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REGULAR ARTICLE

On the properties of natural orbitals for chemical valence

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Abstract Natural orbitals for chemical valence (NOCV) were recently introduced as descriptors of chemical bond. They were shown to provide a valuable bond diagnosis in transition metal complexes (Mitoraj and Michalak in J Mol Model 13:347–355, 2007). The present paper treats the mathematical basis for the proposed method. In particular, the algebraic properties of NOCV, on which this methodology relies, are rigorously proven.

Keywords Natural orbitals for chemical valence · Valence theory

1 Introduction

Recently Mitoraj and Michalak [1,2] introduced Natural Orbitals for Chemical Valence (NOCV) as descriptors of chemical bond. This approach leads to very compact description of the bonding phenomenon because NOCV decompose the deformation density $\Delta\rho$ into diagonal contributions. The analysis of a chemical bond with NOCV was shown to be particularly valuable for transition metal complexes: in this case NOCV provide *quantitative* characterization of σ-donation and π-back-donation effects contributing to ligand–metal bond [1,2].

Natural orbitals for chemical valence are defined as eigenvectors of the *valence operator* of Nalewajski-Mrozek theory [3–7], being the difference of molecular and promolecular density operators:

$$V = 2\sum_{i=1}^{N}\left(|\psi_i\rangle\langle\psi_i| - \left|\psi_i^0\right\rangle\left\langle\psi_i^0\right|\right), \tag{1}$$

where $\{\psi_1,\ldots,\psi_N\}$ and $\left\{\psi_1^0,\ldots,\psi_N^0\right\}$ are occupied molecular and promolecular orbitals, respectively. The promolecule is a reference system for bond formation process consisting of non-interacting fragments placed at their equilibrium positions in the molecule. Naturally, the separation of a given molecule into fragments (i.e. the choice of the promolecule) is arbitrary—it depends on the selection of bond(s) being under investigation.

In the definition of V above (Eq. 1) the molecule and the fragments are assumed to have spin-restricted single-determinant wavefunctions. A straightforward generalization to spin-unrestricted case is possible: valence operator for each spin (↑ and ↓) should be considered separately: the orbitals ψ_i, ψ_i^0 would be then orbitals for the given spin; the factor "2" in Eq. 1 should be omitted.

In the construction of the quantitative measure for σ-donation and π-back-donation effects, the following "pairing property" of NOCV is of primary importance: all nonzero eigenvalues of V (i.e. those which contribute to the bond) appear in pairs of opposite numbers:

$$V\varphi_{\pm k} = \pm\nu_k\varphi_{\pm k} \quad (\nu_k > 0)\,. \tag{2}$$

Above, $(\varphi_{+k},\varphi_{-k})$ is a coupled pair of NOCV. Another, related property concerns the electronic populations ("occupation numbers") of NOCV, which are defined as expectation values of the molecular density operator, P:

$$n_{\pm k} = \langle\varphi_{\pm k}|P\varphi_{\pm k}\rangle\,, \tag{3}$$

Dedicated to Professor Nino Russo on the occasion of his 60th birthday.

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(where $P = 2\sum_{i=1}^{N} |\psi_i\rangle \langle\psi_i|$). It follows that the populations of NOCV in each pair $(\varphi_{+k}, \varphi_{-k})$ satisfy simple relations:

$$\begin{cases} n_{+k} + n_{-k} = 2 \\ n_{+k} - n_{-k} = \nu_k \ . \end{cases} \qquad (4)$$

According to Eqs. (2) and (4) the total electronic transfer due to bond formation might be decomposed into sum of *separated* transfers within pairs of coupled NOCV. For each k, the transfer of ν_k electrons from φ_{-k} to φ_{+k} orbital is observed; during this transfer the total number of electrons in $(\varphi_{-k}, \varphi_{+k})$ pair remains constant and equal exactly to two electrons [1].

The explanation of the algebraic properties of NOCV mentioned above (Eqs. 2, 4), which are the basis of the NOCV-based approach [1,2], will be the subject of the present paper. The proofs will be given for the case of spin-restricted wavefunctions (the extension to spin-unrestricted case is straightforward).

2 The "pairing property" of NOCV eigenvalues

In the proof of Eq. (2) given below we shall explicitly diagonalize the valence operator (1) by employing an auxiliary set of orbitals, which are analogous to the *paired orbitals* due to Amos and Hall [8]; see also the paper by Zilberberg and Ruzankin [9] (Paired orbitals were originally introduced in the context of natural- and spin-orbitals for the UHF-type wave-function.) A mathematical technique used in the contruction thereof is *singular value decomposition* (SVD) [10]. It was already employed in the theory of chemical bonding e.g. by the concept of paired interacting orbitals [11,12].

Let G be the $N \times N$ overlap matrix between occupied molecular and promolecular orbitals, i.e. $G_{ij} = \left\langle \psi_i | \psi_j^0 \right\rangle$. Singular value decomposition exists for G:

$$G = UWU_0^{\dagger},$$

where U, U_0 and W are $N \times N$ matrices; U and U_0 are unitary, whereas W is diagonal ($W_{ij} = w_i \delta_{ij}$).

Let us now define the following auxiliary orbitals:

$$a_i = \sum_{j=1}^{N} \psi_j U_i^j ; \ \ b_i = \sum_{j=1}^{N} \psi_j^0 (U_0)_i^j \quad (i = 1, \ldots, N) \ , \qquad (5)$$

which can be easily proven to satisfy the following orthogonality relations:

$$\begin{cases} \langle a_i | a_j \rangle = \delta_{ij} \\ \langle b_i | b_j \rangle = \delta_{ij} \\ \langle a_i | b_j \rangle = w_i \delta_{ij} \ . \end{cases} \qquad (6)$$

By analogy to the Amos–Hall paired orbitals, introduced for total- and spin-density operators arisen from UHF wavefunction, the orbitals a_i, b_i might be called "the paired orbitals for the valence operator". Using them, V may be easily rewritten as

$$V = 2\sum_{i=1}^{N} \left(|a_i\rangle \langle a_i| - |b_i\rangle \langle b_i| \right) . \qquad (7)$$

Now consider the combined set of orbitals $\{a_i, b_i\}_{i=1}^{N}$. Employing the orthogonality relations (6), one can easily assure that all *distinct* orbitals in this set are linearly independent. (In the other words: the only possible type of linear dependency is the exact equality $a_k = b_k$, which might happen for some k.) This property suggests the partitioning of one-particle Hilbert space $\mathcal{H}$ (spanned by the chosen AO basis) into three disjoint subspaces $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus \mathcal{H}_3$, where:

- $\mathcal{H}_1$ is spanned by those a_k and b_k for which $a_k \neq b_k$ (as noted above, all of them are linearly independent)
- $\mathcal{H}_2$ is spanned by all a_k such that $b_k = a_k$
- $\mathcal{H}_3$ is the linear complement of $\mathcal{H}_1 \oplus \mathcal{H}_2$ to $\mathcal{H}$.

From Eq. (7) one can show easily that $V\xi = 0$ for any $\xi \in \mathcal{H}_2 \oplus \mathcal{H}_3$. Thus, non-trivial (other than zero) eigenvalues of V can be obtained only within $\mathcal{H}_1$. To find them, let us inspect how V operates on the "paired orbitals" a_k, b_k spanning $\mathcal{H}_1$. For each k:

$$\begin{aligned} Va_k &= 2(a_k - w_k b_k) \\ Vb_k &= 2(w_k a_k - b_k) \ . \end{aligned}$$

Hence V—when restricted to $\mathcal{H}_1$ and expressed in the basis of $\{a_k, b_k\}$—is represented by a block-diagonal matrix consisting of 2×2 blocks V_k, where:

$$V_k = 2\begin{pmatrix} 1 & w_k \\ -w_k & -1 \end{pmatrix} . \qquad (8)$$

By explicit diagonalization of (8) one can show that each V_k contributes a pair of opposite eigenvalues $\pm\nu_k$, where

$$\nu_k = 2\sqrt{1 - w_k^2} \ .$$

(The square root above is well defined in the real domain because $|w_k| \leq 1$.) As already noted, all other eigenvalues of V (corresponding to $\mathcal{H}_2 \oplus \mathcal{H}_3$) are exactly zero. This statement finishes the proof.

3 Electronic populations of NOCV

Having the valence operator expressed in the basis of "paired orbitals" (compare Eq. 8) one can easily find its normalized eigenvectors as the combinations of a_k, b_k:

$$\varphi_{\pm k} = \frac{-w_k a_k + (1 \mp \nu_k/2)\, b_k}{\left[2\,(1 \mp \nu_k/2)\left(1 - w_k^2\right)\right]^{1/2}} \,.$$

Putting the above $\varphi_{\pm k}$ into definition (3) and expressing P by means of a_i (analogously to Eq. 7: $P = 2\sum_{i=1}^{N} |a_i\rangle\langle a_i|$) one finally obtains the electronic population of $\varphi_{\pm k}$:

$$n_{\pm k} = 1 \pm \nu_k/2 \,.$$

Such occupation numbers indeed satisfy (4) and this conclusion finishes the proof.

4 Conclusions

The present paper focused on proving the algebraic properties of the NOCV: the symmetry of their eigenvalues and simple relations between their electronic populations. These properties are crucial for the validity of the proposed NOCV-based analysis, which method provides simple but useful bond diagnosis, promising especially for transition metal compounds [1,2].

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