

Bond Indices in Dihydrogen Bonds

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Os índices de ligação de três centros levam a uma descrição nova da ligação di-hidrogênio XH...H'M como sendo uma superposição de uma ponte de hidrogênio usual XHH', mais uma ponte de hidrogênio forte HH'M. O índice de ligação de quatro centros é negativo e o seu valor é intermediário entre os anteriores.

Three-center bond indices lead to a new description for dihydrogen bonds XH...H'M: it may be mainly described as a superposition of a usual hydrogen bond XHH' and a strong hydrogen bond HH'M. The four-center bond index is negative and its value is intermediate between the preceding ones.

Keywords: dihydrogen bonds, multicenter bond index

Introduction

Dihydrogen bonds have deserved plenty of attention in the literature of the last ten years.¹⁻⁸ The first appropriate references belong certainly to the Crabtree group.⁹⁻¹² Doubts have been raised around the possibility of an interaction between protonic and acidic hydrogens, which today would be named a dihydrogen bond, hinted as early as 1934;¹³ as only heavy atoms positions could be actually predicted, the authors postulated a PH...HN interaction. Recently, the ammonium hypophosphite structure has been examined again with a modern diffractometer equipped with a CCD detector, of much higher resolution; this has revealed only conventional NH...O bonds and no close H...H contacts, in agreement with the theoretical study.¹⁴ It seems well established that this unusual type of hydrogen bonding involves a hydridic-to-protonic interaction, with strength and directionality properties in some respects very similar to those of conventional hydrogen bonds.^{4,15} The hydridic hydrogen comes usually from a metal hydride, so that the dihydrogen bond is written as XH...H'M, where XH is the proton donor. Kulkarni¹⁶ has also found stationary structures of several dihydrogen bonded complexes, extending to third-row complexes, which are found weaker than the preceding ones.¹⁷

We desire to propose here a somewhat different approach to the problem, through the molecular orbital multicenter bond index. Several years ago, such an index was proposed, discriminating very satisfactorily between strong and usual hydrogen bonds.¹⁸ In H-bonds, negative values were always obtained for the index. The origin of this negative sign has been extensively analyzed in the literature,¹⁹⁻²² being there associated to electron-rich molecules and the bond, particularly, linked to the three-center four-electron (3c-4e) model. In a treatment employing Grassmann algebra, the index has been also related to the correlation between the fluctuations of the charges in each atomic center from their average values.²³ The multicenter bond index has been the subject of more general treatments through the formalism of Generalized Population Analysis.^{20,24,25} Returning to dihydrogen bonds, among the many theoretical treatments, Grabowski *et al.*^{6,26-30} have performed heavy *ab initio* calculations with different basis, obtaining binding energies with their decomposition, together with the topological parameters derived from the Bader theory of atoms in molecules, AIM.³¹ Alkorta *et al.*³² have calculated a number of dihydrogen complexes, showing their binding energies and harmonic vibrational frequencies; in many of them the MH' stretching frequency is blue-shifted. Recently, extremely short contacts have been found for certain small systems involving the H₂OH⁺...HBeH dimer and its derivatives.⁶ A most recent systematic study carried out by the Alkorta-Elguero group⁸ involves the dihydrogen

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bonds formed between YH (Y = Li, Na, BeH, MgH) and the three weak hydrogen bond donors NCH, CNH, HCCH; different schemes for the interactions are proposed, their conclusion being that the dihydrogen bond is just another type of hydrogen bond.

We shall focus our attention on the pertinent three- and four-center (3c and 4c) bond indices for the complexes appearing in references 28 and 32. The present ones are the first reported results for bond indices in dihydrogen bonds. In doubtful situations such as those mentioned in reference 15, the multicenter bond indices may provide other possible elements in order to diagnose dihydrogen bonds.

Multicenter Bond Index

The first order density matrix in non-orthogonal basis is the product of the charge- bond order matrix P and the overlap matrix S. For closed-shell systems, its idempotency has led to the corresponding generalization^{33,34} of the Wiberg bond index I_{AB} between atoms A and B.³⁵

$$I_{AB} = 4 \sum_{a \in A} \sum_{b \in B} (PS)_{ab} (PS)_{ba} \quad (1)$$

The index is known to be related to the exchange energy³⁶ and has been extended to open shells.³⁷ It is also closely related to effective pair populations and AIM quantities.³⁸

The electronic charge q_A is

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

The 3c bond index I_{ABC} is similarly written as¹⁸

$$I_{ABC} = 8 \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} (PS)_{ab} (PS)_{bc} (PS)_{ca} \quad (3)$$

Multicenter bond indices are thus, more generally, written as³⁹

$$I_{ABC\dots K} = \eta \sum_{a \in A} \sum_{b \in B} \dots \sum_{k \in K} \sum_i \Gamma_i (PS)_{ab} (PS)_{bc} \dots (PS)_{ka} \quad (4)$$

where η is an appropriate normalization constant and Γ_i the permutation operator that interchanges the basis functions labels so as to ensure that the index includes all the terms required.

It may be written⁴⁰

$$I_{AB} = \lambda \sum_C I_{ABC} \quad (5)$$

where λ is an appropriate scaling factor.²⁰

A 3c bond thus contributes to the usual bonds. As in the above formula C may be equal to A and B, in a molecule ABC we have

$$I_{AB} \propto I_{AAB} + I_{ABB} + I_{ABC} \quad (6)$$

The first two terms correct the equipartition of the Mulliken charge,⁴¹ while the last one indicates whether a 3c bond shall contribute to lengthening (if negative) or shortening (if positive) the bond AB. Thus, it is clearly understood why a molecule like CO₂ has a negative 3c-index, for carbon monoxide exhibits a shorter interatomic distance; similarly, C₃ having always a positive 3c-index, its CC distance is shorter than the corresponding one in ethylene, the usual reference.^{21,42}

Likewise, the well known strong hydrogen bonds in diborane and (FHF)⁻ have respectively positive and negative values; the BH distances in the diborane bridge are of course shorter than the others, while the FH distance in the mentioned ion is appreciably longer than the one in hydrogen fluoride.

In a dihydrogen complex X-H...H'-M, we have

$$\begin{aligned} I_{XH} &= \lambda (I_{XXH} + I_{XHH}) + \lambda (I_{XHH'} + I_{XHM}) \\ I_{MH'} &= \lambda (I_{MH'H'} + I_{MMH'}) + \lambda (I_{HH'M} + I_{XHM}) \end{aligned} \quad (7)$$

Hence one would expect *a priori* that the signs of the 3c bonds should indicate whether the XH and MH' bonds shall be longer or shorter than the monomers distances. If longer, as happens in usual hydrogen bonds, the bond stretching frequency will be red-shifted; if shorter, it will be blue-shifted.

Now, the blue shift in hydrogen bonds XH...Y has been the subject of very harsh discussions. Schlegel *et al.*⁴³ have carried out the most thorough and complete study of the physical origin of blue-shifted hydrogen bonds. They have shown that not only carbon as a proton donor leads to a blue-shift, but that also molecules involving Si, N or P show substantial blue-shifts. They conclude that blue-shift means X-H contraction and vice versa; despite this conclusion has been objected and attributed to insufficient extension of the basis used in the calculation,⁴⁴ we think that the mentioned study is very clear and the discussion developed takes into account all the factors involved. Alkorta *et al.*³² have found blue shifts for the M-H' frequency in several of the complexes they studied, we shall return on their results in the discussion. Cybulski *et al.*⁴⁵ have studied some dihydrogen complexes with a variety of approximations; the blue-shift found by them for HCCH...HLi agrees well with that of Alkorta *et al.*

Results and Discussion

The calculations have been carried out in two stages. First, geometry has been optimized with a MP2/6-

bent dihydrogen bonds,^{9,10} the more recent ones^{5,8} are rather inclined towards a linear structure such as we obtained for the other systems.

The Tables show that the main roles of the 3c bonds within dihydrogen bonds are those involving the two hydrogens, namely XHH' and HH'M; the second one more than the first one, its absolute value being significantly higher in all the systems studied. The 3c bond XHM is also significant, in some cases close to XHH', while the XH'M bond is decidedly less important.

The values shown in the Tables make us conclude that the HH'M bond is clearly a strong H bond; so appear to be XHM and XHH' for the charged species, while most of the XHH' bonds and some of the XHM bonds tend to be similar to usual H bonds. Actually, as found in hydrogen bonds,⁴⁸ the indices in the tables go smoothly from strong to usual.

Let us write for $I_{HH'}$ the expression equivalent to equations (7):

$$I_{HH'} = \lambda (I_{HHH'} + I_{HH'H'}) + \lambda (I_{XHH'} + I_{HH'M}); \quad (8)$$

as $I_{XHH'}$ and $I_{HH'M}$ have opposite sign, they have opposite effects. The first one enhances the HH' bond and the other one makes it weaker, so that the resulting effect is a bond weaker than that of the hydrogen molecule.

In all the present instances, as usually happens in other dihydrogen bonds, the HH' distance is considerably longer than that of the hydrogen molecule, ranging from 1.3365 Å for (LiNCH)⁺...H'Li to 2.0497 Å in HCCH...H'Li. The value for $I_{HH'}$ ranges in turn from 0.2500 to 0.0426 respectively. Also, as usual and expected, H is positively charged while H' bears a negative net charge. Very recently,

the shortest intermolecular H...H contacts ever reported have been predicted to be (1.0 – 1.3 Å) for dihydrogen systems between small cations and either BeH₂, HBeF or HBeBeH;⁶ their covalent nature and the details of the H...H interactions are exhaustively discussed. In reference 8 exponential relationships are obtained for the interaction energies plotted vs HH' distances, in the complexes for the same proton donor molecule. We obtain a linear behaviour for E vs $I_{HH'}$, not shown here; this is consistent with the exponential one for I vs r found in the original definition of bond indices for non-orthogonal bases.³³

The signs of the 3c indices agree well with the behaviour of the MH' and XH bonds. While XH bonds exhibit the usual trend, elongating when entering a hydrogen bond, the MH' bonds behave in the opposite sense, becoming shorter; this feature has been found by other authors, although not so generally,^{28,32} and hinted at in the present framework.⁴⁹ The trend of the blue-shift points at the same direction, but there is not a clear correlation as that between the indices and the energies.

Figure 1 represents, on one hand $|I_{XHM} + I_{XHH'}|$ and on the other hand $I_{HH'M} + I_{XH'M}$, as well as $I_{XHH'M}$, all of them as functions of the bond energy. The first two lines are nearly parallel, which means that the elongating effect and the shortening effect reflected by the indices are closely equivalent in terms of the bond energy. The 4c index is also a linear function of the energy, its slope being lower.

Similarly to equation 5, the 3c indices may be written as sums of the 4c ones. There is no need to go into the details of lengthy expressions to understand that, $I_{XHH'M}$ being negative, $I_{HH'M}$ would be even higher if there was no 4c bond, while $I_{XHH'}$ and I_{XHM} become more significant due to the presence of the 4c bond.

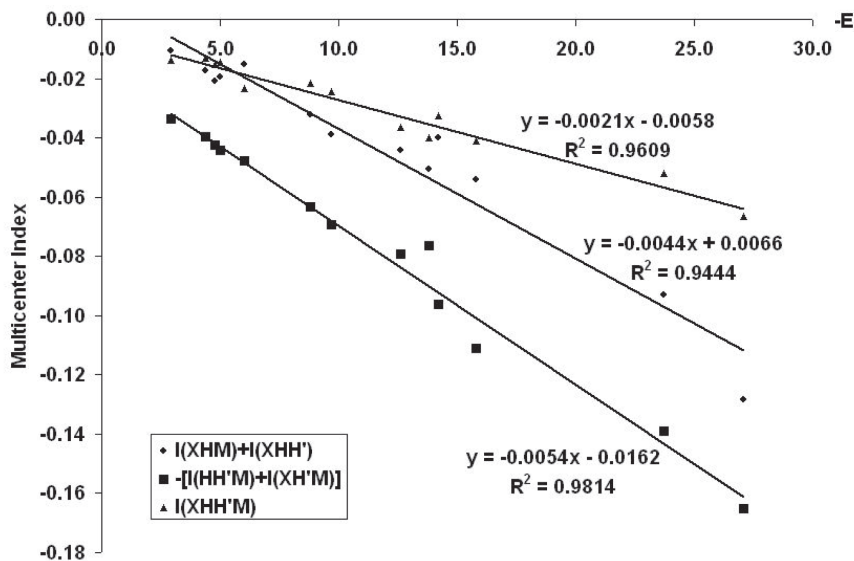


Figure 1. Multicenter bond indices as functions of the bond energy.

Conclusions

A dihydrogen bond appears to involve a strong hydrogen bond HH'M plus another usual hydrogen bond XHH'.

Three-center and four-center indices are linearly correlated to the bond energy.

The sign of the three-center indices indicate that in most dihydrogen bonds the XH bond elongates as in usual hydrogen bonds, while the MH' bond most often contracts.

The four-center indices have a value intermediate between those of the XHH' and the HH'M bonds.

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