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Bond Orbitals from Chemical Valence Theory

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Two sets of orbitals are derived, directly connected to the Nalewajski−Mrozek valence and bond-multiplicity indices: *Localized Orbitals from the Bond-Multiplicity Operator* (LOBO) and the *Natural Orbitals for Chemical Valence* (NOCV). LOBO are defined as the eigenvectors of the bond-multiplicity operator. The expectation value of this operator is the corresponding bond index. Thus, the approach presented here allows for a discussion of localized orbitals and bond multiplicity within one common framework of chemical valence theory. Another set of orbitals discussed in the present work, NOCV, are defined as eigenvectors of the overall chemical valence operator. This set of orbitals can be especially useful for a description of bonding in transition metal complexes, as it allows for separation of the deformation density contributions originating from the ligand → metal donation and metal → ligand back-donation.

Introduction

The concepts such as orbital hybridization, localized orbitals, chemical valence, and bond multiplicity are among those essential for chemistry. These quantities are related to the "classical" Lewis electron-pair picture[1] and the structural formulas of molecules, and as such they provide a link between rigorous description of electronic structure by quantum mechanics, and the language of chemistry. In the case of both the localized orbitals and bond indices, a number of definitions/methods have been proposed in the literature. The invariance of a single-determinantal wave function with respect to a unitary transformation of orbitals[2] allows one to apply different localization criteria, leading to the same wave function and total electron-density distribution. Alternative definitions of the localized orbitals have been widely used in chemical interpretations, starting from the solid-state Wannier functions,[3] through Coulson,[4] Lennard-Jones and Pople,[5−7] Boys,[8] Ruedenberg,[9−12] and Pipek-Mezey[13] up to the bond-order orbitals defined by Jug[14−16] and the related natural-bond orbitals (NBO) by Weinhold et al.[17−21]

It was noticed by Ruedenberg[22] that the canonical MO representation is especially useful for a comparison of different states of the same system, and the localized orbital description facilitates a comparison of different systems in the same state. The utility of localized orbitals was also demonstrated in the NMR interpretation[23−25] as well as in the analysis of response properties.[26] Recently, it has been also shown that the localized orbitals can lead to better CI convergence than the Löwdin natural orbitals.[27]

As in the case of localization schemes, a few alternative definitions of various valence and bond-multiplicity measures have been proposed, starting from Pauling,[28] Coulson,[29] and Wiberg,[30] through Jug[14] and Gopinathan,[31] Mayer,[32] Ciosłowski and Mixon,[33] up to the recently developed two- and three-electron indices of Nalewajski, Köster, Jug, and Mrozek,[34−40] and the Nalewajski information-theory-based concepts.[41,42]

It is worth pointing out that the localization methods which are commonly used nowadays have been developed independently from the most popular bond-multiplicity measures. Due to their obvious interpretational connections, it would be desired to have them unified within one theoretical framework. The first successful attempt of such an unification was presented by Jug.[14−16] It was as well the first contribution where the natural orbitals were used in the theory of chemical valence.

The main purpose of this study was to introduce bond orbitals that are linked to the Nalewajski and Mrozek valence and bond-multiplicity approach. Two sets of orbitals are investigated in the present work: *Localized Orbitals from the Bond-Multiplicity Operator* (LOBO), and the *Natural Orbitals for Chemical Valence* (NOCV). The latter are as well directly connected with the differential density (deformation density), another quantity commonly used in a description of chemical bonding.

Theory and Computational Details

Nalewajski and Mrozek Valence and Bond-Multiplicity Appraoch. Two-electron valence indices have been originally defined by Nalewajski, Köster, and Jug;[34] the modified version was later developed by Nalewajski and Mrozek.[35] These indices were derived by considering changes in the pair-diagonal part of the two-electron density matrix (i.e., two-electron probabilities) due to formation of the molecule from isolated atoms (promolecule). For a single-determinantal wave-functions they can be expressed in terms of the changes in the molecular and promolecular *charge-and-bond-order* (CBO) matrix (first-order density matrix), $\Delta\mathbf{P} = \mathbf{P} - \mathbf{P}^0$.[34,35]

In addition to modified valence indices of ref 35, two alternative sets of Nalewajski−Mrozek indices were proposed and explored in a series of articles.[36−40] They comprise the one- and two-center contributions, both including the covalent ($V^{(1),\mathrm{cov}}$, $V^{(2),\mathrm{cov}}$) as well as ionic ($V^{(1),\mathrm{ion}}$, $V^{(2),\mathrm{ion}}$) parts. Within each set, the sum of all valence indices is preserved,

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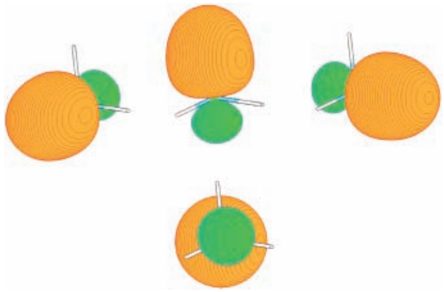

Figure 1. LOBO for ammonia molecule.

i.e., all three sets give rise to the same value of the *overall valence*:

$$V=\sum_{\mathrm{A}}(V_{\mathrm{A}}^{(1),\mathrm{ion}}+V_{\mathrm{A}}^{(1),\mathrm{cov}})+\sum_{\mathrm{A}<}\sum_{\mathrm{B}}(V_{\mathrm{AB}}^{(2),\mathrm{ion}}+V_{\mathrm{AB}}^{(2),\mathrm{cov}}) \tag{1}$$

The overall valence corresponds to the total number of chemical bonds in the molecule.[38−40] Thus, to construct bond-multiplicity indices one has to express the overall valence solely in terms of diatomic contributions:

$$V=\sum_{\mathrm{A}}\sum_{\mathrm{B}}b_{\mathrm{AB}} \tag{2}$$

This was done by splitting the one-center index of an atom among the bonds that this atom forms. Thus, the bond-multiplicity index was calculated as a sum of the relevant two-center part and weighted contributions from one-center indices of the two atoms:[38−40]

$$b_{\mathrm{AB}}=V_{\mathrm{AB}}^{(2)}+w_{\mathrm{A}}^{\mathrm{AB}}V_{\mathrm{A}}^{(1)}+w_{\mathrm{B}}^{\mathrm{AB}}V_{\mathrm{B}}^{(1)} \tag{3}$$

The way of dividing one-center terms is somewhat arbitrary. The proportional weighting factors

$$w_{\mathrm{X}}^{\mathrm{XY}}=V_{\mathrm{XY}}^{(2),\mathrm{cov}}\Big/\sum_{Z}V_{\mathrm{XZ}}^{(2),\mathrm{cov}} \tag{4}$$

were used in all the previous applications.[38−40] They have been shown to give bond-multiplicity values in agreement with the chemical intuition.

It was demonstrated[39] for the spin-restricted case that

$$V={}^{1}/{}_{4}\mathrm{Tr}(\Delta\mathbf{P}^{2})={}^{1}/{}_{2}\mathrm{Tr}(\mathbf{P}\Delta\mathbf{P}) \tag{5}$$

Thus, the right-hand side of eq 5 allows one to formally identify the overall valence V as the expectation value of the valence operator $\hat{V}$:[39]

$$V=\langle\hat{V}\rangle=\langle\Psi|\hat{V}|\Psi\rangle= \mathrm{Tr}(\mathbf{PV})={}^{1}/{}_{2}\mathrm{Tr}(\mathbf{P}\Delta\mathbf{P})=\mathrm{Tr}(\mathbf{P}\,{}^{\mathbf{1}}/{}_{2}\Delta\mathbf{P}) \tag{6}$$

From eq 6 it may be deduced that the matrix form of the valence operator can be

$$\mathbf{V}={}^{\mathbf{1}}/{}_{\mathbf{2}}\Delta\mathbf{P} \tag{7}$$

Localized Orbitals from the Partitioning of the Valence Operator. To define localized orbitals related to the Nalewajski and Mrozek bond multiplicities, we split the valence operator into the diatomic contributions ("bond-multiplicity operators"), in analogy to eq 2:

$$\hat{V}=\sum_{\mathrm{A}<}\sum_{\mathrm{B}}\hat{V}^{\mathrm{AB}} \tag{8}$$

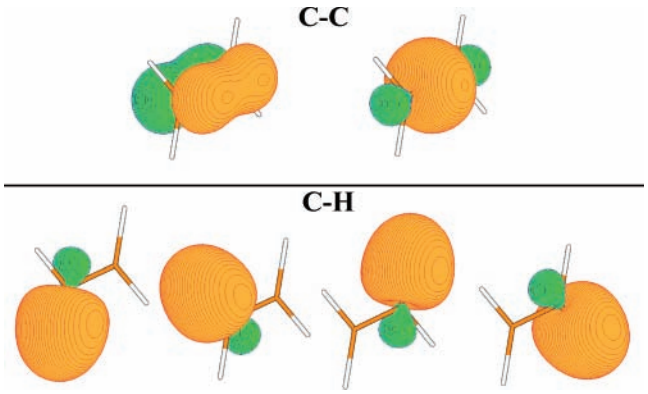

Figure 2. LOBO for ethylene molecule, C_2H_4.

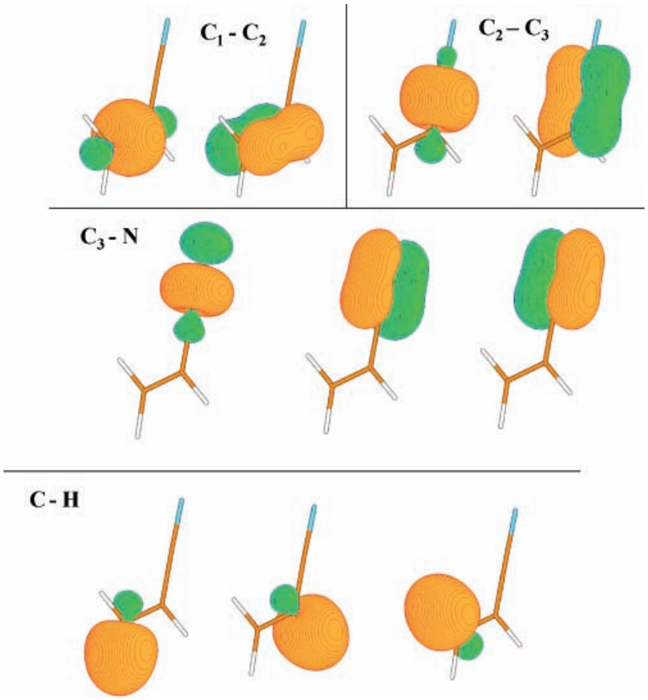

Figure 3. LOBO for acrylonitrile molecule, $CH_2{=}CH_2{-}CN$.

and respectively for the matrix form,

$$\mathbf{V}={}^{1}/{}_{2}\sum_{\mathrm{A}<}\sum_{\mathrm{B}}\Delta\mathbf{P}^{\mathrm{AB}} \tag{9}$$

The diatomic matrices $\Delta\mathbf{P}^{\mathrm{AB}}$ are constructed in such a way that they contain the nonzero atomic and interatomic blocks for two atoms, A and B; the other elements vanish. Thus, in analogy to eqs 2,3 for bond multiplicities, the atomic blocks are split between the "bonds":

$$\Delta\mathbf{P}^{\mathrm{AB}}=\begin{bmatrix} w_{\mathrm{A}}^{\mathrm{AB}}\Delta\mathbf{P}_{\mathrm{AA}} & \Delta\mathbf{P}_{\mathrm{BA}} & 0... \\ \Delta\mathbf{P}_{\mathrm{AB}} & w_{\mathrm{B}}^{\mathrm{AB}}\Delta\mathbf{P}_{\mathrm{BB}} & 0... \\ 0 & 0 & 0... \end{bmatrix} \tag{10}$$

The way to split one-center blocks is certainly arbitrary. We propose here to use the same proportional weighting factors as for bond multiplicities (eq 4) to have a direct correspondence between bond orbitals and bond indices.

The localized orbitals ψ describing the bond between the atoms A and B can be then obtained from diagonalization of

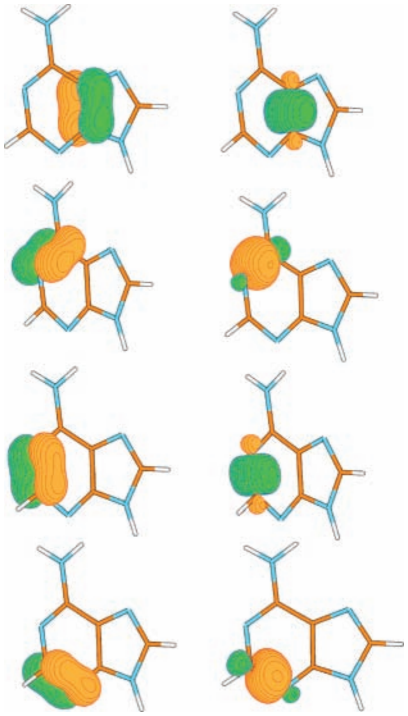

Figure 4. LOBO describing the σ- and π-components of the selected C−C and C−N bonds in the adenine molecule.

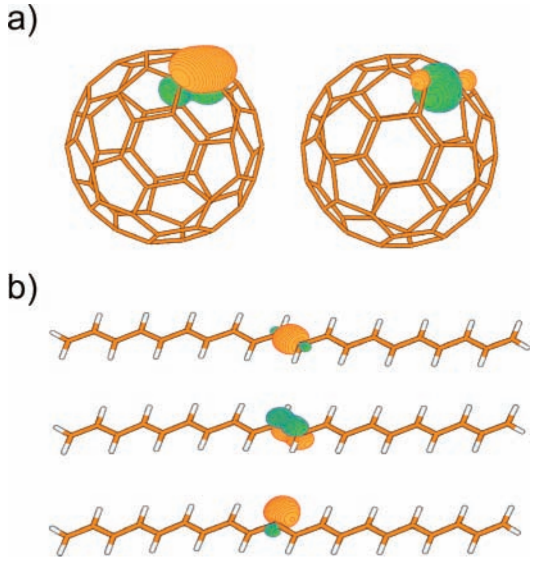

Figure 5. LOBO for selected C−C bond in fullerene C_{60} (panel a). Panel b demonstrates LOBO describing the middle C−C bond and a neighboring C−H bond in the *trans* polyacetylene model ($C_{20}H_{22}$).

the $\Delta\mathbf{P}^{AB}$ matrix. Thus, they are eigenvectors of the operator $\hat{V}^{AB}$:

$$\hat{V}^{AB}\psi_i^{AB} = v_i^{AB}\psi_i^{AB} \qquad i = 1, ..., n \tag{11}$$

Further, it is straightforward to show (see the Appendix) that the bond multiplicity (eq 3) for the bond A-B is the expectation value of the operator $\hat{V}^{AB}$:

$$b_{AB} = \langle\hat{V}^{AB}\rangle = {}^{1}/_{2}\mathrm{Tr}(\mathbf{P}\Delta\mathbf{P}^{AB}) \tag{12}$$

Therefore, we will refer to this set of orbitals as *Localized Orbitals from the Bond-Multiplicity Operator* (LOBO).

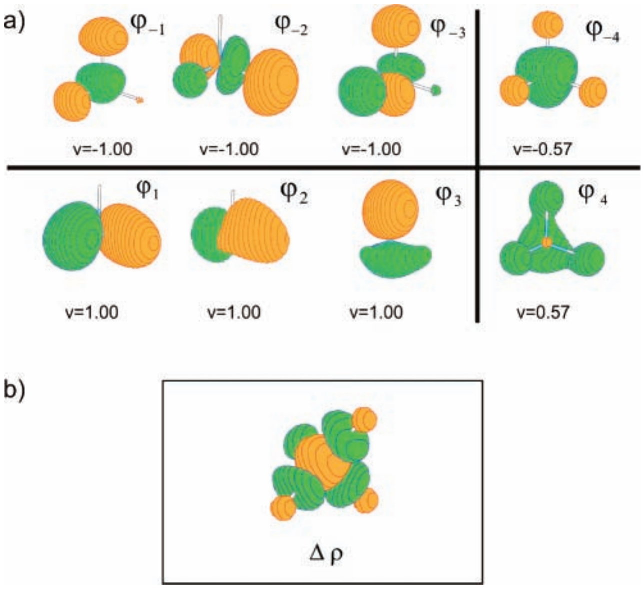

Figure 6. NOCV for ammonia molecule in the atomic resolution (panel a) and the differential density $\Delta\rho = \rho_{mol} - \Sigma\rho_{at}$ (panel b).

In conclusion, it should be noticed that the definition of the bond-multiplicity operator relies on the arbitrary partitioning of one-center terms between the bonds. It is important to emphasize, however, that all the methods referring to the bonds in molecules have some inherent arbitrariness. This is similar to the definitions of atoms-in-molecules.[43]

Natural Orbitals for Chemical Valence (NOCV). Another set of orbitals directly related to the theory of chemical valence can be obtained from diagonalization of the overall $\Delta\mathbf{P}$ matrix. The *Natural Orbitals for Chemical Valence* (NOCV) are defined as the eigenvectors of the valence operator $\hat{V}$:

$$\hat{V}\varphi_i = v_i\varphi_i \qquad \text{where } i = 1, ..., N \tag{13}$$

The eigenvalue v_i describes the contribution from the ith NOCV to the global valence:

$$V = \frac{1}{2}\sum_{i=1}^{N} v_i^2 \tag{14}$$

Let us consider the differential density (deformation density), $\Delta\rho$, commonly used for visualization of chemical bonds, expressed in the terms of atomic orbitals χ:

$$\Delta\rho(r) = \sum_{a}^{AO}\sum_{b}^{AO}\Delta\mathbf{P}_{ab}\chi_a^*(r)\,\chi_b(r) \tag{15}$$

In the NOCV representation the differential density can be written as

$$\Delta\rho(r) = \sum_{i=1}^{N} v_i|\varphi_i(r)|^2 \tag{16}$$

From normalization condition $\int\Delta\rho(r)\,\mathrm{d}r = 0$ and $\int|\varphi_i(r)|^2\,\mathrm{d}r = 1$, and from eq 16 it follows that

$$\sum_{i=1}^{N} v_i = 0 \tag{17}$$

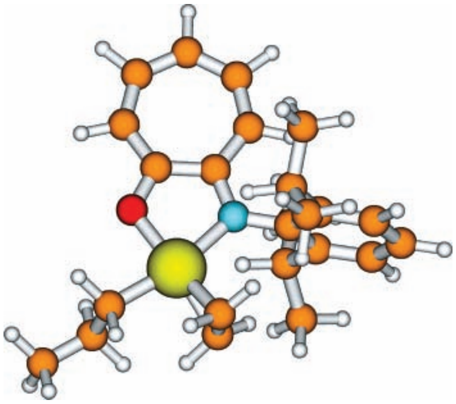

Figure 7. Structure of the ethylene π-complex with the Ni−anilinotropone catalyst for olefin polymerization.

Let us now consider the formation of one single bond (or more precisely: one component, e.g., σ, π, δ), with bond multiplicty equal 1. In contrary to other orbital-based approaches (molecular orbitals, localized orbitals), it is not possible to describe such a bond with a single NOCV. It follows immediately from eq 14 and the normalization condition of eq 17 that at least two orbitals are required, with nonzero eigenvalues; in the case considered here the eigenvalues are $+1$ and -1. For a fractional bond-multiplicity *a*, the corresponding eigenvalues are equal to $+a^{1/2}$ and $-a^{1/2}$.

In the molecular systems with many bonds and/or multiple bonds, NOCV can be grouped in pairs of complementary orbitals corresponding to the same eigenvalue with the opposite sign:

$$\hat{V}\varphi_{-k} = -v_k\varphi_{-k} \qquad \hat{V}\varphi_k = v_k\varphi_k \qquad k = 1, ..., N/2 \qquad (18)$$

It is important that only few pairs of NOCV exhibit nonzero eigenvalues, i.e., describe a formation of chemical bond; the remaining orbitals do not contribute to $\Delta\rho$.

It should be emphasized that this very property, i.e., pairing of the eigenfunctions corresponding to the opposite-sign eigenvalues, is also characteristic to Jug's bond-order orbitals,[14] as well as to the Inter-Reactant-Modes (the charge-flow channels describing changes in atomic populations) defined within the Charge Sensitivity Analysis by Nalewajski et al.[44]

In the case of NOCV this property is especially useful. Namely, using eq **18** the differential density can be expressed in terms of pair contributions:

$$\Delta\rho(r) = \sum_{k=1}^{N/2} v_k[-\varphi_{-k}^{\ 2}(r) + \varphi_k^{\ 2}(r)] = \sum_{k=1}^{N/2}\Delta\rho_k(r) \qquad (19)$$

Interpretation of NOCV follows from eq 19: an eigenvalue v_k corresponds to a fraction of electron density that is being transferred from the φ_{-k} orbital to the φ_k orbital, when the molecule is created from the pro-molecule.

Computational Details. In all the calculations the Amsterdam Density Functional (ADF) program[45−49] was used. The Becke−Perdew exchange-correlation functional[50−52] was applied. A standard double-ζ STO basis with one set of polarization functions was used for main-group elements (H, C, N, O), and a standard triple-ζ basis set was employed for nickel. The 1s electrons of C, N, O, as well as the 1s−2p electrons of Ni 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 potential in each SCF cycle; a fitting procedure applied in ADF is described in refs 45 and 46.

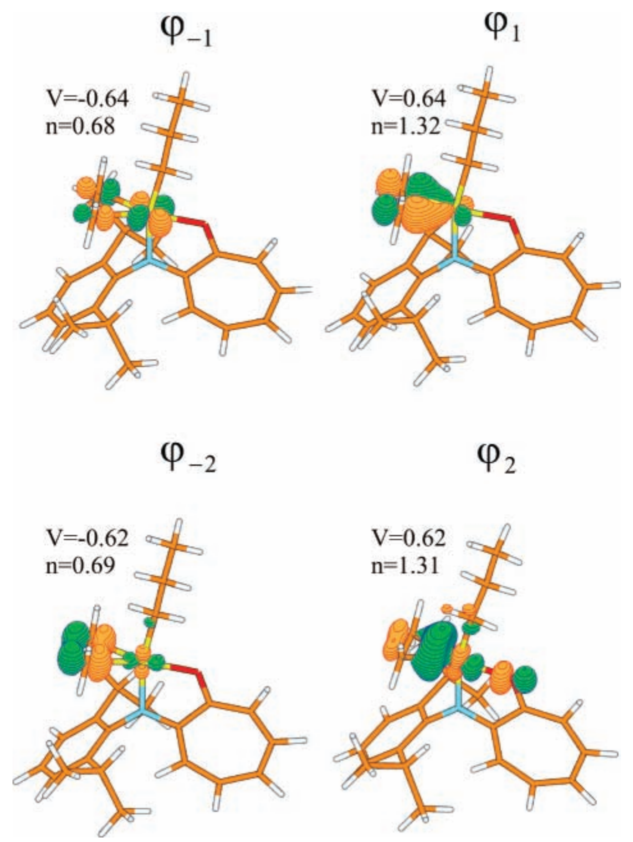

Figure 8. NOCV for the ethylene π-complex with the Ni−anilinotropone catalyst for olefin polymerization. Only the orbitals participating in bonding are shown ($|v| > 0.1$). The numbers denote NOCV eigenvalues (v) and their populations (n).

Results and Discussion

Localized Orbitals from Bond-Multiplicity Operator (LOBO). Figures 1−3 present examples of the Localized Orbitals from the Bond-Multiplicity Operator, determined for ammonia, ethylene, and acrylonitrile. These orbitals were obtained in *atomic resolution,* i.e., for the promolecule resulting from the isolated atoms placed in the same positions as in the molecule.

The orbital contours shown in Figures 1−3 clearly demonstrate a localized character of the LOBO. For the ammonia molecule (Figure 1) we have obtained three equivalent orbitals describing three N−H bonds and an additional orbital describing the lone pair on the nitrogen atom. For ethylene (Figure 2), there are two components of the C−C double bond, a σ-orbital and a π-orbital. The orbitals describing the four C−H bonds are again equivalent.

It should be pointed out that the orbitals that characterize different components of the same bond, i.e., the same pair of atoms, are mutually orthogonal (e.g., the ethylene σ- and π-orbitals for C−C bond). The orbitals determined for different atom-pairs are not orthogonal (e.g., ethylene C−C and C−H bond orbitals). However, the whole set may be orthogonalized, if required.

Another example set of localized orbitals determined for the acrylonitrile molecule is shown in Figure 3. It includes three typical σ-orbitals for the three C−H bonds, three components of the C−N triple bond (a σ- and two π-orbitals), and two components for each of the two C−C bonds (a σ- and a π-orbital). It is worth mentioning that the π-components are obtained for both C−C bonds, C_1−C_2 and C_2−C_3, formally considered as “double” and “single” bonds, respectively. The

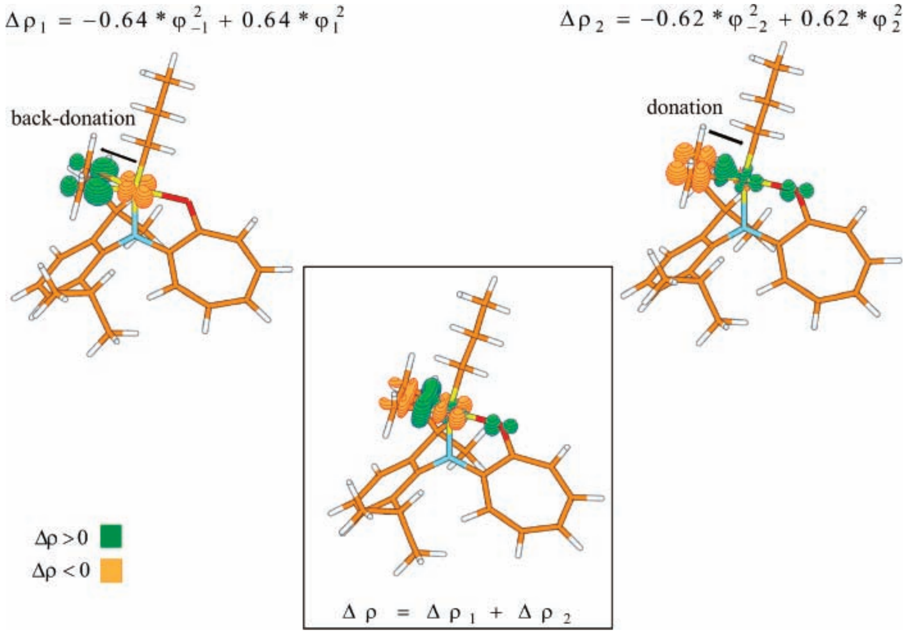

Figure 9. The NOCV back-donation ($\Delta\rho_1$) and donation contributions ($\Delta\rho_2$) to the deformation density ($\Delta\rho$) calculated for the ethylene complex with Ni−anilinotropone catalyst. The $|\Delta\rho| = 0.01$ au contours are shown.

contributions to the bond multiplicities of the two bonds (calculated as the LOBO contributions to Tr($\mathbf{P}\Delta\mathbf{P}^{AB}$); eq 12), originating from the π-component are 0.88 and 0.25. The total bond multiplicities (including σ- and π-components) are 2.08 and 1.18, for C_1-C_2 and C_2-C_3, respectively. For the "triple" C−N bond the calculated bond multiplicity is 3.13.

Thus, this example shows that one of the prospective applications of LOBO can be the assessment of alternative resonance structures and their relative importance.

To demonstrate the applicability of LOBO in a description of larger molecules as well as to assess the extent of their localization, we have determined LOBO for selected bonds in adenine, C_{60} fullerene, and the $C_{20}H_{22}$ molecule as a model for *trans*-polyacetylene chains, $-[CH{=}CH]_n-$, with $n = 10$. The results are presented in Figures 4 and 5.

In the case of adenine, the example orbitals describing the σ- and π-components of selected C−C and C−N bonds are shown in Figure 4. It is clearly seen that LOBO for this system demonstrate strictly localized, two-center character. The same is true for the C−C bonds in C_{60} as well as in $C_{20}H_{22}$. Figure 5 presents the LOBO contours for just one example of σ- and π-components for a C−C (and a C−H bond) for each molecule; for the other bonds the extent of localization is roughly the same. Thus, these examples demonstrate usefulness of LOBO even for the molecules containing aromatic rings or strongly conjugated π-electron bonds.

Natural Orbitals for Chemical Valence (NOCV). The differential nature of the chemical valence operator requires a definition of the promolecular reference state. The most natural choice is the *atomic reference state*, i.e., a promolecule built from isolated atoms, placed in the same positions as in the molecule. However, one can as well consider a *molecular-fragment reference state*, i.e., a promolecule built from larger, multiatomic, noninteracting fragments, positioned as in the molecule. In the following we will discuss the properties of NOCV in *atomic* and *fragment* resolution.

In Figure 6 are displayed NOCV for ammonia molecule, based on atomic reference state. The corresponding differential density plot is shown in Figure 6b. Only those orbitals that correspond to nonzero eigenvalues are shown. For eight of these orbitals, four are characterized by positive and four by negative eigenvalues, to fulfill the normalization condition of eq 17. Six orbitals (three pairs) correspond to $|v| = 1$, and one pair is characterized by eigenvalues of $|v| = 0.57$. The orbitals with negative eigenvalues exhibit "antibonding" character, and those corresponding to positive eigenvalues are mostly "bonding". However, NOCV obtained here are to a large extent delocalized. This comes from the fact that three pairs of orbitals, characterizing three equivalent N−H bonds, correspond to the same value of $|v|$. Thus, any linear combination of those orbitals will correspond to the same eigenvalue. This has the consequence that within the set of degenerate NOCV corresponding to the same $|v|$ (φ_{-1}, φ_{-2}, φ_{-3}, φ_1, φ_2, φ_3), it is not possible to uniquely select pairs of complementary NOCV (eqs 18 and 19). Therefore, only the contribution to $\Delta\rho$ from all those orbitals has a physical meaning.

This example shows that in atomic resolution, in which the valence operator "describes" formation of many bonds, NOCV leads to a delocalized picture with degenerate pairs of orbitals. However, this set of orbitals may be very useful in a resolution of two fragments, i.e., when the corresponding valence operator "describes" formation of only one bond between the fragments.

To illustrate the utility and interpretation of NOCV in the fragment resolution we have determined NOCV for a ethylene complex with the Ni−anilinotropone α-olefin polymerization catalyst,[53] shown in Figure 7. In this case we consider two fragments: ethylene and the organometallic fragment, containing the metal with the anilinotropone and propyl ligands. Thus, the NOCV will describe a bond between the organometallic fragment and ethylene.

Two pairs of complementary NOCV for this system are shown in Figure 8; the remaining NOCV correspond to eigenvalues $|v| < 0.1$, and thus they practically do not participate in the bonding. The contours shown in Figure 8 clearly demonstrate that all four NOCV are localized in the bond region. As in the previous case, the orbitals with negative eigenvalues exhibit antibonding character, and those corresponding to the positive eigenvalues are bonding orbitals. A pair of orbitals characterized by $|v| = 0.64$ (φ_{-1}, φ_1) describes a formation of a π-bond between ethylene antibonding MO and the metal *d* orbital. Second pair of NOCV characterized by $|v| = 0.62$ (φ_{-2}, φ_2) corresponds to a σ-component of the ethylene-metal bond.

It should be pointed out that both orbitals from each pair of NOCV are partially occupied in molecule and promolecule. The populations of NOCV in molecule (n) are shown in Figure 8. As we have already mentioned, the interpretation of NOCV follows from eq 19. In the process of bond formation v_k electrons are transferred from the φ_{-k} to the φ_k orbital. In the case of ethylene−Ni−anilinotropone complex, the populations of φ_{-1} and φ_1 in the promolecule (fragments) are 1.32 and 0.68 e, respectively, and in the final complex they “exchange” their occupations: 0.68 and 1.32 e. Similarly for φ_{-2} and φ_2 the populations are 1.31 and 0.69 e in promolecule, and 0.69 and 1.31 e in the final complex.

Figure 9 shows the deformation density $\Delta\rho = \rho(\text{complex}) - \rho(\text{ethylene}) - \rho(\text{Ni-fragment})$ and the corresponding contributions from the complementary pairs of NOCV. It is clearly seen that the contribution from first pair, φ_{-1} and φ_1, describes transfer of electron from the metal to ethylene. The second pair of NOCV describes the electron donation: ethylene → metal. Thus, this example shows that NOCV allows for a discussion of bonding in transition metal complexes in terms of the “classical” Dewar−Chatt−Duncanson model[54,55] of the ligand → metal donation and the metal → ligand back-donation.

Concluding Remarks

In the present study we have investigated two sets of orbitals directly linked to the Nalewajski−Mrozek valence and bond-multiplicity indices. It was demonstrated that localized orbitals can be obtained from the partitioning of the chemical valence operator into diatomic contributions. It was shown that LOBO, defined as the *eigenvectors of the bond-multiplicity operator*, have the general features of localized orbitals. It was shown in addition that the bond-multiplicity indices can be obtained as the expectation values of the corresponding bond-multiplicity operators. Thus, the approach presented here allows for a discussion of localized orbitals and bond indices within one common framework of chemical valence theory.

Another set of orbitals discussed in the present work are the Natural Orbitals for Chemical Valence. NOCV are defined as *eigenvectors of the overall chemical valence operator*. It was shown that this set of orbitals applied in the two-fragments resolution allows for a separation and quantitative assessment of the contributions to the deformation density from donation (ligand → metal) and back-donation (metal → ligand) electron-transfer processes. Thus, it is especially useful in a description of bonding in transition metal complexes.

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Appendix

Let us assume the spin-restricted case for simplicity. The expectation value of the bond-multiplicity operator, $\hat{V}^{\text{AB}}$, given by $^1/_2\text{Tr}(\mathbf{P}\Delta\mathbf{P}^{\text{AB}})$ may be decomposed into atomic and diatomic terms as

$$\begin{aligned}\frac{1}{2}\,\text{Tr}\mathbf{P}\Delta\mathbf{P}^{\text{AB}} &= \frac{1}{2}\sum_{\alpha}\sum_{\beta}P_{\alpha\beta}\Delta P^{\text{AB}}_{\alpha\beta} = \\ &\frac{1}{2}\sum_{\text{X}}\sum_{\text{x}}^{\text{X}}\sum_{\text{x}'}^{\text{X}}P_{\text{xx}'}\Delta P^{\text{AB}}_{\text{x}'\text{x}} + \sum_{\text{X}<}\sum_{\text{Y}}\sum_{\text{x}}^{\text{X}}\sum_{\text{y}}^{\text{Y}}P_{\text{xy}}\Delta P^{\text{AB}}_{\text{yx}} \\ &= \sum_{\text{X}}\left\{\frac{1}{2}\sum_{\text{x}}^{\text{X}}P_{\text{xx}}\Delta P^{\text{AB}}_{\text{xx}} + 2\sum_{\text{x}<}^{\text{X}}\sum_{\text{x}'}^{\text{X}}P_{\text{xx}'}\Delta P^{\text{AB}}_{\text{x}'\text{x}}\right\} + \\ &\sum_{\text{X}<}\sum_{\text{Y}}\sum_{\text{x}}^{\text{X}}\sum_{\text{y}}^{\text{Y}}P_{\text{xy}}\Delta P^{\text{AB}}_{\text{xy}} \quad \text{(A1)}\end{aligned}$$

From the definition of $\Delta\mathbf{P}^{\text{AB}}$ (eq 10) follows that all terms containing X, Y ≠ A, B vanish. What survives are two atomic terms (A and B) and one diatomic term (AB):

$$\begin{aligned}\frac{1}{2}\,\text{Tr}\mathbf{P}\Delta\mathbf{P}^{\text{AB}} &= \\ &\left\{\frac{1}{2}\sum_{\text{a}}^{\text{A}}P_{\text{aa}}\Delta P^{\text{AB}}_{\text{aa}} + 2\sum_{\text{a}<}^{\text{A}}\sum_{\text{a}'}^{\text{A}}P_{\text{aa}'}\Delta P^{\text{AB}}_{\text{a}'\text{a}}\right\} + \\ &\left\{\frac{1}{2}\sum_{b}^{B}P_{\text{bb}}\Delta P^{\text{AB}}_{\text{bb}} + 2\sum_{\text{b}<}^{\text{B}}\sum_{\text{b}'}^{\text{B}}P_{\text{bb}'}\Delta P^{\text{AB}}_{\text{b}'\text{b}}\right\} + \\ &\sum_{\text{a}}^{\text{A}}\sum_{\text{b}}^{\text{B}}P_{\text{ab}}\Delta P^{\text{AB}}_{\text{ba}} \\ &= w^{AB}_{\text{A}}\left\{\frac{1}{2}\sum_{\text{a}}^{\text{A}}P_{\text{aa}}\Delta P_{\text{aa}} + 2\sum_{\text{a}<}^{\text{A}}\sum_{\text{a}'}^{\text{A}}P_{\text{aa}'}\Delta P^{\text{AB}}_{\text{a}'\text{a}}\right\} + \\ &w^{\text{AB}}_{\text{A}}\left\{\frac{1}{2}\sum_{\text{b}}^{\text{B}}P_{\text{bb}}\Delta P^{\text{AB}}_{\text{bb}} + 2\sum_{\text{b}<}^{\text{B}}\sum_{\text{b}'}^{\text{B}}P_{\text{bb}'}\Delta P_{\text{b}'\text{b}}\right\} + \\ &\sum_{\text{a}}^{\text{A}}\sum_{\text{b}}^{\text{B}}P_{\text{ab}}\Delta P_{\text{ba}} \quad \text{(A2)}\end{aligned}$$

which gives bond multiplicity for the bond A−B, as defined by eq 3

$$\frac{1}{2}\,\text{Tr}\mathbf{P}\Delta\mathbf{P}^{\text{AB}} = w^{\text{AB}}_{\text{A}}V^{(1)}_{\text{A}} + w^{\text{AB}}_{\text{B}}V^{(1)}_{\text{B}} + V^{(2)}_{\text{AB}} \qquad \text{(A3)}$$

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