the development of chemistry more remarkably as the ill-defined qualitative tenet of chemical bond. The crucial step in the understanding of the nature of chemical bond was made by G.N. Lewis,[1] whose idea of chemical bond as shared electron pair has provided a key step toward detailed understanding of the classical structural theory and its description of molecular structure in terms of classical structural formulas. The intuitively discovered relation between the chemical bonding and electronic structure of the molecules was put on safe theoretical basis with the advent of the quantum theory, and it is interesting that the very first method of solving the Schrödinger equation, the so-called VB method[2,3] was also straightforwardly based on the idea of electron pairing. It is not therefore surprising that Lewis model does not cease to represent the challenge for the chemical theory and much effort continues to be devoted to its reconciliation with the rigorous quantum theory.[4−26]

One of the problems that to some extent complicate the demonstration of the mutual compatibility of classical and quantum chemical description of chemical structure is the increased complexity of the wave functions generated using

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modern sophisticated computational methods. To overcome the loss of the transparency of the complicated multielectron wave functions, the introduction of new computational methods is being accompanied by the design of auxiliary theoretical tools and procedures allowing to extract the structural information hidden in the wave function and to "back transform" it into the language close to classical chemical thinking. The important role in this respect belongs to the methods providing the analysis of the wave function in real 3D-space.[7,8,18−33] An example in this respect is the topological analysis of the molecular electron density, introduced some time ago by Bader.[23,24] This method, also known as the quantum theory of atoms in molecules (QTAIM), goes far beyond a simple topological study of a scalar field. It rather provides a full consistent quantum mechanical framework for the definition of the atoms or group of atoms in a molecule and for the treatment of the mechanics of their interaction. QTAIM has also resulted in the introduction of such concepts as bond paths and related bond critical points, whose lack or occurrence may be verified experimentally [see ref 34, and ref 35 for review], but whose interpretation and importance for chemical bonding has been[36,37] and continues to be[35,38−43] the source of several controversies.

The main problem in this respect concerns the fact that the *chemical bond*, as intuitively understood by chemists, is neither measurable nor theoretically definable so that it is questionable to relate its presence or absence to the existence or the lack of the bond path and such a conclusion is also straightforwardly corroborated by the recent study by Bader entitled "Bond Paths are not Chemical Bonds" [Bader, R. F. W. *J. Phys. Chem. A* DOI: 10.1021/jp906341r].

To overcome this ambiguity, the QTAIM theory[24,37] puts more emphasis on physical background and interprets the presence of the bond path as sufficient and necessary condition for atoms to be *bonded* to each other. This definition of bond path covers all kind of bonded atoms and implies all type of interactions,[37] from the very weak to the very strong and it is based upon Ehrenfest's and Feynman's theorems of quantum mechanics governing the interactions between atoms.

Irrespective of the importance and of the fundamental physical aspects behind such a definition for two atoms to be bonded to one another, the above criterion still appears not completely free of limitations when translated to common chemical thinking. For instance, it raises the question of how to consider those interactions among pairs of atoms that are characterized by the lack of an associated bond path but that nonetheless display typical features of a bonded interaction exemplified by a significant electron sharing between the corresponding atoms, quantitatively measured by the delocalization index.[44,45] This is typically the case of systems whose structure diagram evolves through a conflict mechanism[24] and for points of the nuclear configuration space in the neighborhood of the conflict catastrophe point. In this case, there will be two alternative pairs of atoms competing for a bond path[46] and despite the extent of electron sharing for the two pairs of atoms will be almost indistinguishable close to the conflict catastrophe point, one pair will be termed as "bonded" and the other one as "not bonded" according to the bond path criterion and to the electron density topology.

Pendas et al.[46] have recently addressed such issues, and the problems commonly raised by what they have termed the "orthodox" interpretation of the bond path, namely, that its occurrence fulfills the sufficient and necessary conditions for two atoms *to be bonded* to one another.[37] Pendas et al.[46] do not deny the fundamental physical tenets of bond paths, but rather suggest to interpret them as privileged exchange channels, a conceptual progress which easily explains why under certain chemical circumstances a bond path may either be present or not despite the existence of a significant electron sharing between two interacting atoms. This interpretation is strongly supported by the interesting observation that when two pairs of atoms are competing for a bond path, the pair found to be linked by a bond path is always the one with prevailing contribution of exchange energy density.[46] Indeed, it was found that for systems evolving through conflict mechanisms, the exchange energy curves of two competing pairs cross almost exactly at the conflict catastrophe point, where a switch from a bond path linking one pair to one linking the other pair precisely occurs.[46]

Other examples which enlighten the limitations of the orthodox interpretation of a bond path, when this is translated to common chemical thinking, concern the bonding in supported metal carbonyls and the general phenomenon of multicenter bonding.[47,48]

The search for metal−metal bond path has often been invoked in the literature to decide the question of the existence or lack of a direct metal−metal bond. The validity of such a "proof" has been, however, seriously questioned by the observed sensitivity of the topological analysis of electron density to the choice of the computational methods used owing to which the presence or absence of metal−metal bonds in such cases is more related to subtle computational details rather than to the firm existence or lack of the corresponding bond path.[49] Moreover, it has been shown that the extent of electron sharing (delocalization index) between the metal atoms in unsupported binuclear metal carbonyls may be comparable or even smaller than in the corresponding bridged carbonyl compounds, despite the

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metal atoms are found to be linked by a bond path in the former but not in the latter systems.[27]

The lack of a direct detection of multicenter bonding with the bond path criterion is also closely tied with the problem of the classification of the bonding interactions in supported metal carbonyls, where the multicenter bonding of the bridging ligands and direct metal−metal bonds are considered as the possible alternatives[49−52] and the final picture of the bonding depends in any particular case on the delicate balance between the above two alternative bonding modes.[27,52] Using the interpretation of Pendas et al.,[46] this is a delicate case of exchange energy competition; one between the occurrence of bond paths linking the metal to the bridged carbonyl ligands or the contemporary presence of both the metal−ligands and the metal−metal bond paths. Analysis of the delocalization indices for the various atomic pairs involved in the multicenter interaction (or of the corresponding exchange energies) can provide useful insights on such an interaction.[27,52]

Yet a new impetus for the study of the bonding interactions in supported metal carbonyls has recently come from the analysis of the so-called domain averaged Fermi holes.[28−32,53,54] This analysis that represents a new approach to the visualization of the bonding interactions in 3-D space opens, namely, the possibility of direct detection of both metal−metal and multicenter bonding and its applications in the case of supported carbonyls $Fe_2(CO)_9$ and $Co_2(CO)_8$[53] has seriously questioned the existence of direct metal−metal bond and suggested that the binding of the bridging ligands involves multicenter (3c-2e) bonding.

As, however, the relative role of metal−metal and multicenter bonding can to considerable extent be affected by the geometrical structure of the corresponding species, especially by the distance between metal atoms, and the variation of molecular geometry is known to induce the changes in the topology of electron density, it was of interest to check whether or to what extent the picture of the bonding provided by earlier DAFH study[53] of the bonding interactions in $Fe_2(CO)_9$ and $Co_2(CO)_8$ can be affected by the systematic variation of molecular geometry. For this purpose we report in this study the detailed comparison of the QTAIM and DAFH analysis for two supported metal carbonyls, namely, $Fe_2(CO)_9$ and $Co_2(CO)_8$ in which we systematically varied the interatomic distance between the metals under the constraint of keeping the symmetry of the molecule (D_{3h} and C_{2v}, respectively).

We also supplement such study with the evaluation of the delocalization indices[44,45] for the same systems and at the same geometries used in the DAFH analysis. These indices, even when defined over QTAIM atomic basins,[45] have shown to provide a continuous description of bonding evolution with geometry changes,[27,52] which is to be contrasted with the possible discontinuous picture of structural evolution unavoidably inherent to the bond path criterion.

Theoretical

The analysis of domain averaged Fermi holes (DAFH), suggested some time ago as a generalization of the original concept of Fermi hole by Wigner and Seitz,[55] has proved as a new practical tool for the description and the elucidation of the bonding interactions especially in molecules with a nontrivial bonding pattern like hypervalence, multicenter bonding, metal−metal bonding, and so forth. Reported applications of this approach have demonstrated its usefulness for appealing, highly visual description of the bonding interactions in terms close to classical chemical thinking. As the formalism of the analysis was repeatedly described in earlier studies,[28−32] we confine ourselves to only a brief recapitulation of the basic ideas to the extent necessary for the purpose of this study. The most straightforward introduction of DAFH is via the appropriate integration of the so-called pair correlation function[56] (eq 1).

$$C(r_1, r_2) = 2\rho(r_1, r_2) - \rho(r_1)\,\rho(r_2)$$

$$\begin{aligned} g_\Omega(r_1) &= -\int_\Omega C(r_1, r_2)\,\mathrm{d}r_2 \\ &= \rho(r_1)\int_\Omega \rho(r_2)\,\mathrm{d}r_2 - 2\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2 \end{aligned} \qquad (1)$$

In this equation $\rho(r_1,r_2)$ and $\rho(r_1)$ denote the pair and ordinary first order density, respectively, and the integration is over the finite domain of ordinary space Ω. In previous studies we have shown that especially interesting and chemically relevant information can be extracted from these holes if the domain Ω is identified with the Bader atomic domains resulting from the virial partitioning of the electron density. In this case, the holes provide the information about the valence state of the corresponding atoms in the molecule. Generated and analyzed can be, however, also the holes averaged over more complex domains formed by the union of several atomic domains corresponding, for example, to various functional groups or interesting molecular fragments. In such a case the analysis reveals the electron pairs (chemical bonds, lone pairs, etc.) that remain intact in the corresponding fragment, as well as the broken or dangling valences formed by formal splitting of the bonds required for the isolation of the fragment from the rest of the molecule.

The simplest situation is in the case of the Hartree−Fock approximation, where due to the possibility of constructing the pair densities from the first order density matrix, the general formula eq 1 reduces to eq 2

$$g_\Omega(r_1) = 2\sum_i^{occ}\sum_j^{occ} \langle \varphi_i|\varphi_j\rangle_\Omega \varphi_i(r_1)\,\varphi_j(r_1) \qquad (2)$$

where the corresponding matrix elements can be identified with the elements of the so-called atomic overlap matrix (AOM) defined over the QTAIM domain, eq 3,

$$\langle \varphi_i|\varphi_j\rangle_\Omega = \int_\Omega \varphi_i(r)\,\varphi_j(r)\,\mathrm{d}r \qquad (3)$$

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In this connection it is, however, interesting to mention, that because of the close formal similarity of Hartree–Fock and Kohn–Sham wave functions, the formula eq 3 can formally be used also at the DFT level of the theory which is of our concern here.

The analysis consists in the first step in the diagonalization of the matrix that represents the hole eq 1 in appropriate basis. The eigenvalues and eigenvectors resulting from this primary diagonalization are then, in the second step, subjected to the so-called isopycnic transformation,[57] whose goal is to transform the original DAFH eigenvectors that, like the canonical MOs are often delocalized over the whole molecule, into more localized functions reminiscent of classical chemical bonds, lone pairs, and so forth. The structural information is then being extracted from the numerical values of the resulting transformed eigenvalues and the interpretation is greatly facilitated by the visual inspection of the associated localized eigenvectors. Thus, for example, the eigenvectors associated with the eigenvalues close to 2 typically correspond to electron pairs of chemical bonds, lone pairs, and so forth. Similarly the broken valences are generally identified with the localized functions associated for nonpolar bonds, characteristic of ideal sharing of the bonding electron pair, with the eigenvalues close to 1. On the other hand, the formal splitting of polar bonds results in the free valences whose associated eigenvalues can often significantly deviate from unity, and the extent of the deviations from this ideal value then provides the information about the contributions of individual atoms to the unevenly shared electron pair of the corresponding bond.

Computations

The calculations required in this study are of two types. The first one comprises the generation of the reliable wave functions of the studied molecules. This usually involves the complete optimization of the geometry of the corresponding species at the chosen level of the theory.The generated wave functions are then used to determine the corresponding electron densities and Fermi holes, which are then, in the second step subjected to QTAIM and/or DAFH analysis. As, however, the main focus of this study was to confront the visual picture of the bonding provided by DAFH analysis with the changes in the topology of electron density induced by the slight deviations of the molecular geometry in the vicinity of the minimum on the potential energy hypersurface, the above general scenario was modified, and the wave functions were generated also for several non-equilibrium structures characteristic of different metal–metal distance [The geometries of these species are provided in the Supporting Information]. These calculations were performed using Gaussian 98 program[58] at the same B3LYP/LANL2DZ level of the theory used in a previous study,[53] in which the approximate Mulliken-like form of DAFH analysis was used. This approximation concerns the determination of the integrals over the AIM domains, whose calculation via explicit integration was replaced by a Mulliken-like approximation, according to which the electron is in the domain of a certain atom, if it is in an orbital localized on that atom. The main reason for the use of this approximation was that the ECP basis sets, often used in the calculation of transition metal systems, are known to produce the electron densities, whose integration is not always straightforward.[59,60] In such a case the approximate DAFH analysis represents a relatively simple and feasible alternative. Nevertheless, the resolution of these numerical problems using refined integration techniques allowed us in this study to overcome the above limitation and to perform the analysis using an "exact" AIM generalized approach enabling the straightforward comparison both with the traditional QTAIM theory and also with the earlier study[53] based on alternative approximate approach. The DAFH analysis was performed using our own program WinBader which is available upon request, and the traditional QTAIM analysis of the topology of electron density was performed using the PROAIM program (PROAIMV, Version (94, revision B).

Results and Discussion

$Fe_2(CO)_9$. Before reporting the results of the effects of the systematic variation of the interatomic Fe···Fe distance on the picture of the bonding in the studied iron carbonyl, it is first useful to review briefly the results of the previous DAFH study[53] dealing with the analysis of bonding interactions in the ground state equilibrium geometry of this molecule using the approximate Mulliken-like approach. As the complete analysis can be found in the study,[53] we focus here only on the brief discussion of electron pairs involved in the bonding of the bridging ligands. Consistent with the qualitative predictions of the isolobal analogy,[61,62] the DAFH analysis suggests that the bonding of these ligands involves 5 electron pairs whose role in the bonding can straightforwardly be revealed by the inspection of associated DAFH eigenvectors. (Figure 1 left column). The inspection of this Figure shows that 4 out of the 5 bonding electron pairs are involved in localized 2c-2e bonding of two bridging ligands, while the remaining ligand is bonded via a delocalized electron pair with the character of 3c-2e bond. As, however, such a localized description is not compatible with the 3-fold symmetry of the $Fe(CO)_9Fe$ fragment, the final picture of the bonding requires to take into account the resonance of three limiting structures as suggested in the Scheme 1.

As a consequence, each of the $Fe-C_b$ bonds slightly looses the character of localized 2c-2e bonds and as, moreover, the above resonance also assumes the uniform distribution of the electron pair associated with 3c-2e bonding among all three $Fe-C_b-Fe$ bridges, the bonding of the bridging ligands exhibits strongly delocalized character. This result is very important not only because the delocalized multicenter character of the bonding of the bridging ligands is completely consistent with the conclusions of previous theoretical analyses of orbital

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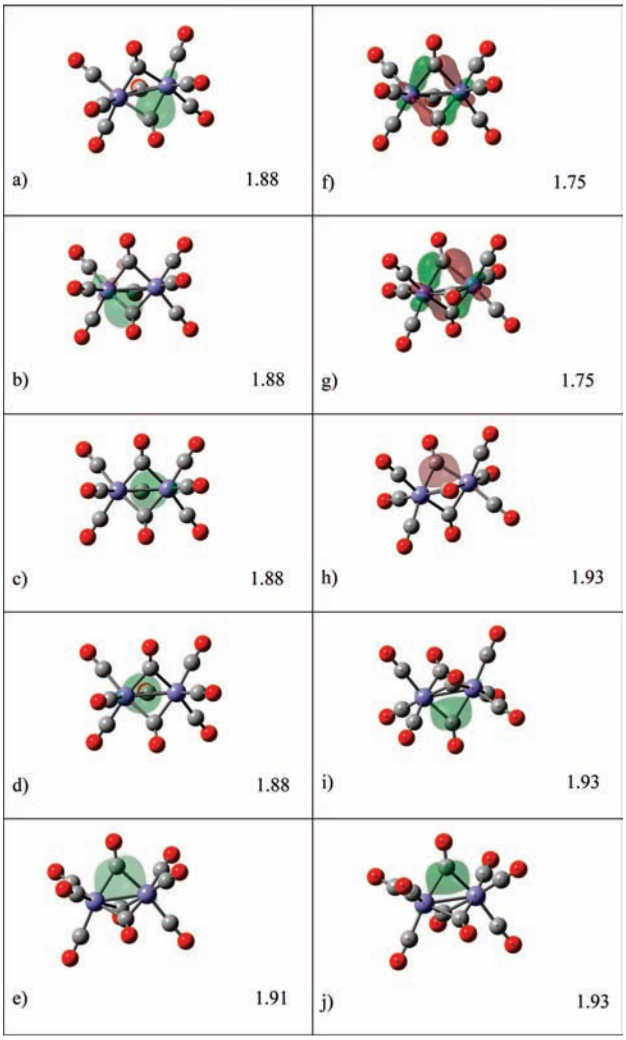

Figure 1. Picture of the bonding provided by the approximate and "exact" DAFH analysis (left and right columns, respectively) for the equilibrium geometry of $Fe_2(CO)_9$. Eigenvectors corresponding to the electron pairs involved in the bonding of the bridging ligands for the hole averaged over the $Fe(CO)_3Fe$ fragment. The numbers indicate the populations of the corresponding eigenvectors (pictures were generated using GaussView program).

interaction diagrams[63-65] but also because the existence of the delocalization reflected in the above resonance scheme can be straightforwardly demonstrated by the comparison of the delocalization indices, whose values for the bridging Fe$-$C$_b$ bonds are considerably lower than the analogous values for the well localized 2c-2e Fe$-$C bonds with terminal ligands (0.596 vs 0.956 respectively). In addition to inducing the delocalized character of the bonding of the bridging metal$-$ligand bond, there is yet another important consquence of the above resonance scheme, namely, the lack of direct metal$-$metal bond. Also this result is very important as the above conclusion of DAFH analysis apparently contradicts the anticipations of 18-electron rule[66] and also the conclusions of several earlier studies,[49,50] in which the authors advocate for the existence of "some, albeit weak Fe···Fe bond" and corroborate their conclusions by invoking the incomplete cancelation of the repulsive and attractive interactions between the metal atoms. Although we do not deny the existence of such interactions, which is reflected in the non-vanishing values of the corresponding delocalization index (δ(Fe,Fe) = 0.252), the picture of the bonding emerging from DAFH analysis rather suggests a slightly different intepretation according to which the non-vanishing Fe···Fe bond index reflects the existence of residual interactions associated with the 3c-2e character of the bonding of the bridging ligands. As demonstrated, namely, in the study,[67] the existence of 3c-2e bonding in an A$-$B$-$C fragment requires the existence of non-vanishing bond orders (bond indices) between all the pairs of atoms so that the non-vanishing Fe···Fe bond indices just represents an important prerequisite enabling the existence of multicenter 3c-2e character of the bonding of the bridging ligands as detected in the DAFH analysis. In addition to the above arguments, the interpretation of non-vanishing Fe···Fe interactions as being due to "some, albeit weak" Fe···Fe bond is also questionable for another reason. In our opinion, for any interaction to be classified as "chemical bond", it must be possible to associate it with an electron pair, but as it is clearly evident from the DAFH analysis, there is no electron pair that could be associated with the Fe···Fe bond. Such a conclusion is also completely consistent with the description of the structure of the above carbonyl in terms of localized molecular orbitals. Such a description reveals, in complete agreement with the anticipations of isolobal analogy, the existence of just 5 bonding electron pairs involved in the bonding of the bridging ligands, and their inspection shows that there is no such orbital (electron pair) corresponding to a direct Fe···Fe bond.

Although the absence of direct metal$-$metal bond is also corroborated by the lack of the corresponding bond path[49,68,69] the fact that the DAFH analysis was performed using the approximate Mulliken-like approach makes its confrontation with the traditional AIM analyses questionable. This limitation is overcome in the present study where the results of the QTAIM approach are straightforwardly compared to the appealing picture of the bonding provided by DAFH analysis using the "exact" QTAIM generalized form of this approach. The main advantage of such a level of comparison between the two approaches is that it not only allows to reveal any eventual bias of the picture of the bonding emerging from the approximate DAFH analysis, but also to contrast the observed sensitivity of topology of electron density to the variations of molecular geometries[23,24,46] with the possible, but not compulsorily large, resulting changes in the DAFH picture of bonding.

Before reporting on these changes with geometry, we focus first on the comparison of the differences emerging from the approximate and the "exact" DAFH analysis for the ground state equilibrium geometry of $Fe_2(CO)_9$.

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Scheme 1

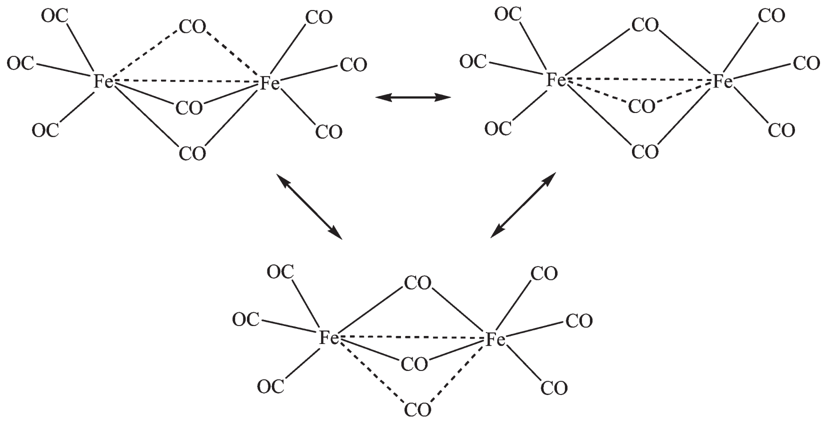

Table 1. Variation of the Topology of Electron Density and of the Metal−Metal (M−M) and Metal−Carbon (M-C_{bridge}) Delocalization Indices, δ, with Increasing Metal−Metal Distance in $Fe_2(CO)_9$ and $Co_2(CO)_8$

$M_2(CO)_x$, symmetry	M−M interatomic distance (Å)	nature of BCP	δ(M,M)	δ(M,C_{bridge})
$Fe_2(CO)_9$, D_{3h}	2.3	(3,-1)	0.358	0.631
	2.4	(3,-1)	0.328	0.618
	2.524 (equil)	(3,+3)	0.299	0.596
	2.6	(3,+3)	0.284	0.581
$Co_2(CO)_8$, C_{2v}	2.3	(3,-1)	0.424	0.672
	2.4	(3, +1)	0.376	0.665
	2.545 (equil)	(3,+1)	0.317	0.653
	2.6	(3,+1)	0.295	0.648
	2.7	(3,+1)	0.263	0.636

For the sake of comparison, the “exact” DAFH analysis was performed at the same B3LYP/LANL2DZ level of the theory as in the study,[53] and the resulting 5 electron pairs responsible for the bonding of the bridging ligands are also summarized in the Figure 1 (right column). The comparison of left and right columns of this figure shows that although the switch from the approximate Mulliken-like to the “exact” AIM generalized description does affect the shape of the corresponding DAFH eigenvectors, the impact of these changes for the final picture of the bonding of the bridging ligands is rather of quantitative than of qualitative character. The inspection of the Figure 1 shows, namely, that in addition to denying the absence of direct Fe···Fe bond, both approaches consistently imply strongly delocalized character of the bonding of the bridging ligands, so that finally the main difference between the two descriptions is that the “exact” approach attributes more importance to multicenter 3c-2e bonding of the bridging ligands.

After having demonstrated the picture of the bonding for the equilibrium geometry of $Fe_2(CO)_9$, we now focus on how the changes in the topology of the electron density induced by the systematic variation of Fe···Fe distance impact on the DAFH picture of the bonding of the corresponding distorted species. The results of a QTAIM analysis of the electron density for several species with the Fe···Fe distance ranging between 2.3 to 2.6 Å are summarized in Table 1. At shorter interatomic distances the QTAIM analysis detects the existence of metal−metal bond path and of the corresponding (3,-1) bond critical point in the middle of the M−M internuclear axis, while further increase in the M−M distance leads to the change in the character of this critical points to (3, +3) (cage critical point) and to the loss of the M−M bond path. In view of this result it was of interest to see whether or to what extent the above changes in the electron density topology and associated structure are also accompanied by the changes in the chemical bonding features of the corresponding species. For this purpose we report in Figure 2 the comparison of the picture of the bonding provided by the “exact” DAFH analysis for distorted iron carbonyls with the Fe···Fe distances of 2.3 Å, 2.524 Å (equilibrium geometry), and 2.6 Å. The inspection of this figure shows that despite dramatic change in the structure as dictated by the topology of electron density, the systematic variation of interatomic Fe···Fe distance has no effect on the form of the corresponding DAFH eigenvectors, and only slight variations are observed in the associated eigenvalues, so that the picture of the bonding, as revealed by the DAFH analysis remains in all cases the same. Not unexpectedly, also the trend of the Fe−Fe and Fe−C_{bridge} delocalization indices with changing Fe···Fe distance complies with the corresponding DAFH variations. Table 1 shows that both delocalization indices, although decreasing with increasing Fe···Fe distance, undergo smooth and marginal changes, with that between the two metal atoms, δ(Fe,Fe), being almost one-half that between a metal and a bridging carbon, δ(Fe, C_{bridge}). Indeed, the ratio between the two indices slightly decreases from 0.56 down to 0.48 along the investigated range of Fe−Fe distances.

As it will be shown, similar discrepancies between the detected changes in the topology of electron density and the actual picture of the bonding are not exceptional and can be observed also for other supported metal carbonyls as, for example, the $Co_2(CO)_8$.

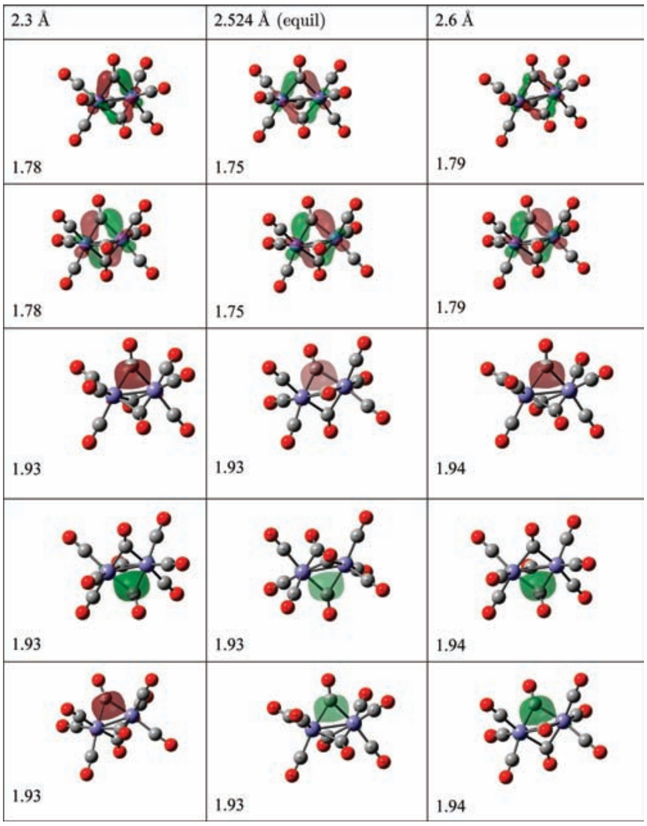

Figure 2. Comparison of DAFH eigenvectors resulting from the "exact" AIM generalized form of the analysis for the systematic variation of Fe···Fe distance in $Fe_2(CO)_9$. Displayed pictures correspond to 5 bonding electron pairs involved in the bonding of the bridging ligands.

$Co_2(CO)_8$. As a second example demonstrating the effect of the systematic variation of the topology of electron density on the picture of the bonding in supported metal carbonyls we report below the comparison of traditional AIM and "exact" DAFH analysis for $Co_2(CO)_8$ in which the metal−metal distance was varied between 2.3 Å to 2.7 Å [The geometries of the corresponding species are again provided in the Supporting Information]. Before reporting the results of such a comparison, we again briefly review, similarly as in the case of $Fe_2(CO)_9$, the picture of the bonding emerging from the earlier approximate Mulliken-like DAFH analysis[53] for the equilibrium structure of the cobalt carbonyl. For the sake of straightforward comparison with the previous study,[53] in which the equilibrium structure of this carbonyl was analyzed using the approximate DAFH analysis, the present "exact" approach has been performed at the same B3LYP/LANL2DZ level of the theory. The comparison of the picture of the bonding provided by the aproximate and exact DAFH approach is summarized in Fig. 3. The comparison shows again the close resemblance of both descriptions, that is reflected not only in denying the existence of direct metal−metal bond but also in suggesting the strongly delocalized character of the bonding of the bridging ligands. The main difference, again rather of quantitative than qualitative nature, is thus that in the approximate description one of the ligands is bonded via two ordinary localized 2c-2e bonds and that the bonding of the second ligand has the character of a 3c-2e bond as suggested in the Scheme 2, whereas the exact description attributes, similarly as in the case of iron carbonyls, more importance to the 3c-2e bonding.

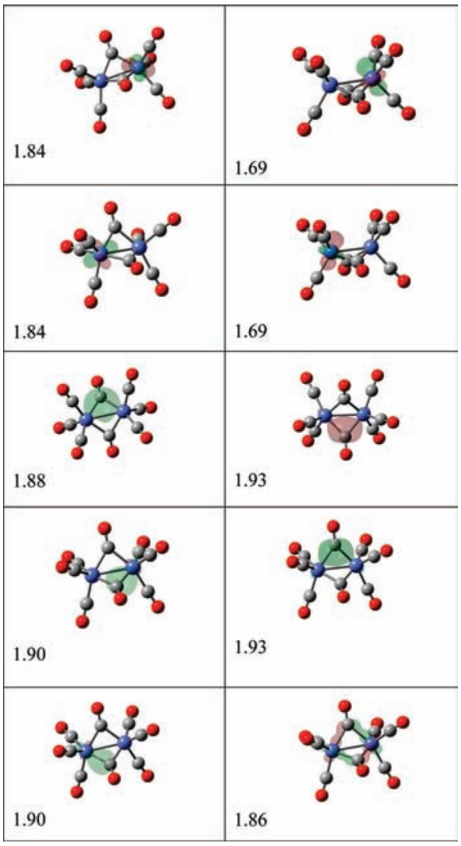

Figure 3. Picture of the bonding provided by the approximate and "exact" DAFH analysis (left and right columns, respectively) for the equilibrium geometry of $Co_2(CO)_8$. Eigenvectors corresponding to the electron pairs involved in the bonding of the bridging ligands for the hole averaged over the $Co(CO)_2Co$ fragment. The numbers indicate the populations of the corresponding eigenvectors.

The delocalized character of the bonding of the bridging ligands can be again, similarly as in the previous case of diiron nonacarbonyl demonstrated by the values of the delocalization indices $\delta(Co,C)$ of metal−ligand bonds, whose values for well localized terminal bonds are again considerably higher (($\delta(Co,C_{term}) = 0.904$) than for the bonds to the bridging ligands ($\delta(Co,C_{term}) = 0.653$). In addition to the above numerical evidence, the existence of the extensive delocalization of the bonding of the bridging ligands, as well as the concomitant lack of direct Co−Co bond, is also straightforwardly consistent with the absence of a Co···Co bond path,[70] and no indication of such a bond has been reported also in the more recent study[71] based on orbital resolution of charge density analysis.

After demonstrating the close resemblance of the exact and approximate DAFH description on the picture of the bonding in the equilibrium structure of $Co_2(CO)_8$, we now focus on the systematic scrutiny of the effect of the systematic variation of interatomic Co···Co distance on the structure of the corresponding distorted species.

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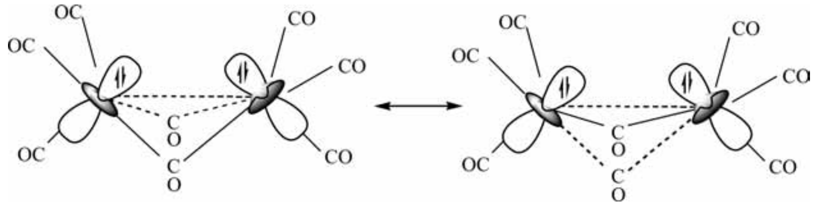
Scheme 2



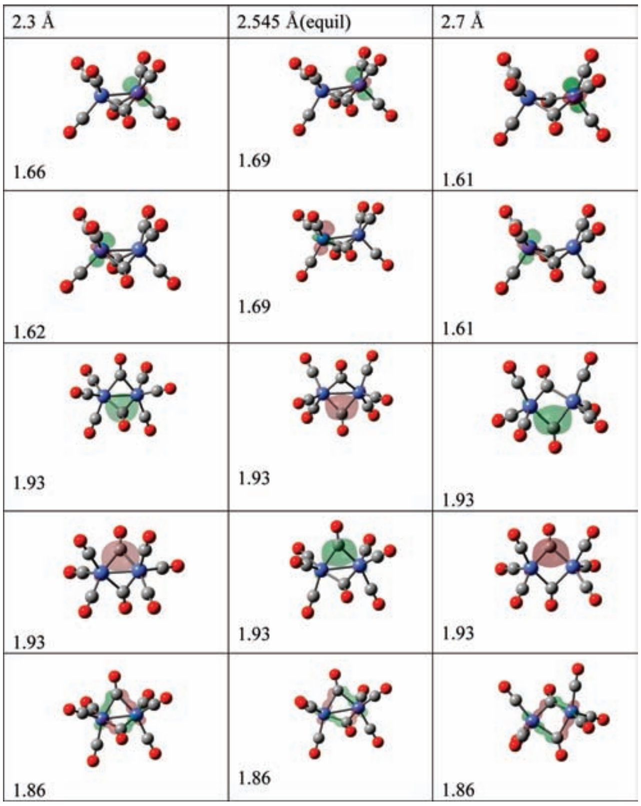


Figure 4. Comparison of DAFH eigenvectors resulting from the "exact" AIM generalized form of the analysis for the systematic variation of Co···Co distance in $Co_2(CO)_8$. Displayed pictures correspond to 5 bonding electron pairs involved in the bonding of the bridging ligands.

The impact of the systematic structural variation on the topology of electron density in the corresponding species is summarized in Table 1. Similarly as in the case of diiron nonacarbonyl, the elongation of the internuclear metal−metal distance is accompanied by the dramatic change of the nature of the critical point in the middle of the M−M internuclear axis. While for short distance (2.3 Å) the QTAIM analysis detects the existence of metal−metal bond path and the corresponding critical point has the character of ordinary (3,-1) bond critical point, for longer distance the nature of the critical point changes to (3,+1) ring critical point and the M−M bond path vanishes. The situation is, however, quite different for the DAFH analysis which remains remarkably insensitive to the above change of topological structure, and the resulting picture of the bonding for all studied Co···Co distances is practically the same. (Figure 4).

Inspection of this Figure shows that even for the shortest Co···Co distances, where the QTAIM analysis detects the existence of the bond path, the DAFH approach denies the existence of direct metal−metal bond and, similarly as in the case of $Fe_2(CO)_9$, suggests that irrespective of the actual M−M distance the bonding of the bridging ligands has the character of delocalized 3c-2e bonding. Similar insensivity of the picture of the bonding to the variation of M−M interatomic distances emerges also from the trend of delocalization indices, δ(Co,Co) and δ(Co,C_{bridge}) (Table 1). Both delocalization indices decrease smoothly with increasing metal−metal distance, with δ(Co,Co) being always much smaller than δ(Co, C_{bridge}). We note, however, that the ratio between the two delocalization indices undergoes a larger variation with metal−metal distance increase than found for $Fe_2(CO)_9$.

Conclusions

The main general conclusion from our work is the observed lack of the straightforward link between the structure description dictated by the topology of electron density and the picture of bonding as obtained from an analysis of bonding descriptors defined in terms of the exchange part of the pair density (DAFH and delocalization indices). This seems to imply that the orthodox QTAIM interpretation of the bond path and of the resulting structure is unable to cope with other bonding descriptions, also based on well-defined physical quantities. The real problem here is the dramatic difference in the nature of both types of description. While the traditional QTAIM analysis reflects the structural variation using often discontinuous changes of the topology of electron density, the effect of the same structural variation on the picture of the bonding provided both by the DAFH analysis and the delocalization indices rather has a character of small continuous changes characteristic for the smooth variation of the exchange part of the pair density. A possible way to reconcile the two visions is to accept to complement the orthodox interpretation of the bond path with its view as a privileged exchange energy channel.[46] Another attempt at revealing deeper insights into the link between the topology of electron density and the nature of the bonding interactions is represented, for example, by the recent study by Zhang et al.[72] in which the traditional interpretation of QTAIM characteristics as, for example, the density at the bond critical point and/or laplacian of electron density has been discussed using the partitioning of electron density into covalent and ionic components.

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Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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