

Bond index: relation to second-order density matrix and charge fluctuations

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It is shown that, in the same way as the atomic charge is an invariant built from the first-order density matrix, the closed-shell generalized bond index is an invariant associated with the second-order reduced density matrix. The active charge of an atom (sum of bond indices) is shown to be the sum of all density-density correlation functions between it and the other atoms in the molecule; similarly, the self-charge is the fluctuation of its total charge.

Key words: Bond index — Second-order density matrix — Density-density correlation function

Biorthogonal (or dual) sets have been introduced in very different frameworks in order to avoid the non-orthogonality problem [4, 9, 12]. Mayer [9] has shown that, when used together with the second quantization formalism, they permit a better understanding of the different terms arising from the partition of the LCAO Hamiltonian. Here, we relate part of this approach to the bond indices which are the generalization of the Wiberg ones to non-orthogonal bases [6, 7 and refs. therein]; we show that their mere introduction amounts to referring to the second-order density matrix.

It is said [3] that "Lowdin showed that the orthogonalizing matrix can be chosen to be $S^{-1/2}$." Yet, it is much more than a *possible* choice, for

$$\det |S^{-1/2}| = J \quad (1)$$

where J is the Jacobian of the transformation from "cartesian" to "curvilinear" coordinates; that is, from orthogonal to non-orthogonal wavefunctions. The

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overlap matrix S is the covariant metric tensor of order two. The contravariant tensor S^{ab} (a, b , atomic orbitals) already appears in the classical Chirgwin-Coulson work [1] and it is used to build a mixed Hamiltonian H_a^b .

The metric tensor is built from the scalar products of a covariant basis $\{\phi_a\}$:

$$S_{ab} = (\phi_a, \phi_b) \quad (2)$$

The contravariant basis associated to it, $\{\phi^a\}$, is given by the tensor contraction

$$\phi^a = \sum_b S^{ab} \phi_b \quad (3)$$

Hence the Chirgwin-Coulson H_a^b becomes simply

$$H_a^b = (\phi^b, H\phi_a) \quad (4)$$

and

$$(\phi^a, \phi_b) = \delta_b^a = S_b^a \quad (5)$$

The two (covariant and contravariant) sets, taken together, therefore lead to a more compact formulation. The creation and annihilation operators corresponding to the ϕ 's are ϕ^+ and ϕ^- .

It is almost universally admitted that a chemical bond arises from a concentration of electron density in the bond region, thereby the first-order density matrix ρ_1 or similar related quantities such as Mulliken's populations are used for describing bonds [5]. However, the pairwise character of the chemical bond is not *fully* reflected by ρ_1 ; it seems most natural to associate a bond to the second-order density matrix ρ_2 .

The first-order reduced density matrix represents a *mixed second order tensor* [7]; the second-order matrix is a fourth rank tensor. Let us show that this fourth-rank tensor is related to the one which we introduced in order to obtain the appropriate generalized bond indices I_{AB} under contraction [7].

If x^{ia} are the contravariant and x_{ia} the covariant coefficients of the a orbital (centered on atom A) in the i th wavefunction of a doubly occupied level (we shall restrict ourselves to a closed-shell case), the idempotent first-order density matrix $2\Pi_a^c$ is

$$2\Pi_a^c = 2 \sum_i x_{ia} x^{ic} \quad (6)$$

which is related to the annihilation-creation operators by [9]:

$$\langle \phi_a^+ \phi^{-c} \rangle = 2\Pi_a^c \quad (7)$$

where c may belong to A or to another atom. By b we shall denote an orbital intended to belong to atom $B \neq A$.

We thus define a bond index I_{AB} and an atomic charge q_A [6, 7]:

$$I_{AB} = 4 \sum_{\substack{a \in A \\ b \in B}} \Pi_a^b \Pi_b^a \quad (8)$$

$$q_A = \left(\frac{1}{2}\right) I_{AA} + \left(\frac{1}{2}\right) \sum_{B \neq A} I_{AB} \quad (9)$$

where $\left(\frac{1}{2}\right) I_{AA}$ is the self-charge and the second term the active charge distributed along formal and effective bonds [6, 14]. This definition of q_A coincides with Mulliken's gross atomic population, with a very different partition of self-charge and active charge. Thus I_{AB} differs appreciably from Mulliken's overlap population [8]. On the other hand, q_A is still

$$q_A = \langle \hat{q}_A \rangle = \left\langle \sum_{a \in A} \phi_a^+ \phi^{-a} \right\rangle \quad (10)$$

i.e. the mean value of the actual LCAO atomic charge operator \hat{q}_A [9, 10].

An atomic orbital charge defined as [7]

$$q_a^a = 2 \sum_c \Pi_a^c \Pi_c^a = 2 \Pi_a^a \quad (11)$$

is *not* an invariant. The only scalar associated with an atom is the atomic population

$$q_A = \sum_{a \in A} q_a^a \quad (12)$$

In orthogonal bases, the second-order density matrix ρ_2 of "elements" d_{ijkl} is written, in terms of creation and annihilation operators χ^\pm , as [2]:

$$d_{ijkl} = \langle \chi_i^+ \chi_j^+ \chi_k^- \chi_l^- \rangle \quad (13)$$

An extension of this to the dual basis can be

$$d_{gh}^{ef} = \langle \phi_g^+ \phi_h^+ \phi^{-e} \phi^{-f} \rangle \quad (14)$$

where [9]:

$$\langle \phi_g^+ \phi_h^+ \phi^{-e} \phi^{-f} \rangle = 4 (\Pi_g^f \Pi_h^e - \Pi_h^f \Pi_g^e) \quad (15)$$

The factorization of the second-order density (15) as products of first-order ones is characteristic of the one-determinant approximation [11]. Equations (14) and (15) satisfy the conditions expected from the antisymmetry of the second-order density matrix:

$$d_{gh}^{ef} = -d_{gh}^{fe} = -d_{hg}^{ef} \quad (16)$$

Let us look for an invariant built from the second-order density matrix. As a bond involves one pair of atoms, we shall ask (15) to contract as

$$\sum_{\substack{a \in A \\ b \in B}} d_{ba}^{ab} \quad (17)$$

Due to the anticommutation relations of [9], this is easily shown to be

$$\begin{aligned} \sum_{\substack{a \in A \\ b \in B}} d_{ba}^{ab} &= \sum_{\substack{a \in A \\ b \in B}} \langle \phi_b^+ \phi_a^+ \phi^{-a} \phi^{-b} \rangle = \sum_{\substack{a \in A \\ b \in B}} \langle \phi_a^+ \phi^{-a} \phi_b^+ \phi^{-b} \rangle \\ &= \langle \hat{q}_A \hat{q}_B \rangle \end{aligned} \quad (18)$$

which in turn, taking into account (8), (11), (12) and (15), is equal to

$$\sum_{\substack{a \in A \\ b \in B}} d_{ba}^{ab} = q_A q_B - I_{AB} = \langle \hat{q}_A \hat{q}_B \rangle \quad (19)$$

If this is added over all atoms A and B it gives the number of electron pairs

$$\frac{1}{2} \sum_A \sum_B q_A q_B - \frac{1}{2} \sum_A \sum_B I_{AB} = (N^2 - N)/2 = N(N-1)/2 \quad (20)$$

as it should. Thus, we have

$$I_{AB} = q_A q_B - \sum_{\substack{a \in A \\ b \in B}} d_{ba}^{ab} \quad (21)$$

which shows that the generalized bond index between atoms A and B arises from the difference between the product of the atomic charges in A and B , and the contraction of d_{gh}^{ef} . This is obviously also valid for orthogonal bases, i.e. for the Wiberg index.

The atomic charge is the atomic invariant built from the first-order density matrix. We have just shown that, in a similar way, the generalized bond index is *an invariant associated to the two-electron density matrix*.

Equation (19) permits a direct calculation of the mean value of the operator $\hat{q}_A \hat{q}_B$, i.e. the probability of atom A having the charge q_A and atom B the charge q_B . Our d_{ba}^{ab} has a form closely similar to that given by Ruedenberg to the pair density for orthogonal bases [13]. He calls "exchange part of the pair density" or "correlative pair density between different electrons" the quantity which, when contracted in a and b , we have defined as bond index.

Let us briefly delay on this statistical side of the bond index. We have just seen that

$$\langle \hat{q}_A \hat{q}_B \rangle - \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle = -I_{AB} \quad (22)$$

Now, the left-hand member is easily shown to be the density-density correlation function

$$\langle (\hat{q}_A - \langle \hat{q}_A \rangle) (\hat{q}_B - \langle \hat{q}_B \rangle) \rangle \quad (23)$$

Hence, *the bond index measures the correlation between the fluctuations of q_A and q_B from their average values*: it vanishes when the motions of the electrons in A are independent from the motions of the electrons in B . The active charge of an atom, $(\frac{1}{2}) \sum_{B \neq A} I_{AB}$, is then half the sum of all correlations between it and the other atoms in the molecule.

If in Eq. (22) we put $A = B$, we obtain

$$\langle \hat{q}_A^2 \rangle - \langle \hat{q}_A \rangle^2 = -I_{AA} \quad (24)$$

that is, *the self-charge of an atom is half the fluctuation of its gross charge*.

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