REMARKS ABOUT THE DEFINITION OF A BOND INDEX

by

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ABSTRACT

The tensor notation elucidates the ambiguities arised in the bond index definition, due to different matrix representations of the electronic charge distribution operator. It is shown that the orthogonalization transformation is the familiar Löwdin matrix $S^{1/2}$.

Key-words: Bond index definition; Non-orthogonal bases; Löwdin transformation.

Recent literature [1-3] has reported a polemics about the definition of a bond index, utilized in turn for a definition of valence [4]. We use the expression "bond index" to avoid confusion with the classical π bond orders introduced by Coulson. We shall discuss here the closed-shell case, this does not limit the argument.

We shall show that the difficulties arisen can be prevented through the consistent employment of the tensor notation of Ref. [5]; the notation simply acknowledges the tensor character of certain matrices appearing in the calculations. Greek letters shall denote indices of the orthogonalized basis $\{\psi_\mu\}$ and Latin letters indices of the non-orthogonal basis $\{\phi_a\}$ or $\{\phi^b\}$; let us remind that the variance of the first ones is indistinguishable, while the variance of the second ones <u>must</u> be discriminated [6]. The corresponding creation and annihilation operators are $\psi^+(\phi^+)$ and $\psi^-(\phi^-)$. The transformation linking these operators is written as

$$\tilde{\psi}_\mu^+ = \sum_a T^a_\mu \tilde{\phi}_a^+$$

$$\tilde{\psi}_\nu^- = \sum_b T_{\nu b} \tilde{\phi}^{-b}$$

(1)

We have chosen to put the creation operators as covariant and the annihilation operators as contravariant, but the opposite is equally valid; the transformation properties of covariant and contravariant quantities must obey

$$\sum_a T^a_\mu (T^a_\nu)^\dagger = \sum_a T^a_\mu T_{a\nu} = \delta_{\mu\nu} \tag{2}$$

For this reason we have put the indices as they stand, although the transformation matrices themselves are not tensors [7]. The position of the Greek indices, as we have just said, is irrelevant.

The metric tensor S_{ab}

$$S_{ab} = (\phi_a, \phi_b) \tag{3}$$

is the familiar overlap matrix, and S^{ab} its inverse. The T matrices are related to the metric by [7]

$$S_{ab} = \sum_\mu T_{a\mu} T_{b\mu} \tag{4}$$

Therefore, the transformation relating orthogonal and non-orthogonal bases is the Löwdin orthogonalization [5,8]

$$T_{a\mu} = (S^{1/2})_{a\mu} \tag{5}$$

The electronic charge distribution operator $\hat\rho$ in non-orthogonal bases may be written as [9]

$$\hat\rho = \sum_{a,b}' \hat\phi_a^+ \hat\phi^{-b} \phi^a \phi_b \tag{6}$$

The matrix elements of the first-order density matrix 2Π are

$$2\Pi_a^b = \langle \hat\phi_a^+ \hat\phi^{-b} \rangle = \sum_c P^{bc} S_{ac} \tag{7}$$

where

$$P^{bc} = 2 \sum_i^{occ} x^{ib} x^{ic} \tag{8}$$

and x^{ib} is the contravariant coefficient of the b orbital, belonging to atom B, in the i-th wavefunction of a doubly occupied level. Similarly, in the orthogonalized (Löwdin) bases $\bar{\rho}$ is

$$\bar{\rho} = \sum_{\mu,\nu} \psi_\mu \psi_\nu \hat{\psi}_\mu^+ \hat{\psi}_\nu^- \qquad (9)$$

and the matrix elements of the first-order density matrix P' are

$$P'_{\mu\nu} = \langle \hat{\psi}_\mu^+ \hat{\psi}_\nu^- \rangle = (S^{1/2} P S^{1/2})_{\mu\nu} \qquad (10)$$

P is the matrix of which the elements are defined in (8).

It is easily shown that, by means of T (or $S^{\pm 1/2}$), eqs. (7) and (10) are linked by a similarity transformation

$$P'_{\mu\nu} = (S^{1/2} 2\Pi S^{-1/2})_{\mu\nu} = (S^{1/2} P S^{1/2})_{\mu\nu} \qquad (11)$$

If one works with an orthogonalized basis, the Wiberg index [10] must be used:

$$W_{AB} = \sum_{\substack{\mu \in A \\ \nu \in B}} P'^2_{\mu\nu} \qquad (12)$$

Borisova and Semenov adopted eq.(12) for IEH calculations [11]; it has been used without modification in "ab initio" cases [12].

Non-orthogonal bases require the generalized Wiberg bond index which we proposed [13] and applied to different systems [13,14]:

$$I_{AB} = 4 \sum_{\substack{a \in A \\ b \in B}} \Pi_a^b \Pi_b^a \qquad (13)$$

The introduction of the bond index $W_{AB}(I_{AB})$ amounts to referring to the second-order density matrix [5]. This one leads to W_{AB} or to I_{AB} depending on whether the operator $\tilde{\rho}$ is represented by matrix elements in orthogonalized or non-orthogonal bases; obviously, different bases shall yield different numerical results. The Mulliken atomic charge is an invariant associated with the first-order density matrix in non-orthogonal bases [15]; if orthogonalized bases are used, the invariant will be the Löwdin charge. Similarly, $I_{AB}(W_{AB})$ is the invariant arising from the second-order density matrix [5].

In either case, valence V_A is expressed in the same way [4,15]

$$V_A = \sum_B W_{AB} \qquad \text{or} \qquad V_A = \sum_B I_{AB} \qquad (14)$$

As to the comparison of the Mulliken and Löwdin atomic charges made in Ref. [3], let us recall that they differ in second order in the commutator [H,S] [16], where H is the Hamiltonian matrix. (Actually, in Ref. [16] the comparison involves the Chirgwin-Coulson charges, which are equal to Mulliken's [6]). Elsewhere, the appearance of negative orbital populations has been discussed [17]; by the way, as orbital populations are not scalars [5], this feature may have only a relative importance.

In short, the tensor notation has proven helpful in the elucidation of the bond index definition. The quantities I_{AB} and W_{AB} are related through a similarity transformation, characteristic of the Löwdin orthogonalization procedure. Perhaps we could say that there has been "much ado about nothing".

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