Restoring orbital thinking from real space descriptions: bonding in classical and non-classical transition metal carbonyls

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A combined strategy that unifies our interacting quantum atoms approach (IQA), a chemically intuitive energetic perspective within the quantum theory of atoms in molecules (QTAIM), the domain natural orbitals obtained by the diagonalization of the charge-weighted domain-averaged Fermi hole (DAFH), and the statistical analyses of chemical bonding provided by the electron number distribution functions (EDF) is presented. As shown, it allows for recovering traditional orbital images from the orbital invariant descriptions of QTAIM. It does also provide bonding indices (like bond orders) and bond energetics, all in a per orbital basis, still invariant manner, using a single unified framework. The procedure is applied to show how the Dewar, Chatt, and Ducanson model of bonding in simple transition metal carbonyls may be recovered in the real space. The balance between the number of σ-donated and π-backdonated electrons is negative in classical compounds and positive in non-classical ones. The energetic strength of backdonation is, however, smaller than that of donation. Our technique surpasses conventional orbital models by providing physically sound, quantitative energetics of chemical bonds (or interactions) together with effective one-electron pictures, all for arbitrary wavefunctions.

1. Introduction

The vast majority of the concepts related to chemical bonding that we may find in a practicing chemist’s toolkit stem from the orbital model. Orbitals are easy to parameterize, and orbital-based explanations have reached a high degree of predictivity over the years.1 However, any of such explanations is necessarily not invariant under general transformations that however preserve the wavefunction. This undesirable dependence is absent in real space theories of chemical bonding, which extract chemical information from invariant reduced density matrices. Many of them use the topology of a scalar field to partition the space into regions which are endowed with intuitive chemical meaning, for instance, the quantum atoms from the Quantum Theory of Atoms in Molecules (QTAIM),2 or the core, bonding, and lone pair basins obtained from the electron localization function (ELF) of Becke and Edgecombe.3

As a whole, these methods are becoming increasingly preferred over orbital based ones to analyze chemical bonding issues.

A salient feature of the QTAIM is that it provides not only a wealth of bonding indices by examining well defined scalars at a finite set of distinguished points (the critical points of the ρ scalar field), but that it allows for exact partitions of the molecular energy. Bonding and binding (cohesion) may then be examined on the same footing. Our Interacting Quantum Atoms approach (IQA)4–8 has been shown to provide a chemically appealing framework which unifies the standard QTAIM with a general theory of cohesion valid for any molecular geometry. In IQA, every pair of QTAIM quantum atoms interact among themselves, and on doing so their proper energies (self-energies) are altered. Binding appears as a competition between the promotion energy (deformation energy or self-energy change) of the atoms which is usually destabilizing, and their interatomic interaction energies, usually stabilizing. The interaction energies come from adding classical (or ionic-like), and quantum mechanical (or covalent-like) terms. IQA has been applied to shed light on a number of problems in chemical bonding.9–13 and we have recently analyzed the M–CO link in both classical and non-classical carbonyls.14

However elegant these procedures may be, the penetration of real space reasonings in the chemical literature depends on the ability of the new methodologies to recast the orbital language into the new formalism without losing predictive
power. This enterprise has not yet succeeded entirely, and the QTAIM, for instance, still lacks the predictivity of standard orbital-based models.

A possible way out of this situation is allowing the chemist to still use the deeply rooted orbital models within real space theories by endowing them with a one-electron operating mode. This may be done by reintroducing effective domain-averaged one-electron descriptions from purely invariant objects. These effective electrons may then be safely used to decompose our IQA atomic or interatomic quantities into orbital contributions, thus restoring orbital thinking from real space descriptions. In this work we develop such a strategy combining the IQA approach with the domain-averaged Fermi hole (DAFH) perspective introduced by Ponec.\textsuperscript{15,16} We have recently shown\textsuperscript{17} that a link exists between the DAFHs and the electron number distribution functions (EDFs)\textsuperscript{15,18–20} that provide the statistics of the electron population among different basins. This link shows that the DAFHs and their effective one electron functions are intimately linked to bonding concepts.

Our purpose in this paper is twofold. On the one hand, we will briefly present our IQA/DAFH/EDF combined strategy. On the other, we will apply it to show how to recover the Dewar, Chatt, and Duncanson model\textsuperscript{21,22} (DCD) of organometallic chemistry in simple carbonyls that is taken as a successful example of insights provided by orbital-based models.

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In the above expressions, $N_{\Omega}$ is the electron population of basin $\Omega$, $\lambda^{\Omega}$ is $\Omega$’s localization index, a measure of the number of electrons that do not delocalize to other regions of space, and $\delta^{\Omega,\Omega'}$ is $\Omega$’s localization index between basins $\Omega$ and $\Omega'$, a standard measure of the covalent bond order in real space techniques.\textsuperscript{26}

Effective one-electron functions may be defined by diagonalizing the DAFH on the basis of occupied orbitals.\textsuperscript{15,16} In this way, $G^2(r) = \sum_{\ell\mu} \mu_{\ell}(\phi_{\ell\mu}(r))^2$, the $\phi_{\ell}$’s being one-electron functions or domain natural orbitals (DNOs), and the $n$’s a set of occupation numbers that reconstruct by summation $N_{\Omega}$. A nice link (exact for single determinant descriptions) between these DNOs, their occupation numbers, and the statistics of domain electron population exists.\textsuperscript{17} It establishes that the effective electrons described by the DNOs are statistically independent, so that $\rho_{\ell}(r) = \frac{1}{n_{\ell}}$, the probability of finding exactly $n_{\ell}$ electrons in basin $\Omega$, and $n_{\ell'} = N - n_{\Omega}$ electrons in basin $\Omega' = \mathbb{B} - \Omega$ is given by a binomial distribution constructed from a set of $N$ independent events (or coin tosses). Each of the electrons, described by one different $\phi_{\ell}$ has a probability $p(\Omega) = n_{\ell}/\lambda^{\Omega}$ of being found in basin $\Omega$ (so that $p(\Omega') = 1 - n_{\ell}$). We should notice\textsuperscript{17} that...
the statistics of basin electron populations is intimately linked to electron localization and delocalization, and thus to chemical bonding.24,25

The DNOs obtained for a given basin \( \Omega \) come out in three basic flavors. Each \( \phi_i \) may be either extremely localized in \( \Omega \), with \( n_i \approx 1 \), extremely localized in \( \Omega' \), with \( n_i \approx 0 \), or partially delocalized between both, with an extreme case being \( n_i = 0.5 \). DNOs are neither strictly localized orbitals (even though many of them are in fact localized in one basin), nor delocalized functions (even though some of them may be very delocalized). We prefer to use the term adaptive, for them, which reflects their more general nature more faithfully. It is easy to show that DNOs display the local symmetry of the \( \Omega \) basin. In high symmetry situations this property is undesirable, and it is customary to break it by performing an isopycnic localization.27

This is a linear transformation, non-unitary, in general, that bonding orbitals only appear from valence canonical functions, recovering textbook ideas. Mostly, any bonding orbital is only delocalized between two basins, but sometimes it covers non-negligibly the space of several. This allows for a simple real space mapping of multireference bonding concepts, which have sometimes been said to lie beyond the QTAIM. \( \delta \)'s are easy to generalize to what are called multireference delocalization indices,28–33 which quantify the bond order associated to \( n \)-center links. These indices might also be used to define easy to compute quantities which correlate with back-bonding in more complex contexts. For instance, simple two-center metal–carbon delocalizations will fail to separate \( \sigma \) and \( \pi \) contributions in side on metal–olefin coordination complexes. We will pursue this issue in future publications.

Eqn (2) may also be rewritten in terms of DAFH orbitals. Considering a closed-shell single determinant for simplicity,

\[
\rho_{xc}(r_1, r_2) = 4 \sum_{ij} \phi_i(r_1) \phi_j^*(r_2) \rho_{ij} \phi_j(r_2),
\]

\[
V_{xc}^{\Omega,\Omega'} = 4 \sum_{ij} \rho_{ij} \frac{\phi_i(r_1) \phi_j^*(r_1) \phi_j^*(r_2) \phi_j(r_2)}{r_{12}}
\]

As we have already explained,17 the orthogonality of the DNOs in both \( \Omega \) and \( \Omega' \) will make the non-diagonal (\( i \neq j \)) contributions to \( V_{xc}^{\Omega,\Omega'} \) very small (strictly vanishing in the absence of the \( r_{12} \) denominator). Moreover, the diagonal \( i = j \) terms will be dominated, by large, by orbitals delocalized between \( \Omega \) and \( \Omega' \). DNOs localized either in \( \Omega \) or in \( \Omega' \) will contribute to one of the \( r_1 \) or \( r_2 \) domains, respectively, but not to the other. In the end, the total \( V_{xc}^{\Omega,\Omega'} \) energy will mainly come from diagonal delocalized, i.e. bonding, terms, and

\[
V_{xc}^{\Omega,\Omega'} \approx \sum_{\phi_i \text{ bonding}} V_{xc}^{\Omega,\Omega'} (ii).
\]

We have found this expression to recover about 90% \( V_{xc} \) in standard cases, deviations coming basically from non-diagonal terms that couple different bonding orbitals. For instance, in \( \text{Li}_2 \), \(-251.688\) out of \(-251.709\) kJ mol\(^{-1}\) of total \( V_{xc}^{\text{Li}_2}\) is due to diagonal terms. In \( \text{N}_2 \), with a much larger \( V_{xc}^{\text{NN}} = -2486\) kJ mol\(^{-1}\), 264 kJ mol\(^{-1}\) are due to non-diagonal contributions.

All these ideas provide a rather compact framework that expands considerably the applicability, predictability, and usefulness of real space bonding analyses for the practicing chemist. This is the first work in which such a strategy is presented jointly and applied to a chemically interesting case. Our combined strategy provides: (i) a QTAIM atomic partition, with its associated critical points, atomic interaction lines, and the enormous amount of wisdom accumulated from correlations among chemical concepts and properties at critical points; (ii) an exact (IIA) energetic decomposition, valid at any molecular geometry, that introduces intuitive chemical concepts like atomic promotion energies or ionic and covalent contributions to the interaction energy between every pair of atoms in the system; (iii) a set of statistically independent one electron functions (DAFH orbitals) which give additive contributions to bond orders between basins, and approximately additive terms to the above covalent energies, substantiating...
bond order–bond energy relationships; (iv) a chemically appealing picture of covalency in terms of delocalization of electrons.

3. Selected examples and computational details

One of the most attractive characteristics of chemical bonding in transition metal complexes is that paired electrons belonging to one of the two counterparts (the metal or the ligand) can be mutually donated. Thus, together with the donation of electron pairs from the ligand (similar to what occurs in Lewis acid–base complexes of main group elements) we have a back-donation from the metal to the ligand. The two mechanisms are not exclusive and usually they both concur to the bonding. One of the most well known donation/back-donation scheme is that proposed by Dewar, Chatt, and Duncanson (DCD)\textsuperscript{21,22} widely adopted to explain bonding in metal olefins\textsuperscript{34–37} or metal carbonyl complexes.\textsuperscript{38–45}

As the M–CO bond is regarded, and grossly speaking in standard orbital parlance, a σ-donation from the HOMO of CO into an empty orbital of M is accompanied by π-backdonation from a d orbital of M into the LUMO of CO. Such a simple model explains a large set of experimental facts, and even though it has been questioned many times, particularly after the discovery of non-classical carbonyls\textsuperscript{46–47} with CO stretching frequencies larger than those of free CO, it has essentially survived up-to-date. The energetic role of σ and π contribution to bonding has also been examined, for instance through the energy decomposition analysis (EDA) technique.\textsuperscript{48} In our opinion, the root of some of these controversies lies in the absence of a single consistent, physically rooted method that provides, simultaneously, the bonding energetics and the orbital picture to interpret it. Our approach provides one.

In our previous paper on bonding in metal carbonyls,\textsuperscript{14} we selected a relatively wide set of systems described at the HF, DFT, and CASSCF levels that spanned both the classical and non-classical regimes and we analyzed them in terms of IQA. Succinctly, the ionic contributions to M–CO (ML) bonding were shown to depend heavily on the coordination index of M and the formal charge of the complex, evolving from positively to negatively charged metals.\textsuperscript{51} IQA/DAFH/EDF analyses were done with our PROMOLDEN\textsuperscript{52} and EDF\textsuperscript{53} codes. PROMOLDEN integrations were performed using typically tight parameters, truncated at \(l_{\text{max}} = 10\), so that interaction energies are significant to about 4–5 kJ mol\(^{-1}\). We have previously shown\textsuperscript{54} how small core ECPs may be safely used in QTAIM/IQA studies by using interatomic surfaces obtained through core reconstruction.

4. Results and discussion

We will examine in this section our results. We will first present in detail the Ni(CO)\(_4\) tetracarbonyl, a balanced system very well studied\textsuperscript{55,56} in which more or less half the stabilization is due to σ-donation, and the other half to π-backdonation. Then we will switch to show how that landscape evolves on changing the metal in the d\(^{10}\) systems. After this we will again discuss the square planar [Ni(CO)\(_4\)]\(^{2+}\) system in some detail, and show the clear bonding differences found in this non-classical compound. Since the decomposition of covalent energies into DNO contributions is extremely CPU-intensive, we have decided not to explore here the rest of the systems that may be found in our previous contribution.\textsuperscript{14} Recent DAFH analyses of binuclear carbonyls have been published,\textsuperscript{57,58} although their spirit is quite different to that of this work.

4.1 The Ni(CO)\(_4\) complex

Let us first consider the DNOs obtained by: (i) diagonalizing the charge-weighted Fermi hole averaged over the metal basin; (ii) subjecting the resulting orbitals to an isopycnic localization (vide supra).

Since we are interested in ML bonding, we will only analyze those DNOs with occupation numbers, \(n_o\), significantly different from zero, i.e. DNOs totally or partially localized on M. There are 13 of them in our three tetrahedral compounds. Fig. 1 shows them for the Ni(CO)\(_4\) case. The first four displaying \(n_o > 0.999\) are almost entirely localized in the metal basin, and may intuitively be associated to the 3s and 3p valence orbitals of the Ni atoms (let us not forget that the [Ar]
orbitals. Only 0.033 electrons described by they are adequately interpreted as to be equal to 0.128, and 0.838 in the corresponding CO, so the probability of finding the electron in the M basin turns out

Fig. 1 Isopycnic DNO orbitals that are significantly localized on the Ni basin for the Ni(CO)₄ tetracarbonyl. Isosurfaces displayed at the |φ| = 0.05 a.u. level. Only one of the four equivalent σ-like bonding orbitals is displayed. The order is from top to bottom, left to right, ϕ₃s, 3 × ϕ₃p, ϕ₂s, 5 × ϕ₁d.

core has been substituted by an ECP). They do not participate in bonding.

The remaining nine functions are also immediately classified. Four of them (ϕᵢₛ, i = 1,...4, only one shown in the figure) are σ orbitals delocalized over the metal and each of the four ligands, with an eigenvalue n = 0.117. According to our EDF interpretation, they describe effective electrons that contribute to the ML bond. Notice that these bonding orbitals are rather polarized. If we obtain the domain integrals of ϕᵢ's, the probability of finding the electron in the M basin turns out to be equal to 0.128, and 0.838 in the corresponding CO, so they are adequately interpreted as σ-donating carbonyl orbitals. Only 0.033 electrons described by ϕᵢₛ are delocalized among the other three remaining ligands. Another rationalization path would say that each ligand’s ϕᵢₛ donates 0.117 × 2 = 0.234 electrons to the metal, making a grand total of about 0.935 electrons (see Table 1). The total delocalization index (bond order) between M and L is found to be δ⁽ML⁾ = 0.895. With our decomposition, the contribution to this value coming from ϕᵢₛ is 0.407 (0.364 from the ligand’s C, 0.027 from the ligand’s O, and 0.015 from the residual delocalization among the other three ligands). This value is only slightly smaller than half the total δ⁽ML⁾. The rest up to 0.895 is due to the contribution of the five remaining DNOs, which, as seen in the figure are d-like functions very localized in the Ni basin, i.e. π-backdonating orbitals. We would like to stress how the adaptive localizability of the isopycnic DNOs provides a frame which recovers the DCD ideas straightforwardly.

A first point regarding these backdonating functions is that they do not localize over one particular CO moiety, contrarily to what the four σ functions do. This points towards a very important difference between σ-donation and π-backdonation in these tetracarbonyls. In the former case, four isolated ML functions linking two-groups exist, while in the latter ML bonding must involve several ligands at a time, i.e. π contributions are multiligand in nature. The five d DNOs come out to be slightly split in a 3 + 2 fashion with n’s equal to 0.892 and 0.894, respectively. This splitting reminds the T₂ + E decomposition in T₄ symmetry. Notice, however, that isopycnic orbitals do not rigorously transform as irreducible representations of the local point group, so that this resemblance should not be taken too far. Actually (see below), none of the five slightly split DNOs bind equally the four CO ligands, so that care is to be taken when labelled according to T₄ irreducible representations. Each of the five d functions backdonates 0.213 electrons to each of the ligands, making a total of 1.058 electrons. The topological charge of the metal in the complex, +0.122, may be viewed as coming from the balance of a d⁰ system backdonating 0.122 more electrons than those received from σ-donation from the ligands. In any case, five very localized d-like functions exist upon the metal, so our procedure allows us to assign a clear metallic configuration to this system.

On average, each of the d functions provides a total bond order with the rest of the system of 0.381, of which 0.317 (about 85%) is due to bonding with only two out of the four carbonyls. Each d function thus links preferentially the metal

<table>
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<th>M</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(MC)</td>
<td>1.766</td>
<td>1.924</td>
<td>2.296</td>
</tr>
<tr>
<td>Δd(CO)</td>
<td>0.024</td>
<td>0.002</td>
<td>−0.010</td>
</tr>
<tr>
<td>Δν’</td>
<td>−295</td>
<td>−64</td>
<td>90</td>
</tr>
<tr>
<td>Q’’’</td>
<td>0.189</td>
<td>0.122</td>
<td>0.802</td>
</tr>
<tr>
<td>n₀</td>
<td>0.131</td>
<td>0.117</td>
<td>0.056</td>
</tr>
<tr>
<td>n₀(T₂-like)</td>
<td>0.729</td>
<td>0.892</td>
<td>0.974</td>
</tr>
<tr>
<td>n₀(E-like)</td>
<td>0.848</td>
<td>0.894</td>
<td>0.975</td>
</tr>
<tr>
<td>N₀</td>
<td>1.047</td>
<td>0.935</td>
<td>0.448</td>
</tr>
<tr>
<td>N₅</td>
<td>2.235</td>
<td>1.058</td>
<td>0.254</td>
</tr>
<tr>
<td>δ⁽ML⁾</td>
<td>1.319</td>
<td>0.895</td>
<td>0.337</td>
</tr>
<tr>
<td>δ⁽MC⁾</td>
<td>1.153</td>
<td>0.798</td>
<td>0.313</td>
</tr>
<tr>
<td>δ⁽ML⁽ϕᵢₛ⁾</td>
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<td>0.407</td>
<td>0.196</td>
</tr>
<tr>
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<td>0.850</td>
<td>0.477</td>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>ρ⁽ML⁽ϕ₀ϕ₀⁾</td>
<td>−0.033</td>
<td>−0.026</td>
<td>−0.005</td>
</tr>
</tbody>
</table>
Given the very polarized nature of these, each of the two ligands at the top left and top right. From described by the depicted function in the metal center, and the product of the probabilities of finding an electron in normalization are available, so we will just provide the triple product is about 0.002, to be compared with 1/27 equivalent three-center index in the ideal 3\( \delta_{LL} \) bond in H\( ^+ \). A first point regards the general nature of the DNOs. The same general structure found for the Ni case is repeated in all the systems. We have found extremely localized 3s and 3p functions that do not participate in bonding, plus a set of four equivalent localized \( \phi_\sigma \) donating and five delocalized \( \phi_d \) backdonating orbitals. According to this view, all these systems may be described as d\(^{10} \) complexes. We should notice how the DNOs occupation numbers evolve on going from the copper to the cobalt complex: (i) \( n_\sigma \) increases, so the \( \sigma \)-donating functions become more delocalized over the metal; (ii) \( n_d \) decreases, and the \( \pi \)-backdonating orbitals delocalize better over the ligands; (iii) the \( T_2 - E \) like splitting increases such that \( n_d(T_2) \) becomes smaller and the participation of the \( T_2 \)-like functions in ML bonding more important, as we should intuitively expect from standard molecular orbital arguments related to ML overlap.

As in Ni(CO)\(_4\), the \( d \) functions delocalize over more than one ligand. The pattern found in [Cu(CO)\(_4\)]\( ^+ \) is exactly the same as already presented in Ni(CO)\(_4\), but as the \( T_2 - E \)-like gap increases, a shift is seen towards another pattern.
In $[\text{Co(CO)}_4]^{-}$, the $e$-like functions link the four ligands at a time in a symmetric manner, while the $t_2$-like ones do only delocalize over three ligands, see Fig. 3. The multicenter (multiligand) character of backdonation thus increases as the formal charge of the complexes becomes more negative.

From the point of view of electron population, it is clear that both $\sigma$-donation and $\pi$-backdonation increase in the Cu to Co direction. This is clearly related to the decrease in MC distance. Overall, the topological charge on the metal may be seen as a balance between donation and backdonation over the ideal $d^{10}$ configuration. As we shift from the copper towards the cobalt molecule, more electrons (thus stronger ML interaction) are delocalized both in the donating and backdonating channels. However, their mutual ratio changes completely. In the Cu case, the number of $\sigma$-donated ($N_d$) electrons almost doubles those $\pi$-backdonated ($N_b$). These numbers are roughly equal in the Ni molecule, but $N_b$ more than doubles $N_d$ in the Co complex. Thus, the positive topological charge of cobalt is the result of backdonating 2.235 $|e|$ but receiving only 1.047 $|e|$ from the ligands on top of its ideal $-1$ oxidation state.

Quantification of electron sharing (or electron delocalization) provides a similar picture, although backdonation (if not too large) is slightly more effective than donation to delocalize electrons. For that reason, the ratios of the $\pi$ to $\sigma$ contributions to $\delta_{\text{ML}}$ are slightly larger than their equivalents obtained from the total number of electrons transferred, except in the $[\text{Co(CO)}_4]$ case. In this latter system, the number of electrons shared via $\pi$-backdonation doubles those shared via $\sigma$ channels.

The energetic scale is again a product of these considerations, if we take into account that, as explained above, $\pi$ links do provide smaller bond energies than $\sigma$ ones. First, we notice that diagonal orbital terms account for about 90% of the total ML covalent energy. This fact corroborates the goodness of our approximations. Again, the only important non-diagonal terms providing contributions to $V_{\text{xc}}$ in these systems are the $\sigma-\pi$ ones, although in Co, very small other terms have also been found. Second, and contrarily to what it is found on examining charge transfers or electron delocalizations, the backdonation share in the ML covalent energy does not overcome the $\sigma$ contribution, although their ratio increases steadily from 0.5 to about 0.93 along the Cu to Co path. In the cobalt complex, each $d$ function contributes, on average, about $-272 \text{ kJ mol}^{-1}$ to the ML covalent energy.

An important point regards the use of simple correlations as measures of all these effects. Fig. 4 shows that the total $\delta_{\text{MO}}$ value, as proposed by Macchi et al., may actually be taken as a reasonable measure of either $\delta_{\text{ML}}(\phi_d)$ or $V_{\text{xc}}(\phi_d)$, i.e. as an indirect measure of $\pi$-backdonation.

Finally, we note in passing that the change in CO distance and CO stretching frequency, basic parameters in the DCD model that we have successfully related in our previous work with the intensity of $V_{\text{xc}}$ is connected in the present picture to the $N_d-N_b$ balance. This may again be quantified within our approach, but we will not pursue this point further in this work.

### 4.3 The $[\text{Ni(CO)}_4]^2+$ non-classical carbonyl

Let us now discuss the clearly non-classical $d^8$ square planar $[\text{Ni(CO)}_4]^2+$ molecule. Our HF calculation shows a decrease in d(CO) of 0.02 Å, coupled to an increase in the CO stretching frequency of about 170 cm$^{-1}$. Only 12 isocyclic functions show non-negligible occupancies at the metal site. Fig. 5 shows them. Again, four of them, that may be made to correspond to the metal 3s and 3p valence, display $n_i > 0.998$ values, and do not contribute to bonding. We also recognize four equivalent $\sigma$-donating orbitals (only one shown), and four occupied $\pi$-like functions. The $d$ space spans the $A_{1g} \oplus B_{1g} \oplus B_{2g} \oplus E_g$ set of representations in $D_{4h}$ symmetry, but the $B_{1g}$-like representant is lacking from our DNOs. This indicates that the system may be described as a $d^0$ one, again in agreement with formal electron counting. More interestingly, the unrepresented function, $d_{z^2-r^2}$, is the only one having a zero overlap with a $\pi$ ligand contribution, reinforcing the intuitive role of the $d$ functions as backbonding entities.

The four equivalent localized $\phi_{\sigma}$'s display $n = 0.086$, and are again very polarized. The probability that one of these
effective electrons lies in the M basin is equal to 0.100, and 0.853 that it is found in its corresponding carbonyl, so about 0.047 electrons are found over other basins, basically in the trans carbonyl ligand (0.032 of them). As delocalization is concerned, \( \delta^{ML} = 0.499 \), and its contribution coming from \( \phi_\sigma \) is \( \delta^{ML}(\phi_\sigma) = 0.294 \). Only 6% of this value is due to MO delocalization. The other three \( \sigma \) functions contribute very little to the ML \( \delta \), a mere total of 0.016.

The \( d \) functions are very localized in the M basin, with \( n \)'s equal to 0.976 \times 2, 0.988, and 0.969 in the \( d_{xc} \equiv d_{xz},d_{yz},d_{xy} \) order. They contribute to ML delocalization with \( \delta^{ML}(\phi_d) = 0.107 \). Backdonation is therefore not large, but non-negligible.

The four occupied \( d \) functions contribute differently to this value, the largest contribution being 0.041 for \( d_{xz} \) if \( L \) lies along the \( z \) axis, for instance, and the smallest, 0.012 for \( d_{yz} \), all in entire agreement with chemical intuition. We should notice that the \( d_{xy} \)-like function does not backdonate to \( \pi \)-like ligand functions, but to \( \sigma \)-like components.

Overall, 0.693 electrons are \( \sigma \)-donated to the metal, and only 0.184 backdonated to the ligands, making the total topological charge of the metal equal to 1.490, the value reported in our earlier paper. Notice that in the copper tetrahedral compound \( N_0 \) was about 55% \( N_0 \), but that here that figure has decreased to 26%. The multicenter character of backdonation is again clear, the \( d_{xz} \) and \( d_{xy} \)-like DNOs backdonating equally to all the four ligands, while the \( d_{xy} \) backdonate exclusively to two ligands trans to each other. Interestingly, \( \sigma \)-donation is also affected by this multicenter delocalization, and each \( \phi_\sigma \), as stated before, delocalizes slightly over its trans situated ligand. All these features are shown in Fig. 6. Notice that what is found here is the existence of direct delocalization channels that affect trans located ligands so that a perturbation at a given \( L \) will be transmitted directly to its trans partner. This effect may hold clues about the origin of the trans effect and deserves further exploration.

Finally, the total \( V_{xc}^{ML} = -230 \text{ kJ mol}^{-1} \) is partitioned in the following way: -180 \text{ kJ mol}^{-1} are due to \( \phi_\sigma \), with only -4 \text{ kJ mol}^{-1} coming from the MO contribution, and -42 \text{ kJ mol}^{-1} are provided by the four \( \phi_d \) functions, so backdonation provides less than 20% of the total ML stabilization energy. Even more interesting is that 80% of the backdonation stabilization is due to two \( d \) functions: the \( d_{xy} \) and the appropriate \( d_{xz} \) or \( d_{yz} \) component. Finally, the remaining 8 \text{ kJ mol}^{-1} needed to make the grand total of -230 are due to \( \sigma \)-\( d \) non-diagonal terms in \( V_{xc} \). So as far as covalency is regarded, backdonation is energetically small, but it clearly plays a role in bonding in these non-classical systems, in agreement with modern thinking.

5. Conclusions

We have presented in this paper a combined IQA/DAFH/EDF strategy that allows us to recover effective one-electron functions from invariant descriptions coming from the Quantum Theory of Atoms in Molecules. Our Interacting Quantum Atoms approach (IQA) allows for a chemically appealing, exact real space decomposition of the total molecular energy at any geometrical configuration in terms of atomic self-energies and interatomic ionic and covalent interaction energies. Upon this invariant structure, the charge-weighted domain averaged Fermi hole natural orbitals originally defined by Ponec\textsuperscript{15,16} are obtained. We have recently shown them to be intimately linked to the statistics of the electron population (our electron distribution functions, EDF\textsuperscript{13,18}) in real space basins.\textsuperscript{17} In fact, these effective electrons are statistically independent in one-determinant descriptions, and are adaptively localized or

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Fig. 5 DAFH isopinac orbital significantly localized on the Ni basin of the \([\text{Ni(CO)}_4]^2^+\) tetracarbonyl. Isosurfaces displayed at the \( |\phi| = 0.1 \text{ a.u.} \) level. Only one of the four equivalent \( \sigma \)-like bonding orbitals is shown. The order is from top to bottom, left to right, \( \phi_{3\mu}, 3 \times \phi_{3\pi}, \phi_\sigma, 4 \times \phi_d \).

Fig. 6 Multicenter character of relevant DNOs in \([\text{Ni(CO)}_4]^2^+\). Isosurfaces displayed at the \( |\phi| = 0.007, \) and 0.003 a.u. level for the \( d \) and \( \sigma \) contributions, respectively.
delocalized according to their non-bonding or bonding character. In the proposed strategy, only delocalized electrons contribute to bonding between two or more given QTAIM basins, and make an additive contribution to their mutual covalent bond order, as measured by the delocalization index, \( \delta \). Since the strategy relies on a IQA energetic decomposition, the contribution of each of these electrons to the covalent energy may also be determined. In this way, a common framework that starts from the topology of the electron density to determine QTAIM atomic basins includes a detailed energetic view of bonding energies in terms of atomic deformations and electrostatic and covalent contributions, and provides an even thinner decomposition of the interaction energies in terms of one-electron functions is constructed.

We have applied this strategy to examine the Dewar-Chatt-Duncanson model of bonding in simple transition metal carbonyls, and selected a subset of the systems previously analyzed at the IQA level.\(^1,4\) Our results show how we may easily recover \( \sigma \)-donation and \( \pi \)-backdonation from orbital invariant data, and quantify their role upon bonding, measured either as bond order (from delocalization indices) or bond strength (from IQA \( V_{cc} \) values). DNOs support the formal d electron configurations traditionally assigned to the metals, and explain their globally positive topological charges in terms of the balance between the total number of donated and backdonated electrons. Even non-classical carbonyls display non-negligible backdonation, although the ratio of the strength of backbonding with respect to \( \sigma \)-donation is clearly smaller than one in these systems. In terms of the ML covalent energies, backdonation is weaker than \( \sigma \)-donation, and in none of the systems explored does the covalent energy coming from \( \pi \) contributions exceed that emerging from \( \sigma \) terms.

Another interesting point regards the multicenter character of ML bonding due to d-like contributions. It increases with the strength of backdonation, and is related to the well known trans effect in square planar compounds. Finally, our results confirm that \( \delta^{MO} \) is well correlated to the strength of backbonding, either measured by bond orders or bond energies, and that it may be used as an indirect index for it.

The strategy here developed shows how the chemical intuition developed through orbital arguments may indeed be used within real space theories of chemical bonding, moving us a step closer to obtaining chemically appealing one-electron images from general wavefunctions. At the time being, it offers unambiguous interatomic (or intergroup) interactions characterized by quantitative bond orders, with energies written as a sum of ionic and covalent contributions. The latter (and the bond orders) may be further decomposed into effective one-electron contributions which may be visualized in real space and used to develop standard orbital-like arguments. No other technique, to our knowledge, offers at the same time a quantitative energetic picture of bonding compatible with a one-electron (i.e. orbital) image.

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References


