ORIGINAL PAPER

Natural orbitals for chemical valence as descriptors of chemical bonding in transition metal complexes

Mariusz Mitoraj · Artur Michalak

Abstract Natural orbitals for chemical valence (NOCV) are defined as the eigenvectors of the chemical valence operator defined by Nalewajski et al.; they decompose the deformation density (differential density, $\Delta\rho$) into diagonal contributions. NOCV were used in a description of the chemical bond between the organometallic fragment and the ligand in example transition–metal complexes: heme–CO ([$FeN_5C_{20}H_{15}$]–CO), [Ni–diimine hydride]–ethylene ([N^N–Ni–H]–C_2H_4, N^N=–NH–CH–CH–NH–), and [Ni(NH_3)$_3$]–CO. DFT calculations were performed using gradient-corrected density functional theory (DFT) in the fragments resolution, using the fragment/ligand Kohn–Sham orbitals as a basis set in calculations for the whole fragment–ligand complex. It has been found that NOCV lead to a very compact description of the fragment–ligand bond, with only a few orbitals exhibiting non-zero eigenvalues. Results of NOCV analysis, compared with Mulliken populations analysis and Zigler–Rauk interaction–energy decomposition, demonstrate that the use of the natural valence orbitals allows for a separation of the σ-donation and π-back-donation contributions to the ligand–fragment bond. They can be also useful in comparison of these contributions in different complexes.

M. Mitoraj · A. Michalak (✉)
Department of Theoretical Chemistry, Faculty of Chemistry,
Jagiellonian University,
R. Ingardena 3,
30-060 Cracow, Poland
e-mail: michalak@chemia.uj.edu.pl

Introduction

The development of *ab initio* methods of quantum chemistry, and in particular density functional theory (DFT), together with a fast increase in computational power of modern computers has given rise to fast progress in the theoretical description of transition–metal complexes based on high-quality computations. Both aspects of theoretical organometallic chemistry, the electronic structure of transition–metal based compounds, [1, 2] and reactions involving such systems [1–3] are the subject of extensive theoretical studies. However, some fundamental problems still exist that are important for understanding the nature of chemical bonds in these compounds. Recently, considerable attention has been paid to the relationship between the geometrical structure and hybridization, a role of the metal *p*-orbitals in bonding, as well a description of the electronic structure with models that assume covalent character of the bonds. These problems are still a subject of discussion, and are summarized in an excellent review by Frenking [1].

In a description of the bond between the transition–metal-based fragment and a ligand, the Dewar–Chatt–Duncanson model [4–6] is commonly used. It describes bond formation as a synergic process with donation of electrons from the ligand to the metal, and back-donation of electrons from a *d*-orbital of the metal into the empty orbital of the ligand.

In the present article the *Natural Orbitals for Chemical Valence* (NOCV) will be introduced and applied in a

description of the bond between the ligand and the transition-metal-fragment. These orbitals are the eigenvectors of the chemical valence operator of the Nalewajski–Mrozek theory of valence and bond-orders [7–12]. It will be shown in this article that NOCV decompose the deformation density (differential density), $\Delta\rho(r)$, into contributions that correspond to donation and back-donation. Deformation density is one of the basic quantities commonly used to visualize the chemical bond. However, the standard density difference plots do not allow for the separation between the σ- and π-bond components, neither do they allow for the separation of donation and back-donation processes.

The natural orbitals will be analyzed for three systems: the heme/CO ([FeN$_5$C$_{20}$H$_{15}$]–CO), [Ni–diimine hydride]$^+$/ethylene ([N^N–Ni–H]$^+$–C$_2$H$_4$, N^N=–NH–CH–CH–NH–), and [Ni(NH$_3$)$_3$]$^{2+}$/CO. The first complex is a model for the well known complex of biological importance [13]. The second system is an intermediate in the catalytic processes of ethylene polymerization and copolymerization, [14, 15] and the third was chosen to facilitate the comparison between the systems, as it contains the same ligand as one of the systems (CO), and the same kind of transition–metal fragment as the other one (d^8-Ni-based complex). In the following we will first briefly introduce the theoretical background of NOCV, and then present their use in a description of bonding, and in particular, in analysis of donation and back-donation contributions.

Theoretical background

One of the basic quantities in the Nalewajski–Mrozek theory of valence and bond–order indices [7–12] is the

overall chemical valence, V. For a given molecular system, the value of V corresponds to the number of chemical bonds in the system [10–12]. A decomposition of V into diatomic contributions allows for defining the bond–order indices (bond-multiplicities) [10–12].

It has been shown [11] that for the one-determinental wavefunctions and a closed-shell system, the chemical valence can be expressed as

$$V = \tfrac{1}{4}\mathrm{Tr}\left(\Delta\mathrm{P}^2\right) = \tfrac{1}{2}\mathrm{Tr}(\mathrm{P}\Delta\mathrm{P}) \tag{1}$$

where $\Delta P = P - P^0$, P is the standard charge-and-bond-order (CBO) matrix in a molecule and P^0 stands for the CBO matrix in a promolecule, consisting of non-interacting atoms (or larger molecular-fragments) placed in the positions of the nuclei in a given molecular system complex. For open-shell systems, the corresponding relation is expressed in terms of the corresponding spin-resolved CBO matrices.

Therefore, the chemical valence can be defined as the expectation value of the valence operator [11]:

$$V = Tr(P^1/_2\Delta P) = Tr(PV) = \;<\Psi|\widehat{V}|\Psi> \;=\; <\widehat{V}> \tag{2}$$

The operator of chemical valence can be thus written in terms of the molecular/pro-molecular (KS) orbitals Ψ/Ψ^0 and their occupations as

$$\widehat{V} = \frac{1}{2}\Delta\widehat{P} = \frac{1}{2}\left(\widehat{P} - \widehat{P}^0\right) = \frac{1}{2}\left(\sum_i^{MO}|\Psi_i> n_i <\Psi_i| - \sum_j^{MO}\left|\Psi_j^0> n_j^0 <\Psi_j^0\right|\right) \tag{3}$$

In the present work we consider the *natural orbitals for chemical valence*, φ, defined as the eigenvectors of $\widehat{V}$:

$$\widehat{V}\varphi_i = v_i\varphi_i, \; i = 1,\ldots,n \tag{4}$$

where n is a number of the basis functions.

Such orbitals decompose the deformation density (differential density), $\Delta\rho$, into diagonal contributions:

$$\Delta\rho(r) = \sum_{i=1}^n v_i\varphi_i^2(r) \tag{5}$$

Also, the overall chemical valence can be written in terms of the eigenvalues as:

$$V = \frac{1}{4}\sum_{i=1}^n v_i^2 \tag{6}$$

Let us consider the molecular system A–B, consisting of two molecular fragments A and B. The molecular wavefunction (electron density) can be expressed in the basis of the fragment orbitals. The deformation density (differential density) can be defined with respect to the fragment densities, $\Delta\rho(\rho) = \rho^{AB}(r) - \rho^A(r) - \rho^B(r)$.

In such a molecular fragment resolution, the eigenvalues of $\widehat{V}$ have an interesting property. They can be coupled in

pairs, each of them grouping two complementary orbitals characterized by eigenvalues of opposite sign and the same absolute value:

$$\widehat{V}\varphi_{-k} = -v_k\varphi_{-k}, \widehat{V}\varphi_k = v_k\varphi_k \quad k = 1,\ldots,n/2 \quad (7)$$

It can be expected that few of such pairs contribute to the bond between the fragments, as the deformation density is predominantly localized in the bond region. Thus, a large number of orbitals must describe the fragment electron density without participation in bonding. This means that such NOCV are characterized by the zero eigenvalues, as only the orbitals corresponding to non-zero eigenvalues contribute to the deformation density (Eq. 5).

The interpretation of the natural orbitals in the fragment resolution follows from Eqs. 5 and 7. The deformation density can be expressed as:

$$\Delta\rho(r) = \sum_{k=1}^{n/2} v_k \left[-\varphi_{-k}^2(r) + \varphi_k^2(r) \right] \equiv \sum_{k=1}^{n/2} \Delta\rho_k(r) \quad (8)$$

where the summation goes over the pairs of NOCV.

Thus, the eigenvalue v_k represents the number of electrons transferred from the orbital φ_{-k} ('antibonding') to the orbital φ_k ('bonding') in a process of bond formation. It should be emphasized that in general both orbitals of each pair have fractional occupations in the molecule, as well as in the promolecule.

In the following we will present a few examples of the NOCV, determined in a two-fragment resolution, and their contributions to the deformation density, focusing on the ligand bonding in transition metal complexes.

Computational details and the model systems

The optimized geometries of the model complexes studied in the present work are shown in Fig. 1. The fragment–ligand bond was characterized for the heme–CO ([FeN$_5$C$_{20}$H$_{15}$]–CO, panel **a**), [Ni–diimine hydride]$^+$–ethylene ([N^N–Ni–H]$^+$–C$_2$H$_4$, N^N=–NH–CH–CH–NH–, panel **b**), and [Ni(NH$_3$)$_3$]$^{2+}$–CO (panel **c**). All the calculations were performed in a fragment resolution, i.e. using the fragment/ligand KS orbitals as a basis set for the whole fragment–ligand system. DFT calculation based on the Becke–Perdew exchange-correlation functional [16–18] were performed using the modified version of the Amsterdam Density Functional program (ADF 2004) [19–24]. The 'standard' STO basis sets, included in the ADF program, [19] were used in all the calculations. Double–zeta STO basis sets were used for the H, C, N and O atoms, while triple–zeta basis sets were used for Ni and Fe atoms. The 1s electrons of C, N, O as well as the 1s−2p electrons
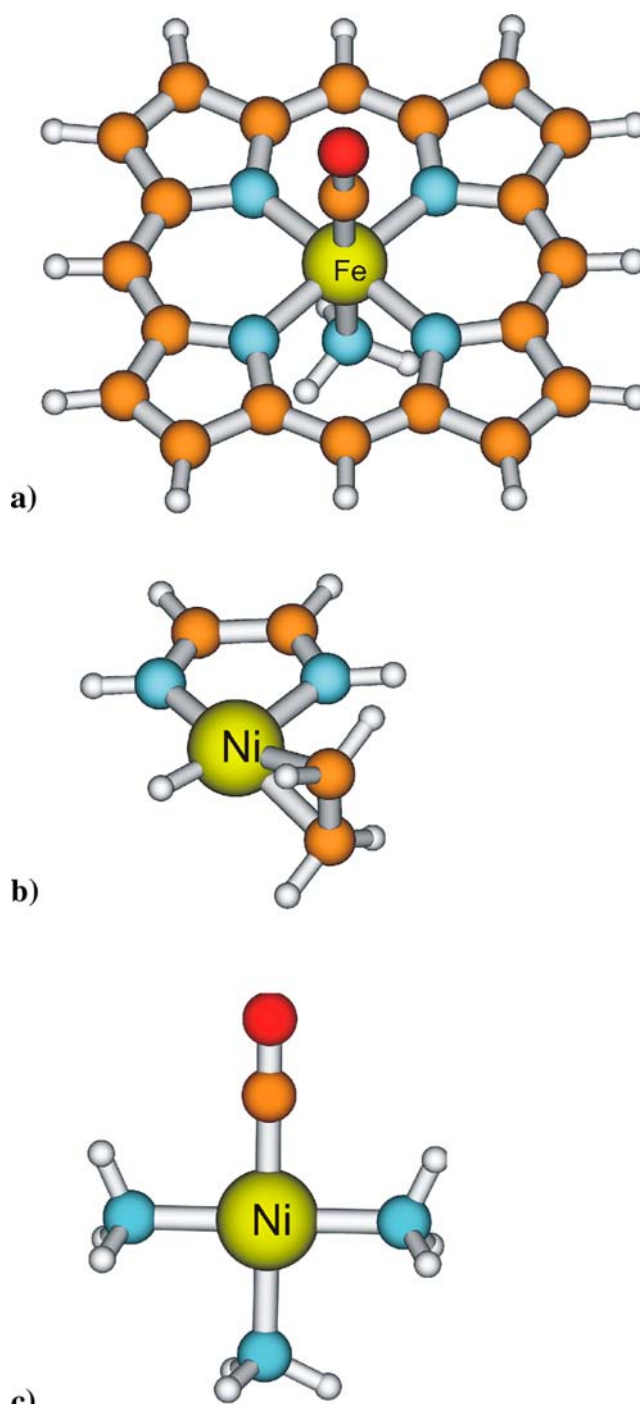

a)

b)

c)

Fig. 1 The molecular systems studied in the present work: the model heme–CO complex ([FeN$_5$C$_{20}$H$_{15}$]–CO, (**a**) [Ni–diimine hydride]$^+$–ethylene ([N^N–Ni–H]$^+$–C$_2$H$_4$, N^N=–NH–CH–CH–NH–, (**b**) and [Ni(NH$_3$)$_3$]$^{2+}$–CO (**c**)

of Ni and Fe were treated as frozen core. Auxiliary s, p, d, f and g STO functions, centered on all nuclei, were used to fit the electron density and obtain accurate Coulomb and exchange potentials in each SCF cycle. The donation/back-donation effects were also analyzed in terms of the Mulliken population analysis, [25] and the Ziegler–Rauk bond-energy decomposition [26, 27].
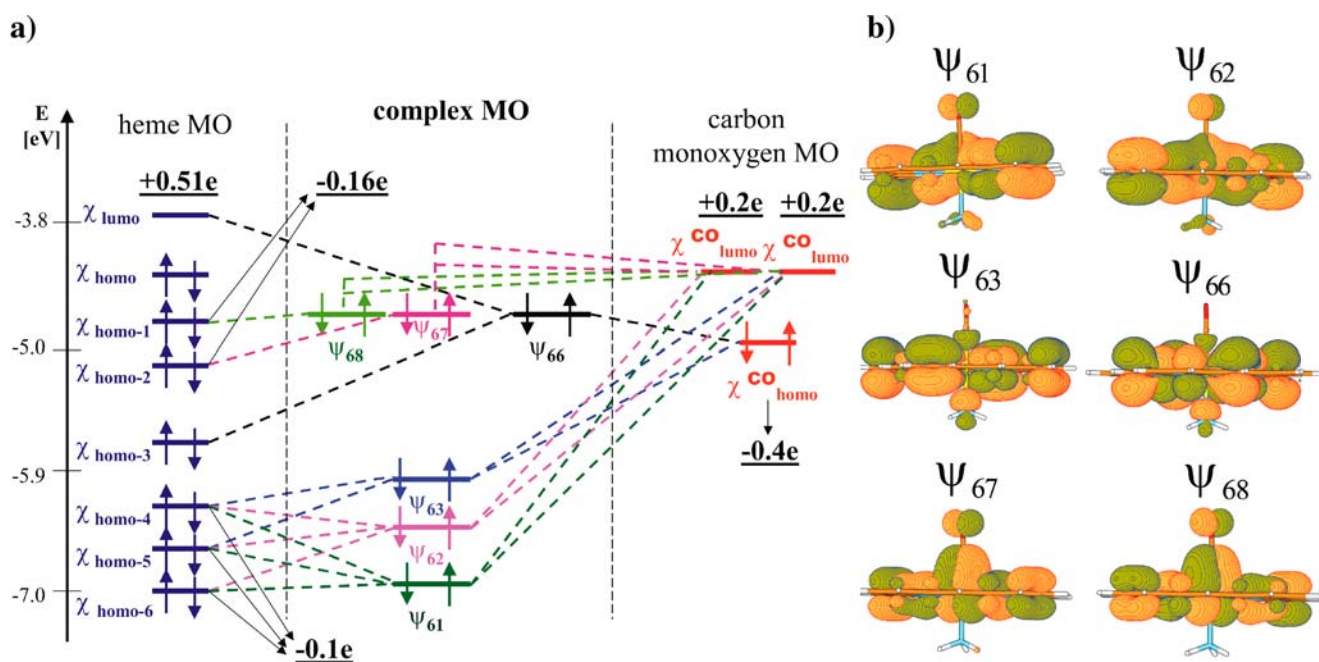
a)

b)

Fig. 2 Molecular orbital interaction diagram (**a**) and the contours ($|\Psi|$=0.1 a.u.) of the molecular orbitals contributing to the bond between heme and CO (**b**). The changes in Mulliken populations of the fragment orbitals in the complex with respect to the promolecule (separated fragments) are shown in the MO diagram

Results and discussion

In the following, the natural orbitals for chemical valence will be presented and analyzed for the three model systems shown in Fig. 1. We begin the discussion with the heme–CO complex (Fig. 1a). In Fig. 2, the molecular orbital interaction diagram is shown (panel **a**) together with the contour plots of the molecular orbitals that participate in the CO bonding (panel **b**). The MO diagram of Fig. 1a was obtained from the DFT calculations in the basis set built of the Kohn–Sham orbitals of non-interacting fragments. There are six orbitals participating in the Fe–CO bond (labeled as ψ_{61}, ψ_{62}, ψ_{63}, ψ_{66}, ψ_{67}, and ψ_{68}); the two omitted orbitals (ψ_{64}, ψ_{65}) are entirely localized on the heme fragment. From contour plots of Fig. 2b, it is possible to determine the symmetry of MO; it is clear that orbitals ψ_{63} and ψ_{66} participate in the σ-bond, while the remaining orbitals exhibit π-character. The contour plots show that these MOs are delocalized over the whole iron–porphyrine–CO system. The MO diagram of Fig. 2a emphasizes that these MOs are a complicated combination of a few fragment orbitals. Thus, their interpretation, e.g. in terms of donation/back-donation can be quite difficult. In this respect, the Mulliken population analysis can be helpful. In Fig. 2a, the changes of Mulliken populations of the fragment MO are added. The HOMO of CO loses 0.4 e, while the LUMO of heme gains 0.5 e; this corresponds to the CO → heme donation. Similarly, the LUMO of CO

gain 0.4 e, mostly as a result of the heme → CO back-donation from a few occupied orbitals of heme; in total they lose ca. 0.6 e. It should be pointed out that the increase in population of LUMO on one fragment and the decrease in populations of HOMO on the other fragment do not cancel each other. This reflects the intra-fragment polarization of their MO.

The natural orbitals for chemical valence describing the heme–CO bond formation are shown in Fig. 3. There are three pairs of complementary orbitals with eigenvalues significantly higher than zero ($|v|$>0.1). Thus, the other natural orbitals barely participate in bonding, as their contribution to $\Delta\rho$ depends on v^2 (here v^2<0.01). The first pair, φ_{-1} and φ_1, exhibit σ-character; the remaining are π-orbitals. Each of the NOCV contains contributions from both fragments. However, the positive-eigenvalue orbitals are mostly localized in the bonding region, between Fe and C atoms; thay exhibit bonding character. The negative eigenvalue orbitals are antibonding. The population of the antibonding orbital φ_{-1} in a promolecule is 1.37 e, and of the bonding orbital φ_1 0.63. In the process of bond formation from the fragments, the former loses 0.74 e, and the latter gains the same amount. In a molecule, their populations are 'switched' compared to the promolecule (0.63 e for φ_{-1} and 1.37 e for φ_1). This is schematically illustrated in an NOCV diagram of Fig. 4a; here the size of the balls corresponds to the occupations of the NOCV in the promolecule/molecule.
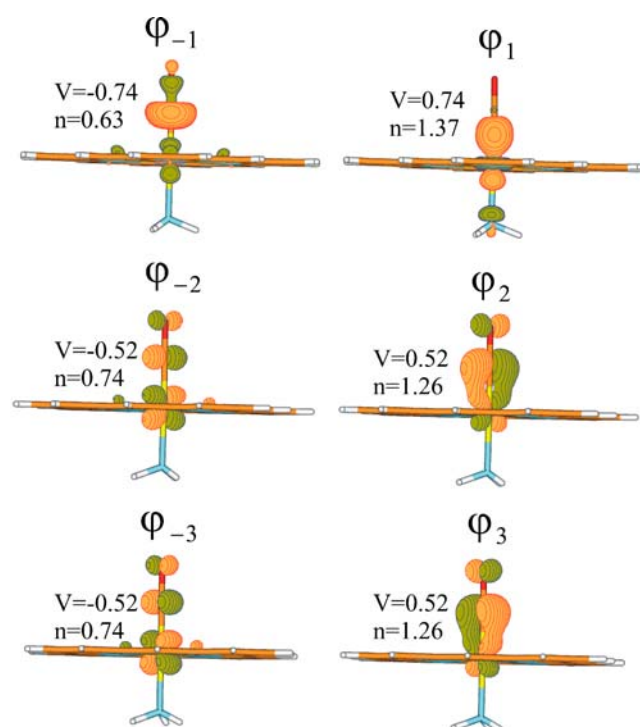
Fig. 3 Natural orbitals for chemical valence for the heme/CO system. Only the orbitals participating in bonding ($|v|>0.1$) are shown. The numbers in the figure denote the eigenvalue (V), and the population (n) of the natural orbital in a molecule

It can be concluded from Eq. 8 and the discussion above, that the interpretation of the NOCV in the two-fragment resolution may be depicted as a scales. This is illustrated in Fig. 4b. If the electrons are localized mostly in the first orbital of the complementary pair (negative eigenvalue, antibonding orbital, left scale), there is no bond. As they flow to the other one (positive eigenvalue, bonding orbital, right scale), the bond is formed.

The picture of π-bonding in the heme–CO system is analogous. The two negative-eigenvalue orbitals, φ_{-2} and φ_{-3} are populated by 1.26 e each in promolecule. As the bonds are formed, 0.52 e flows to their complementary partners, φ_2 and φ_3, respectively; the occupations of the two bonding orbitals in the molecule become 1.26 e.

Finally, the contributions of the NOCV to the deformation density $\Delta\rho$ are shown in Fig. 5. The contributions from the three pairs of orbitals determine the complete shape of $\Delta\rho$ (Fig. 5d), as the eigenvalues of the remaining orbitals are negligible. Figure 5a shows the contribution from the first pair, φ_{-1} and φ_1. It is clearly seen from the contour plot of $\Delta\rho_1 = v_1\left[-\varphi_{-1}^2 + \varphi_1^2\right]$ that this pair of orbitals participates in the donation from CO to heme: the negative contributions (outflow of electrons) are practically localized on CO and the positive changes (increase in the number of electrons) are visible exlusively on the heme fragment.

On the contrary, the contributions from the other two pairs of complementary orbitals, $\Delta\rho_2$ and $\Delta\rho_3$ (Fig. 5c,d), clearly correspond to π-back-donation from heme to CO. The negative changes are localized on a d-orbital of the iron atom, while the positive on CO molecule (mostly on carbon).

Thus, the contributions from NOCV to the deformation density allow for a separation of the σ-donation and π-back-donation charge–flows. As such the natural orbitals for chemical valence provide a useful tool in a description of the bonding in organometallic systems in terms of the intuitive quantities well established in chemistry. It is worth emphasizing that the overall deformation density of Fig. 5d does not provide any information on the σ-/π-donation/back-donation contributions, as they partially cancel in some regions of physical space.

Let us discuss the second system studied in the present work. Figure 6 shows the most important natural orbitals for chemical valence (panel **a**) and their contributions to the deformation density (panel **b**) calculated for the π-complex of ethylene with the Ni–diimine–hydride system of Fig. 1b. There are two pairs of complementary NOCV: one of σ-character (φ_{-1} and φ_1) and another of π-character (φ_{-2} and φ_2).

The first orbital of the σ-pair φ_{-1} exhibits antibonding character. The second orbital of the pair is clearly a σ-bonding orbital, localized predominantly in the bond region. The populations of φ_{-1} and φ_1 in promolecule are 1.28 e and 0.72 e. Formation of the molecule from promolecule is accompanied by a charge–flow of 0.56 e from φ_{-1} to φ_1; as a result the population of φ_{-1} decreases to 0.72 e and the population of φ_1 increases to 1.28 e. Thus, similarly to the previous system discussed in this article, the two orbitals 'switch' their populations.

The same is true for the π-pair of NOCV, φ_{-2} and φ_2. The former is an antibonding orbital, while the latter is a π-bonding combination of fragment orbitals. The charge flow of 0.46 e from φ_{-2} to φ_2 decreases the population of the former from 1.23 to 0.77, and increases the population of the latter from 0.77 to 1.23. The two orbitals have practically no contributions from atoms other than those directly involved in bonding (Ni and ethylene C atoms).

Figure 6b shows the contributions from the two pairs of NOCV to the deformation density. The contribution from the first pair, $\Delta\rho_1 = v_1\left[-\varphi_{-1}^2 + \varphi_1^2\right]$, is negative in the ethylene part (outflow of electrons), and positive on the catalyst (inflow of electrons). Thus, as in the case of the previous molecular system, the first pair contributes to σ-donation from ethylene to the Ni–diimine complex. The second pair of NOCV contributes to π-back donation from the catalyst to ethylene, as the catalyst (mostly the metal atom) loses electrons, and there is an increase in electron density in the region close to ethylene carbon atoms. The total deformation

Fig. 4 The natural orbital population diagram (**a**) for the heme/CO system. The complementary orbitals (φ_{-k} and φ_k) are grouped in pairs; size of a circle corresponds to a population of a given NOCV in a promolecule/molecule. The eigenvalues, corresponding to a charge transfer from φ_{-k} and φ_k, are displayed on top of each diagram. Panel **b** illustrates the 'scales' interpretation of NOCV (see text); as an example the first pair of complementary orbitals (φ_{-1} and φ_1) was used. If the electrons are 'localized' in the first orbital of the complementary pair (in promolecule), there is no bond; as they flow to the other one, the bond is formed (see also Eq. 8)
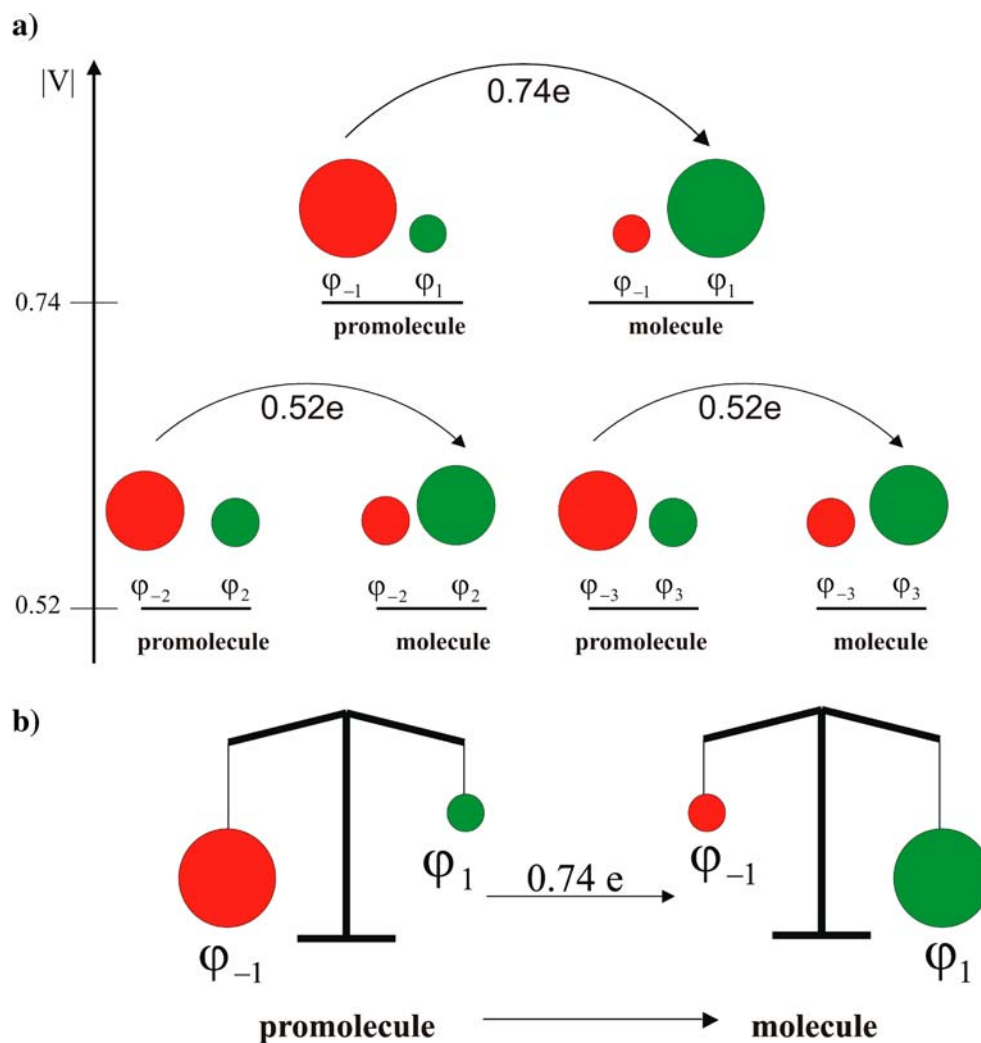

Fig. 5 The donation (**a**) and back-donation (**b** and **c**) contributions to the deformation density ($\Delta\rho$, **d**) for the heme/CO system, originated from the three pairs of complementary of NOCV shown in Fig. 3. The $|\Delta\rho|=0.01$ a.u. contours are shown
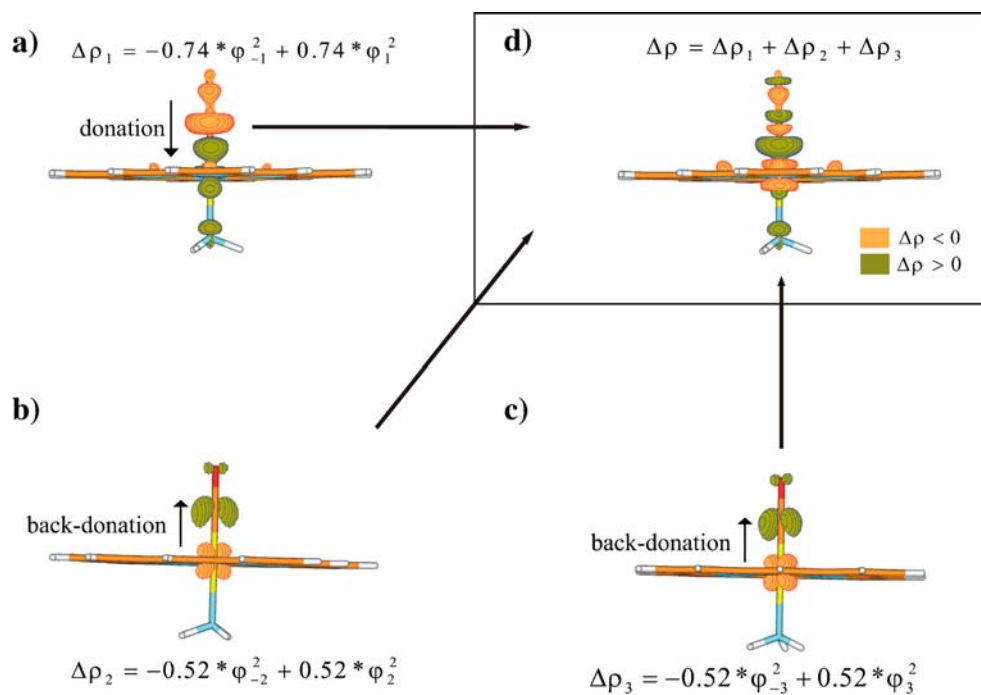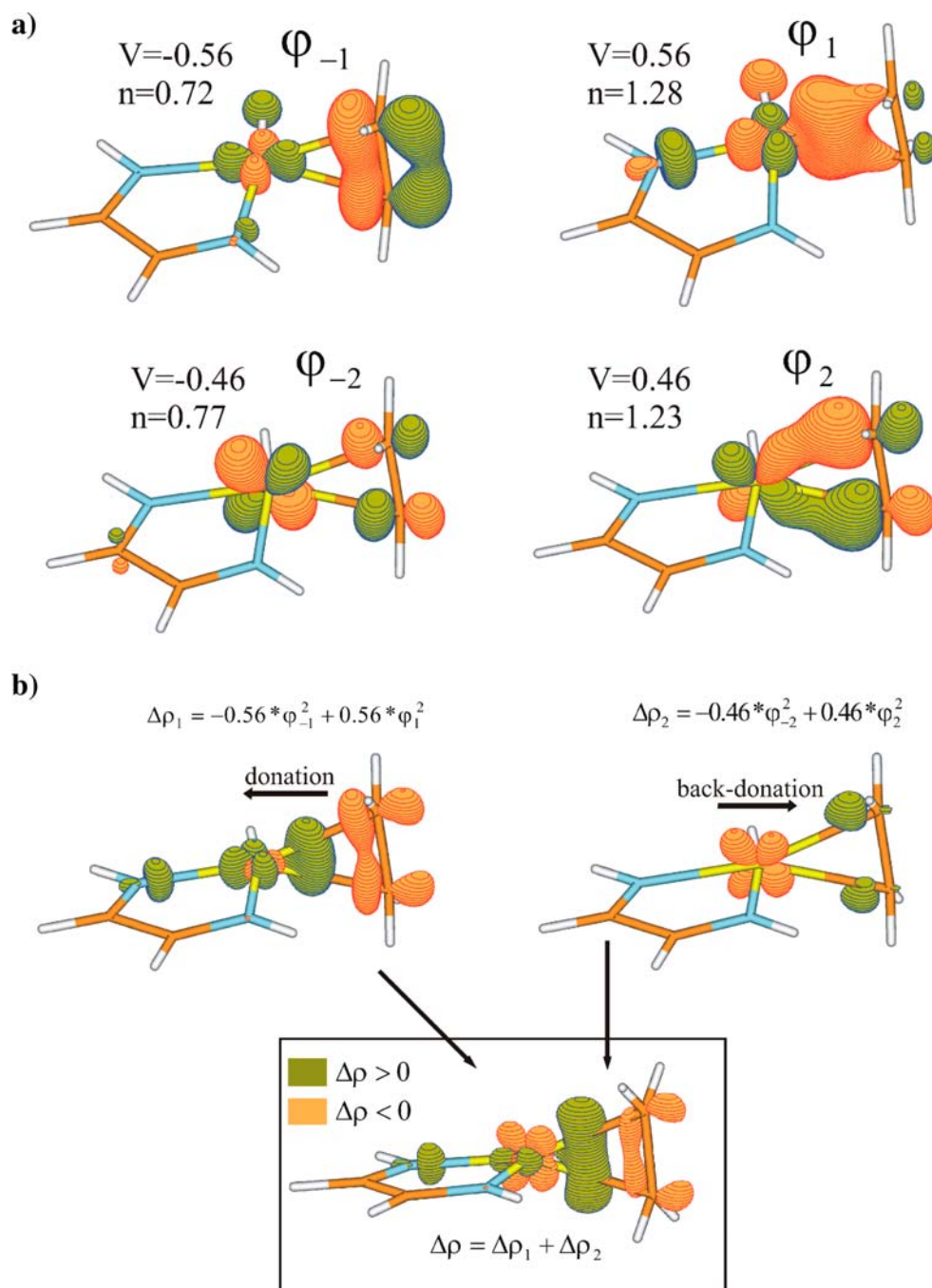
Fig. 6 The natural orbitals for chemical valence (**a**) and their contributions to $\Delta\rho$ (**b**), for the [Ni–diimine–hydride]/ethylene system. The details as in Figs. 3 and 5

density, $\Delta\rho$, contains both contributions, and thus, it is characterized by an increase of electron density in the bond region.

The basic features of NOCV are also similar in the case of the third system studied (Figs. 7 and 8). Three pairs of NOCV contribute to the metal–CO bond, one of σ-character and two pairs of π-symmetry. This is quite similar to the heme–CO system discussed earlier. However, there is a slight difference in the eigenvalues of the π-pairs (±0.37 and ±0.30 for $\varphi_{\pm2}$ and $\varphi_{\pm3}$, respectively). This comes as a result of an asymmetry of –NH$_3$ ligands. The

$\Delta\rho$ contribution from the first pair of NOCV again describes ligand → metal donation, and from the other two pairs corresponds to the metal → ligand backdonation. However, $\Delta\rho_2$ and $\Delta\rho_3$ exhibit a non-negligible, negative contributions at the oxygen atom of CO.

Table 1 compares the NOCV-eigenvalues determined for the three systems discussed above. These numbers are collected together with the estimates of donation/back-donation charge transfer from Mulliken population analysis (changes in HOMO/LUMO occupations) and the results of the Ziegler–Rauk bond-energy decomposition. In the case
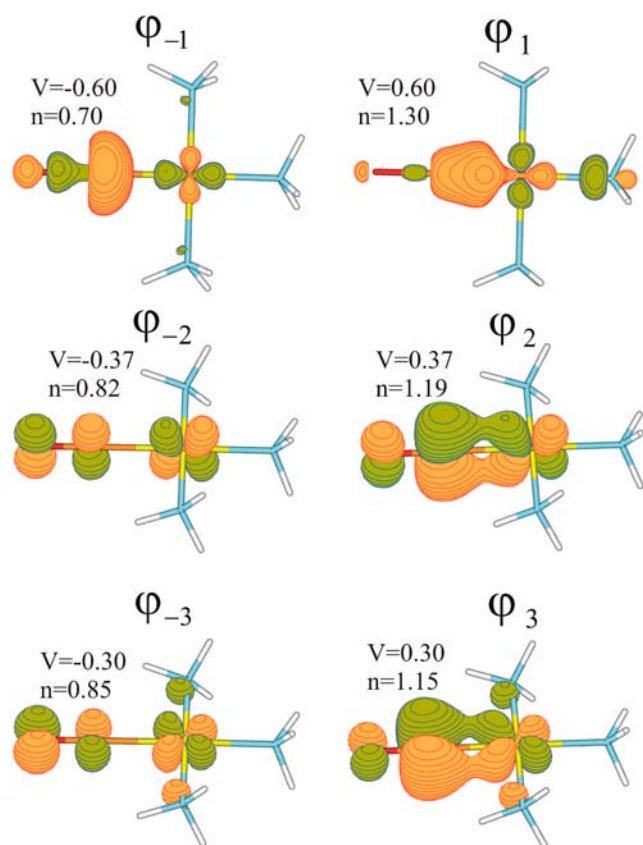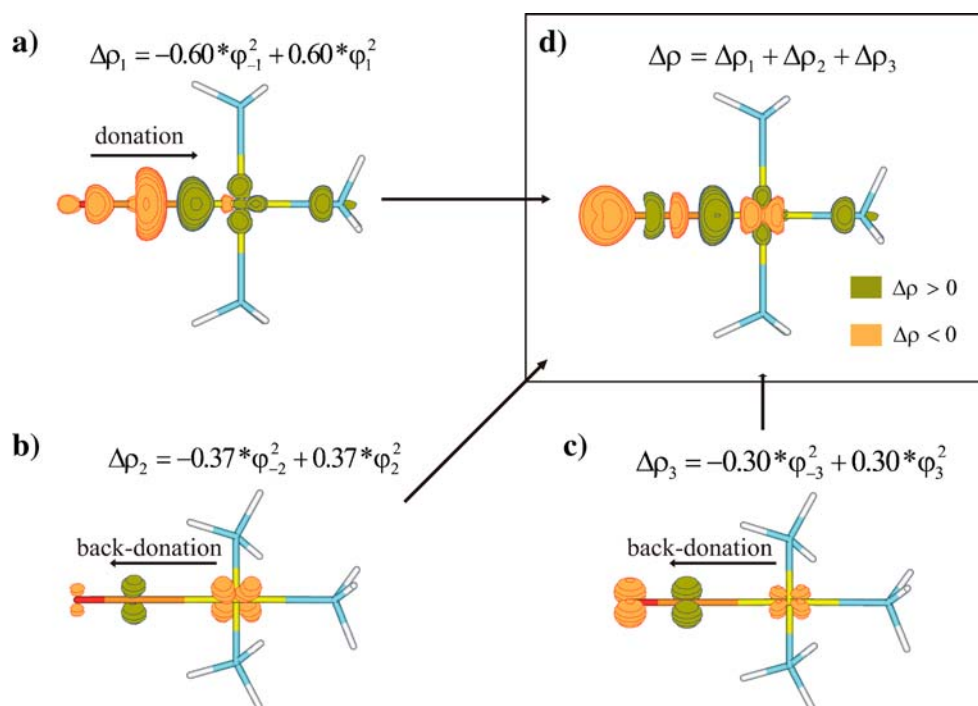
Fig. 7 The natural orbitals for chemical valence for the [Ni(NH$_3$)$_3$]/CO system. The details as in Fig. 3

of the bond-energy decomposition, the orbital interaction energy, ΔE_{orb} comprises both contributions (from donation and back-donation). Therefore, it is reasonable to compare

these values with the sum of the NOCV-charge transfer measures (sum of absolute values of eigenvalues).

The eigenvalues for the σ-orbitals (donation) change in the order: heme–CO >[Ni(NH$_3$)$_3$]$^{2+}$–CO >Ni–diimine–hydride–ethylene complex. The same order is observed for the back-donation measures (sum of π-eigenvalues).

The trend following from the eigenvalues is confirmed by both Mulliken population analysis, and Ziegler–Rauk bond-energy analysis: the correlations between $(V_d + V_{bd})$ and $\left(V_d^{Mull} + V_{bd}^{Mull}\right)$ as well as between $(V_d + V_{bd})$ and ΔE_{orb} are linear (both with $R^2=0.99$). It should be pointed out that the total bonding energy ΔE_{total} also includes the steric (electrostatic+Pauli repulsion) contributions. Therefore, ΔE_{total} cannot be expected to correlate well with the NOCV eigenvalues. Indeed, the correlation between $(V_d + V_{bd})$ and ΔE_{total} is worse ($R^2=0.82$), although the trend is preserved for the systems studied.

Thus, it can be concluded that the NOCV not only provide a compact description of the fragment-ligand bond and allow for separation of the donation and back-donation contributions, but they can also be useful in a comparison of these contributions in different complexes.

Concluding remarks

In the present article we used the natural orbitals for chemical valence (NOCV) for a description of the bond between the ligand and the transition-metal-based fragment in the example complexes including the heme/CO, Ni–diimine–hydride/ethylene, and [Ni(NH$_3$)$_3$]$^{2+}$/CO system.

Fig. 8 The donation (**a**) and back-donation (**b** and **c**) contributions to the deformation density ($\Delta\rho$, **d**) for [Ni(NH$_3$)$_3$]/CO the system, originated from the three pairs of complementary NOCV shown in Fig. 7. The $|\Delta\rho|=0.01$ a.u. contours are shown

Table 1 The donation and back-donation measures for the system studied in the present work, obtained from the NOCV analysis, Muliken populations of the fragment MO, and the Ziegler–Rauk interaction energy decomposition

	heme–CO	[Ni(NH$_3$)$_3$]–CO	[N^N–Ni–H]–C$_2$H$_4$
V_d[a]	0.74	0.60	0.56
V_{bd}[b]	1.04	0.67	0.46
$V_d + V_{bd}$	1.78	1.27	1.02
V_d^{Mull}[c]	0.51	0.39	0.33
V_{bd}^{Mull}[d]	0.40	0.24	0.14
$V_d^{Mull} + V_{bd}^{Mull}$	0.91	0.63	0.47
ΔE_{orb}[e]	−96.90	−69.30	−50.60
ΔE_{total}[f]	−41.3	−39.7	−36.01

[a] The eigenvalue for NOCV describing the donation processes.
[b] The eigenvalue (sum of eigenvalues) for NOCV describing the back-donation processes.
[c] Changes in Mulliken populations of MO involved in the donation process.
[d] Changes in Mulliken populations of MO involved in the back-donation process.
[e] The total orbital interaction energy between the fragments (kcal mol^{-1}).
[f] The total bonding energy between the fragments (including orbital-interaction, Pauli repulsion, and electrostatic terms).

We demonstrated that NOCV lead to a very compact description of the fragment-ligand bond, with only a few orbitals exhibiting non-zero eigenvalues. For the systems studied here, NOCV allow for a clear separation between the σ-donation and π-back-donation contributions to $\Delta\rho$. The conclusions on donation/back-donation magnitude resulting from NOCV were validated by a comparison with the results of the Mulliken population analysis of fragment molecular orbitals and the Zigler–Rauk interaction-energy decomposition. Therefore, it may be concluded that NOCV allow us to quantify the 'classical' concepts of donation and back-donation. We would like to point out that this is done without the arbitrariness introduced by a population analysis. Thus, natural orbitals for chemical valence in a fragment resolution can be useful in a description of bonding in various organometallic systems.

References

1. Frenking G, Frohlich N (2000) Chem Rev 100:717–774 (and references therein)
2. Dedieu A (2000) Chem Rev 100:543–600 (and references therein)
3. Niu S, Hall MB (2000) Chem Rev 100:353–405 (and references therein)
4. Dewar MJS (1951) Bull Soc Chim 18:C71–C79
5. Chatt J, Duncanson JA (1953) J Chem Soc 3:2939–2943
6. Cotton FA, Wilkinson G (1988) Advanced Inorganic Chemistry. Wiley, New York
7. Nalewajski RF, Mrozek J, Formosinho SJ, Varandas AJC (1994) Int J Quant Chem 52:1153–1176
8. Nalewajski RF, Mrozek J (1994) Int J Quant Chem 51:187–200
9. Nalewajski RF, Mrozek J (1996) Int J Quant Chem 57:377–389
10. Nalewajski RF, Mrozek J, Mazur G (1996) Can J Chem 74:1121–1130
11. Nalewajski RF, Mrozek J, Michalak A (1997) Int J Quant Chem 61:589–601
12. Nalewajski RF, Mrozek J, Michalak A (1998) Polish J Chem 72:1779–1791
13. Stryer L (1995) Biochemistry. In: Freeman WH (ed) San Francisco
14. Ittel SD, Johnson LK, Brookhart M (2000) Chem Rev 100:1169–1203 (and references therein)
15. Mitoraj M, Michalak A (2005) J Mol Model 11:341–350
16. Becke A (1988) Phys Rev A 38:3098–3100
17. Perdew JP (1986) Phys Rev B 34:7406–7406
18. Perdew JP (1986) Phys Rev B 33:8822–8824
19. te Velde G, Bickelhaupt FM, Baerends EJ, Fonseca Guerra C, van Gisbergen SJA, Snijders JG, Ziegler T (2001) J Comput Chem 22:931–967 (and references therein)
20. Baerends EJ, Ellis DE, Ros P (1973) Chem Phys 2:41–51
21. Boerrigter PM, te Velde G, Baerends EJ (1988) Int J Quantum Chem 33:87–113
22. Versluis L, Ziegler T (1988) J Chem Phys 88:322–328
23. te Velde G, Baerends EJ (1992) J Comput Phys 99:84–98
24. Fonesca Geurra C, Visser O, Snijders JG, te Velde G, Baerends EJ (1995) In: Clementi E, Corongiu G (eds) Methods and Techniques in Computational Chemistry METACC-9. STEF: Cagliari, pp 303–395
25. Mulliken RS (1955) J Chem Phys 23:1833–1841
26. Ziegler T, Rauk A (1978) Theor Chim Acta 46:1–9
27. Ziegler T, Rauk A (1979) Inorg Chem 18:1755–1759