

# Multicenter Bond Index: Grassmann Algebra and N-Order Density Functional

*by*

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## **Abstract**

Through the N-order density functional introduced using Grassmann algebra, a straightforward meaning is attached to multicenter bond indices within the Hartree-Fock approximation; they represent the correlation between the fluctuations of the charges in each atomic center from their average values.

**Key-words:** Multicenter bond index; Grassmann algebra; N-order density functional.

Recently, we have introduced a multicenter chemical bond index intended for closed-shell systems in the one-determinant Hartree-Fock approximation [1]. We shall now link it to the  $N$ -order density functional ( $N$  being the number of electrons in the system considered).

One of us [2] has used Grassmann algebra as an alternative formulation of the wavefunction antisymmetry description. Let us briefly summarize this approach.

State vectors are defined from the generators of a multilinear space  $\mathcal{G}$ , which is introduced as an  $N$ -linear alternating application of the Hilbert space  $\mathcal{H}$ . Spin orbitals may be written as exterior products between generator elements  $\xi_\mu$  of the  $\mathcal{G}$  space. An  $N$ -linear alternating map in the space  $\mathcal{H}$  is then [2, 3]:

$$\Lambda : \mathcal{H} \times \mathcal{H} \times \cdots \times \mathcal{H} \rightarrow \mathcal{G} \quad (1)$$

and  $\mathcal{G}$  is called a Hilbert-Grassmann vector space. The state vector of an  $N$ -electron system takes the form

$$|12 \cdots N\rangle = \xi_1 \wedge \xi_2 \wedge \cdots \wedge \xi_N \quad (2)$$

If any two  $\xi$ 's are equal, this vanishes as it should (Pauli principle);  $\xi_\mu \wedge \xi_\nu$  is a tensor product [2]. These multilinear alternating maps can be understood as generalization of determinants [2, 4].

We shall denote as  $\xi_\mu$  the generators belonging to  $\mathcal{G}$  and as  $\xi^\mu$  those belonging to  $\mathcal{G}^+$  (the dual space of  $\mathcal{G}$ ) having respectively the same properties as the conventional annihilation and creation operators [2].

As the Hilbert space is provided with an inner product, we may consider the  $2N$ -linear form  $\Gamma : \mathcal{H} \times \mathcal{H} \times \cdots \times \mathcal{H} \rightarrow R$  (the field of all real numbers) as defined, in the Hartree-Fock approximation, in the following way [5]

$$\Gamma(\xi_1, \cdots, \xi_N; \xi^1, \cdots, \xi^N) = (\xi_1 \wedge \xi_2 \wedge \cdots \wedge \xi_N) \cdot (\xi^1 \wedge \xi^2 \wedge \cdots \wedge \xi^N) \quad (3)$$

The dot indicates inner product. This in turn is

$$\det(\langle \xi_\mu \cdot \xi^\nu \rangle) \det(\mathcal{D}_N) = d_{12 \cdots N}^{12 \cdots N} \quad (4)$$

For monoelectronic spin orbitals  $\xi_\mu$ ,  $\mathcal{D}_N$  [2, 5] takes the form

$$\mathcal{D}_N = \begin{vmatrix} \langle \xi_1 \cdot \xi^1 \rangle & \langle \xi_1 \cdot \xi^2 \rangle & \cdots & \langle \xi_1 \cdot \xi^N \rangle \\ \langle \xi_2 \cdot \xi^1 \rangle & \langle \xi_2 \cdot \xi^2 \rangle & \cdots & \langle \xi_2 \cdot \xi^N \rangle \\ \vdots & \vdots & & \vdots \\ \langle \xi_N \cdot \xi^1 \rangle & \langle \xi_N \cdot \xi^2 \rangle & \cdots & \langle \xi_N \cdot \xi^N \rangle \end{vmatrix} \quad (5)$$

This expression is much more general than the application we do here of it.

Let us take the generalized inner products in (5) as being equal to the first-order spin density matrix  $\rho_1$ :

$$(\xi_\mu \cdot \xi^\nu) = (\rho_1)_\mu^\nu = \rho_1(x_\mu; x^\nu) \quad (6)$$

If we separate the spin-space coordinates  $x$  into space and spin coordinates, we may write:

$$(\rho_1)_\mu^\nu = \delta_{\sigma_\mu \sigma_\nu} \sum_i x_{i\mu} x^{i\nu} = \Pi_\mu^\nu \delta_{\sigma_\mu \sigma_\nu} \quad (7)$$

where  $\sigma_{\mu(\nu)}$  is the spin orbital  $\mu(\nu)$  and  $x_{i\mu}(x^{i\nu})$  are the covariant (contravariant) coefficients of the  $i$ -th molecular orbital ( $MO$ ) (5,6,7). In orthogonal bases and the one-determinant Hartree-Fock approximation, the functional in (5) is the  $N$ -density matrix  $\rho_N$ , assuming the more familiar form [8]

$$\rho_N = \begin{vmatrix} \rho_1(x_1; x'_1) & \rho_1(x_1; x'_2) & \cdots & \rho_1(x_1; x'_N) \\ \rho_1(x_2; x'_1) & \rho_1(x_2; x'_2) & \cdots & \rho_1(x_2; x'_N) \\ \vdots & \vdots & & \vdots \\ \rho_1(x_N; x'_1) & \rho_1(x_N; x'_2) & \cdots & \rho_1(x_N; x'_N) \end{vmatrix} \quad (8)$$

In eq. (3),  $\Gamma$  is an alternating multilinear from both in the rows and in the columns of the  $\mathcal{D}_N$  functional, i.e. is alternating separately in the  $\xi'_\mu$ s and the  $\xi^\nu$ 's.

Taking electron pairs in eq. (4), summing over all spins for  $N = 2$ , a result is obtained under a different form than those obtained previously [2, 9]

$$\sum_{\substack{a \in A \\ b \in B}} \sum_{\sigma_a, \sigma_b} \det(\mathcal{D}_2) = \langle \hat{q}_A \hat{q}_B \rangle = \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle - I_{AB}/2 \quad (9)$$

where  $\hat{q}_A$  is the  $A$  atom charge operator and  $I_{AB}$  the bond index between atoms  $A$  and  $B$  (generalization to non-orthogonal bases of the Wiberg index [10]):

$$\langle \hat{q}_A \rangle = 2 \sum_{a \in A} \Pi_a^a ; \quad I_{AB} = 2^2 \sum_{\substack{a \in A \\ b \in B}} \Pi_a^b \Pi_b^a \quad (10)$$

Eqs. (9) and (10) are intended for closed-shell systems of wavefunctions written as a single determinant [6, 7]. We have then [2, 9]

$$\langle (\hat{q}_A - \langle \hat{q}_A \rangle) (\hat{q}_B - \langle \hat{q}_B \rangle) \rangle = -I_{AB}/2 \quad (11)$$

As  $I_{AB}$  represents the correlation between the fluctuations of  $q_A$  and  $q_B$  from their average values, it must be due to exchange, the only correlation recognized in the Hartree-Fock approximation.

The above concepts may be extended through  $\mathcal{D}_3$  and  $\mathcal{D}_4$ . Thus, carrying out a bit lengthy developments which do not involve further difficulties, it may be shown that

$$\begin{aligned} \sum_{\substack{a \in A \\ b \in B \\ c \in C}} \sum_{\sigma_a, \sigma_b, \sigma_c} \det(\mathcal{D}_3) &= \langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle = \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle \langle \hat{q}_C \rangle + I_{ABC}/2 - \\ &- \frac{1}{2} \langle \hat{q}_A \rangle I_{BC} - \frac{1}{2} \langle \hat{q}_B \rangle I_{AC} - \frac{1}{2} \langle \hat{q}_C \rangle I_{AB} \end{aligned} \quad (12)$$

The three-center bond index  $I_{ABC}$  [1] corresponds to the correlations between the fluctuations of  $q_A, q_B$  and  $q_C$  from their average values:

$$\begin{aligned} \frac{1}{2} I_{ABC} &= \langle (\hat{q}_A - \langle \hat{q}_A \rangle) (\hat{q}_B - \langle \hat{q}_B \rangle) (\hat{q}_C - \langle \hat{q}_C \rangle) \rangle ; \\ I_{ABC} &= 2^3 \sum_{\substack{a \in A \\ b \in B \\ c \in C}} \Pi_a^b \Pi_b^c \Pi_c^a \end{aligned} \quad (13)$$

Similarly, some algebra starting from  $\mathcal{D}_4$  leads to

$$\begin{aligned}
 \langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = & \\
 & \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle \langle \hat{q}_C \rangle \langle \hat{q}_D \rangle + (\langle \hat{q}_A \rangle I_{BCD} + \langle \hat{q}_B \rangle I_{ACD} + \\
 & + \langle \hat{q}_C \rangle I_{ABD} + \langle \hat{q}_D \rangle I_{ABC})/2 - (\langle \hat{q}_A \rangle \langle \hat{q}_B \rangle I_{CD} + \\
 & + \langle \hat{q}_A \rangle \langle \hat{q}_C \rangle I_{BD} + \langle \hat{q}_A \rangle \langle \hat{q}_D \rangle I_{AB} + \langle \hat{q}_B \rangle \langle \hat{q}_C \rangle I_{AD} + \\
 & + \langle \hat{q}_B \rangle \langle \hat{q}_D \rangle I_{AC} + \langle \hat{q}_C \rangle \langle \hat{q}_D \rangle I_{AB})/2 + (I_{AB}I_{CD} + I_{AC}I_{BC} + \\
 & + I_{AD}I_{BC})/2 - 3I_{ABCD}/4
 \end{aligned} \tag{14}$$

or

$$\begin{aligned}
 \langle (\hat{q}_A - \langle \hat{q}_A \rangle)(\hat{q}_B - \langle \hat{q}_B \rangle)(\hat{q}_C - \langle \hat{q}_C \rangle)(\hat{q}_D - \langle \hat{q}_D \rangle) \rangle = & -3I_{ABCD}/4 \\
 I_{ABCD} = & 2^4 \sum_{\substack{a \in A \\ b \in B \\ c \in C \\ d \in D}} \Pi_a^b \Pi_b^c \Pi_c^d \Pi_d^a
 \end{aligned} \tag{15}$$

We may infer, from eqs. (11) (13) and (15), that *bond indices (of two or more atomic centers) indicate the correlation between the fluctuations of the atomic charges from their average values*, for closed-shell systems in the one-determinant Hartree-Fock approximation.

Sannigrahi and Kar [11] have remarked that L-center indices can be calculated from M-center indices ( $L > M$ ), but not vice versa. This is because there exist recursive relations between the  $\mathcal{D}_i$  and the  $\mathcal{D}_{i+1}$  density functionals [12].

$I_{AB}$  uses to be positive (although it is not positive definite in non-orthogonal bases). Eq. (11) thus means that if  $q_A$  fluctuates in one sense from its average value,  $q_B$  fluctuates in the opposite sense. As to  $I_{ABC}$ , it may assume positive or negative values. This has been discussed [11, 13] and we intend to analyse it elsewhere [14]. Meanwhile, let us note that the three fluctuations in  $q$  are not likely to be all in the same sense; if two are in one sense and one in the opposite sense, either positive or negative values are to be found, with no “a priori” distinction. And so on for indices related with more than three centers.

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