On the electron-pair nature of the hydrogen bond in the framework of the atoms in molecules theory

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Abstract

Delocalization indices, as defined in the atoms in molecules theory, have been calculated between hydrogen-bonded atoms in 20 molecular complexes that are formed between several H-donor and acceptor molecules. In general, the delocalization index associated to an intermolecular hydrogen bond depends on the interaction energy of the complex, but also on the nature of the H-donor and acceptor atoms. The intermolecular delocalization index appears to be strongly correlated to the orbital interaction energy term as obtained from an energy decomposition scheme based on conceptual Kohn–Sham theory. Both the atoms in molecules theory and the energy decomposition analysis allow for a characterization of the hydrogen bonds in these complexes. In general, both kinds of analysis reveal that hydrogen bonding in these systems is not an essentially electrostatic interaction.
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1. Introduction

The hydrogen bond (HB) plays a fundamental role in the stabilization of molecular complexes, with an special importance in molecular recognition and solvation in water. In general, the interaction energies associated to HBs lie between 0.2 and 40 kcal/mol. According to the interaction energy, HBs can be classified as strong, medium, and weak. From an electronic point of view, the typical HB can be considered as an interaction between a partially positively charged $H^{\delta+}$ atom, which is bonded to an atom A in the donor molecule, and a partially negatively charged atom in the acceptor molecule, $X^{\delta-}$, having a lone pair in the direction of the H atom. Thus the HB interaction can be represented according to the following scheme: $A–H^{\delta+}\cdots|X^{\delta-}$. Indeed, the electronic nature of the HB has been the subject of much research in recent years [1–4]. In particular, many discussions have been centered on establishing the degree of covalent or electrostatic character of the HB. For instance, there exist several energy decomposition schemes that allow to analyze the interaction energy in terms of different components [5–8]. Morokuma and coworkers [5,6] have found that medium HBs have a dominant electrostatic contribution, which decreases with the electronegativity

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of the acceptor atom. The dispersion term has also been found to be important for any kind of HB interaction. Recently, Fonseca et al. [7–10] have studied the HBs that take place between purine- and pyrimidine-derived nucleic bases. According to their results, both covalent and electrostatic interactions contribute substantially to the interaction energy between base pairs. From an experimental point of view, Isaacs and coworkers [11] have recently carried out X-ray scattering measures to study hydrogen bonding in ice, concluding that HBs in ice are also partially covalent.

Topological methods are one of the most useful tools to investigate electron density distributions in molecules and aggregates [12–25]. The characterization of hydrogen bonding from the point of view of the atoms in molecules (AIM) theory has recently received some interest. In particular, Koch and Popelier [14] have put forward a set of topological criteria that a bond must fulfill in order to be considered a HB. Furthermore, Espinosa and coworkers [15–17] have attempted a classification of HBs using the topological and energetic properties of intermolecular bond critical points (bcp) derived from experimental electron densities. Also, Grabowski [18–20] has used the AIM theory as a measure of hydrogen bonding strength in conventional and unconventional HB systems. Several authors [21,22] have investigated recently the dependence of the topological properties of bcp's on the HB distance. Fuster and Silvi [23] have analyzed the electron localization function in several HB complexes and have established topological criteria to distinguish between weak, medium, and strong HBs.

More insight on the electronic structure of molecules can be gained by using the localization index

$$\lambda(\mathbf{A}) = -\int_{\mathbf{A}} (2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)) \, d\mathbf{r}_1 \, d\mathbf{r}_2, \quad (1)$$

and the delocalization index,

$$\delta(\mathbf{A}, \mathbf{B}) = -2\int_{\mathbf{A},\mathbf{B}} (2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)) \, d\mathbf{r}_1 \, d\mathbf{r}_2, \quad (2)$$

where $\rho(\mathbf{r})$ and $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ in Eqs. (1) and (2) are the one- and two-electron densities, respectively. The integrations are carried out through one or two atomic basins, as defined from the condition of zero-flux gradient in $\rho(\mathbf{r})$ in the AIM theory [12]. The localization index (LI) measures the number of electrons that are localized in one atom, while the delocalization index (DI) is a measure of the number of electrons delocalized between two atoms. Localized and delocalized electrons can be related to the concepts of non-shared and shared electrons, respectively, in the Lewis model [24]. Recent studies have shown that LI and DI are useful descriptors of molecular structure (see [25] for a recent review).

Recently, Fulton and Perhacs [26] have investigated the HBs in some complexes by using an index that describes the sharing of electronic charge between two centers. Fulton's sharing index is equivalent to the DI at the HF level of theory. In addition, LI and DI have been recently used to investigate the differences between *normal*, red-shifting, and improper, blue-shifting HBs [27]. The aim of this work is to carry out a preliminary study on the hydrogen-bonding characteristics of a series of representative hydrogen-bonded complexes from the point of view of the electron-pair structure. We have chosen to analyze only the DIs that are relevant for the analysis of the intermolecular H-bonding interactions. Furthermore, an energy decomposition analysis is also carried out for these complexes.

2. Methodology

For all the monomers and dimers in this study, molecular geometries were optimized at the B3LYP/6-31++G(d,p) level of theory [28]. Calculation of DIs at the DFT level of theory cannot be performed exactly, because the electron-pair density is not available at this level of theory. As an approximation, we used the Khon–Sham orbitals obtained from the DFT calculation to calculate HF-like DIs,

$$\delta(\mathbf{A}, \mathbf{B}) = 4 \sum_{i,j}^{N/2} S_{ij}(\mathbf{A}) S_{ij}(\mathbf{B}). \quad (3)$$

The summations in Eq. (3) run over all the occupied orbitals. $S_{ij}(A)$ is the overlap of the orbitals i and j within the basin of atom A. Eq. (3) does not account for electron correlation effects, which generally lead to a decrease of interatomic delocalization between covalently bonded atoms. In practice, the values of the LIs and DIs obtained using this approximation are generally closer to the HF values than to the correlated ones (e.g., Configuration Interaction) [29].

In order to analyze the factors that contribute to the HB energy, we have carried out an energy decomposition analysis based on the conceptual framework of the Kohn–Sham MO theory, using a Morokuma type decomposition [6]. The estabilization energy due to the formation of the HB (ΔE_{HB}) can be divided into deformation energy (ΔE_{def}), which is needed to bring the fragments to the geometry that they adopt in the HB complex, and interaction energy (ΔE_{int}). The ΔE_{def} term is usually small (1–2 kcal/mol) for HB complexes [7–10]. For each dimer, the interaction energy between the monomers is decomposed into Pauli repulsive orbital interactions (ΔE_{Pauli}), classical electrostatic interaction (ΔV_{elst}) and attractive orbital interactions (ΔE_{oi}); that is, $\Delta E_{int} = \Delta E_{Pauli} + \Delta V_{elst} + \Delta E_{oi}$. The energy decomposition was carried out by means of the ADF program [30], using the BP86 functional and the TZ2P basis set at the B3LYP/6-31++G(d,p) geometries. TZ2P is a basis set of Slater functions, and is of triple-ζ quality for all atoms. Two sets of polarization functions are included: 3d and 4f for heavy atoms, and 2p and 3d on H atoms. Diffuse functions are also included. The 1s core shells of the heavy atoms were treated by the frozen-core approximation. Comparison of HB energies and interaction energies for all the complexes studied (see Table 1) reveals that they are similar for all the complexes, with the larger difference being ca. 1.6 kcal/mol for the water dimer. Thus, one can assume that the deformation energy term is small, and that the two theoretical levels used (B3LYP/6-31++G(d,p) and BP86/TZ2P) are roughly equivalent. This allows us

Table 1

Hydrogen bond energy (ΔE_{HB}) (kcal/mol), H · X distance (Å), H · X electron delocalization (a.u.), electron delocalization between monomers (a.u.), density at the bond critical point (a.u.), laplacian at the bond critical point (a.u.), orbital interaction energy (a.u.) and electrostatic component of the interaction energy (a.u.)

	ΔE_{HB}[a]		R_{HX}	$\delta(H \cdot X)$	$\delta(M_1 \cdot M_2)$	$\rho_{bcp}(\boldsymbol{r})$	$\nabla^2 \rho_{bcp}(\boldsymbol{r})$	ΔE_{oi}[b]	ΔV_{elst}[b]
NH_4^+–H_2O	−22.11[c]	(−21.17)	1.627[c]	0.140	0.259	0.052	0.147	−17.00	−23.61
H_2O–HCC^-[c]	−19.41[c]	(−20.89)	1.596[c]	0.168	0.377	0.046	0.062	−17.34	−29.76
HF–NH_3[c]	−15.26[c]	(−14.65)	1.644[c]	0.150	0.319	0.059	0.114	−16.44	−22.87
HF–H_2O[c]	−10.39[c]	(−8.96)	1.673[c]	0.103	0.225	0.044	0.139	−9.67	−13.95
HF–H_2CO[c]	−8.64[c]	(−8.28)	1.699[c]	0.098	0.226	0.042	0.130	−9.47	−12.59
HF–PH_3	−5.83	(−5.58)	2.304	0.094	0.220	0.024	0.036	−6.85	−7.16
HF–H_2S	−5.81	(−5.64)	2.420	0.100	0.212	0.025	0.046	−6.85	−7.12
HF–HF	−5.10	(−4.02)	1.808	0.057	0.131	0.026	0.093	−4.06	−6.37
H_2O–NH_3[c]	−7.81[c]	(−6.54)	1.931[c]	0.104	0.216	0.031	0.075	−6.62	−11.88
H_2O–H_2O[c]	−6.02[c]	(−4.41)	1.917[c]	0.078	0.161	0.026	0.077	−4.27	−8.11
H_2O–H_2CO[c]	−5.07[c]	(−4.08)	1.981	0.067	0.172	0.024	0.068	−3.87	−7.34
H_2O–PH_3	−2.66	(−2.11)	2.632	0.062	0.136	0.013	0.031	−2.48	−3.49
HCl–NH_3	−11.06	(−11.29)	1.683	0.213	0.387	0.058	0.102	−20.03	−21.82
HCl–H_2O	−6.81	(−5.22)	1.840	0.119	0.217	0.032	0.088	−7.16	−10.02
HCl–PH_3[c]	−3.65[c]	(−3.21)	2.476[c]	0.113	0.218	0.019	0.031	−5.34	−5.36
HCl–H_2S[c]	−3.64[c]	(−3.33)	2.658	0.120	0.211	0.020	0.035	−5.34	−5.37
HCl–HCl	−1.64	(−1.12)	2.583	0.069	0.115	0.011	0.032	−2.03	−2.08
H_2S–NH_3	−4.47	(−3.40)	1.973	0.119	0.204	0.024	0.049	−5.31	−7.55
H_2S–H_2S[c]	−1.46	(−0.92)	2.826[c]	0.072	0.116	0.009	0.024	−1.59	−2.13
H_2S–PH_3[c]	−1.33	(−0.77)	2.925[c]	0.063	0.113	0.009	0.021	−1.43	−1.89

[a] In parenthesis interaction energies (with no nuclear relaxation) obtained at B3LYP/6-31++G(d,p)//BP86/TZ2P.

[b] BP86/TZ2P//B3LYP/6-31++G(d,p) energies.

[c] Obtained from [24].

to carry out comparisons of the results obtained with the two kinds of analysis (see below).

3. Results and discussion

Fig. 1 depicts the structures of the 20 complexes analyzed. Interaction energies of the dimers and topological properties of the intermolecular HBs are gathered in Table 1. $\delta(H,X)$ corresponds to the delocalization between the two atoms forming the intermolecular HB, whereas $\delta(M_1, M_2)$ is the total delocalization between the two fragments forming the dimer. For these complexes, $\delta(H,X)$ generally accounts for approximately half of the total electron delocalization between the fragments. DIs between relevant atom pairs in the monomers and dimers are collected in Table 2. For the HF, HCl, H_2O, H_2S, NH_3 and PH_3 isolated molecules, the DIs calculated at the B3LYP/6-31++G(d,p) level with the approximation discussed above are very close to previous results obtained at the HF/6-311++G(2d,2p) level [24]. The values with more interest in Table 2 (in italics) are those related to
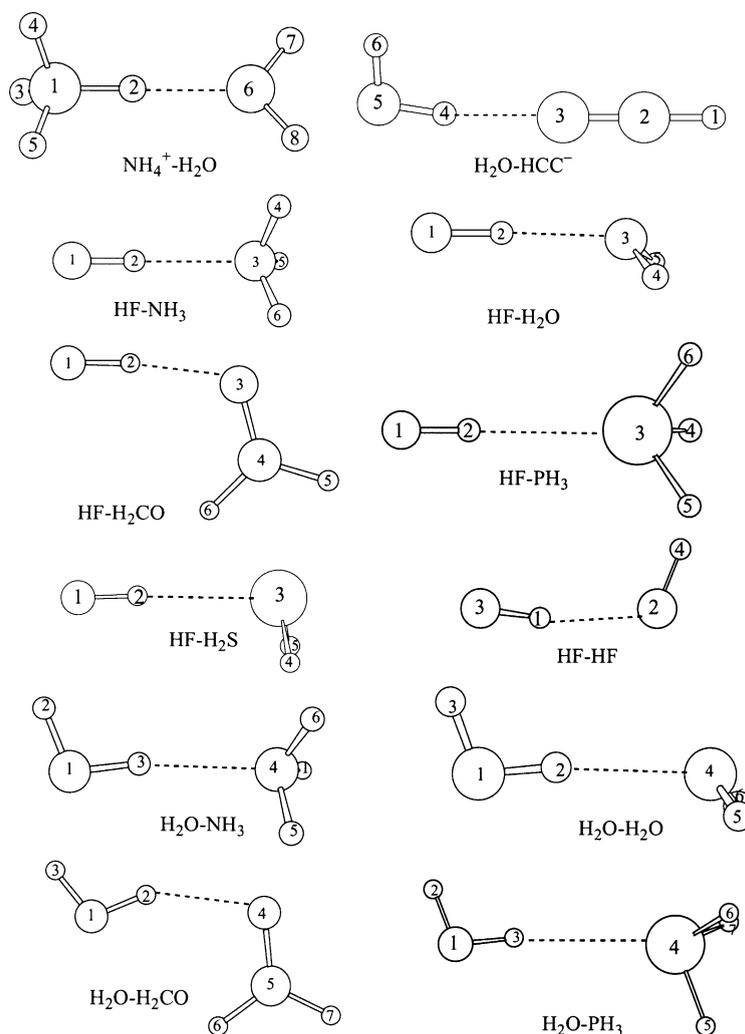

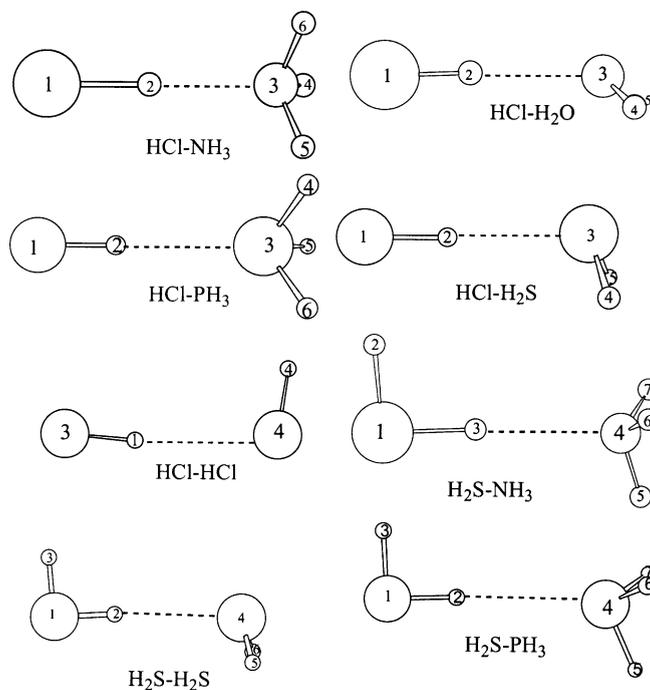Fig. 1. Molecular structure of the dimers.

Fig. 1. (*continued*)

the A–H $\cdots$ X intermolecular HB. For instance, δ(A,H) depends mainly on the nature of atom A, increasing in the direction: F < O < N < Cl < S. In general, these values are consistent with the A–H bond being a covalent polar bond, ranging from strongly polarized bonds (F–H) to nearly apolar covalent bonds (Cl–H, S–H). Actually, the Cl–H and S–H bonds exhibit DIs between bonded atoms larger than one, which means that there is some delocalization of the non-bonded lone pairs of the Cl and S atoms into the H basin.

With respect to the monomer, the formation of the dimer leads to significant changes in the electron density distribution of the donor and acceptor molecules. In particular, δ(A,H) decreases significantly upon formation of the intermolecular A–H $\cdots$ X bond, in all the complexes, while significant delocalization is found between the H and X atoms (see Table 2). The actual δ(H,X) values depend on the atoms involved, and generally increase with the strength of the HB. In many cases, the delocalization between A and X can be also significant. In general, DIs between atoms not in-volved directly in the HB do not change significantly between the monomers and the dimer.

Intermolecular HBs can also be characterized from the analysis of the associated bcp's. In general, all the intermolecular bcp's in the complexes studied exhibit low $\rho_{bcp}(\boldsymbol{r})$ values and positive $\nabla^2\rho_{bcp}(\boldsymbol{r})$ values, which are typical of HB interactions. Fig. 2 shows that there is a good relationship between $\rho_{bcp}(\boldsymbol{r})$ and the interaction energy for all the neutral complexes (the two outliers in Fig. 3 correspond to the charged complexes). Fig. 3 graphs $\nabla^2\rho_{bcp}(\boldsymbol{r})$ values with respect to the inter-action energy, revealing that these two quantities are also related. According to Figs. 2 and 3, the properties of the bcp appear to be approximately related to the HB energy, for all kinds of donor and acceptor atoms. Other studies have found similar relationships between properties of the bcp and interaction energies or H $\cdots$ X distances [15–22].

More information on the electronic nature of the HB can be obtained by looking at δ(H,X) values. In general, according to the results of

Table 2
Electron delocalization for A · B pair in dimer and monomer

Dimer	Atom A[a]	Atom B[a]	$\delta(AB)_{Dimer}$	$\delta(AB)_{Mon}$	Dimer	Atom A[a]	Atom B[a]	$\delta(AB)_{Dimer}$	$\delta(AB)_{Mon}$
$[NH_4–H_2O]^+$	1	2	0.523	0.708	$H_2O–H_2O$	1	2	0.560	0.673
	1	*6*	*0.101*			*1*	*4*	*0.076*	
	2	*6*	*0.140*			*2*	*4*	*0.078*	
	6	7,8	0.592	0.673	$H_2O–H_2CO$	1	2	0.577	0.673
$[H_2O–HCC]^-$	1	3	0.097	0.107		*1*	*4*	*0.066*	
	3	*4*	*0.168*			*2*	*4*	*0.067*	
	3	*5*	*0.161*			4	6	0.118	0.128
	4	5	0.463	0.673	$H_2O–PH_3$	1	3	1.069	0.673
$HF–NH_3$	1	2	0.374	0.501		*1*	*4*	*0.031*	
	1	*3*	*0.151*			*3*	*4*	*0.062*	
	2	*3*	*0.150*		$HCl–NH_3$	1	2	0.732	1.022
$HF–H_2O$	1	2	0.389	0.501		*1*	*3*	*0.150*	
	1	*3*	*0.114*			*2*	*3*	*0.230*	
	2	*3*	*0.103*		$HCl–H_2O$	1	2	0.861	1.022
$HF–H_2CO$	1	2	0.397	0.501		*1*	*3*	*0.090*	
	1	*3*	*0.104*			*2*	*3*	*0.119*	
	2	*3*	*0.098*		$HCl–PH_3$	1	2	0.912	1.022
	3	5	0.115	0.128		*1*	*3*	*0.071*	
	3	6	0.118	0.128		*2*	*3*	*0.113*	
	5	6	0.049	0.056	$HCl–H_2S$	1	2	0.913	1.022
$HF–PH_3$	1	2	0.439	0.501		*1*	*3*	*0.080*	
	1	*3*	*0.091*			*2*	*3*	*0.120*	
	2	*3*	*0.094*		$HCl–HCl$	*1*	*2*	*0.069*	
$HF–H_2S$	1	2	0.438	0.501		1	3	0.966	1.022
	1	*3*	*0.102*			*2*	*3*	*0.045*	
	2	*3*	*0.100*			2	4	1.010	1.022
$HF–HF$	*1*	*2*	*0.057*		$H_2S–NH_3$	1	3	1.000	1.110
	1	3	0.425	0.501		*1*	*4*	*0.071*	
	2	*3*	*0.073*			*3*	*4*	*0.119*	
	2	4	0.471	0.501	$H_2S–H_2S$	1	2	1.066	1.110
$H_2O–NH_3$	1	3	0.536	0.673		*1*	*4*	*0.036*	
	1	*4*	*0.096*			*2*	*4*	*0.072*	
	3	*4*	*0.104*		$H_2S–PH_3$	1	2	1.114	1.110
						1	*4*	*0.031*	
						3	*4*	*0.063*	

Delocalization between atoms from different monomers are written in italic.
[a] The numbering is referred to Fig. 1.

previous studies, in bonds formed by two atoms sharing an electron-pair, the DI between the two atoms is related to the polarity of the bond. In these cases, the DI takes values between 1, for a perfectly shared electron-pair (e.g., H_2), and close to zero, for a totally ionic bond (e.g., LiF). For the set of complexes studied, $\delta(H,X)$ takes values between 0.06 and 0.21. In general, one could expect that complexes with larger interaction energies should exhibit larger intermolecular delocalization, but Fig. 4 shows that there is not a clear correlation between ΔE_{HB} and $\delta(H,X)$. Indeed, the

actual values of $\delta(H,X)$ depend also on the acceptor and donor atoms of the $A–H \cdots X$ bond. For instance, the $HCl–NH_3$ complex is only ca. 0.6 kcal mol^{-1} more stable than the $HF–H_2O$ one, but the $\delta(H,X)$ of the former complex is more than twice that of the latter. Thus, the HB in $HCl–NH_3$ involves a significant sharing of electrons between the H and N atoms, while there is practically no sharing of electrons between the H and O atoms in $HF–H_2O$. At this point, it is interesting to look at the results of the energy decomposition analysis for these two complexes (see Table 1). Both the
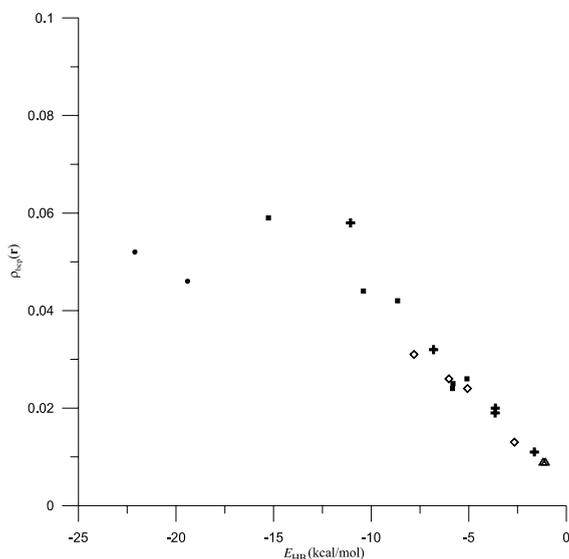
Fig. 2. Density at the bond critical point versus ΔE_{HB}. ■, HF as a donor; ♦, H_2O as a donor; +, HCl as a donor; △, H_2S as a donor; and ●, charged systems.
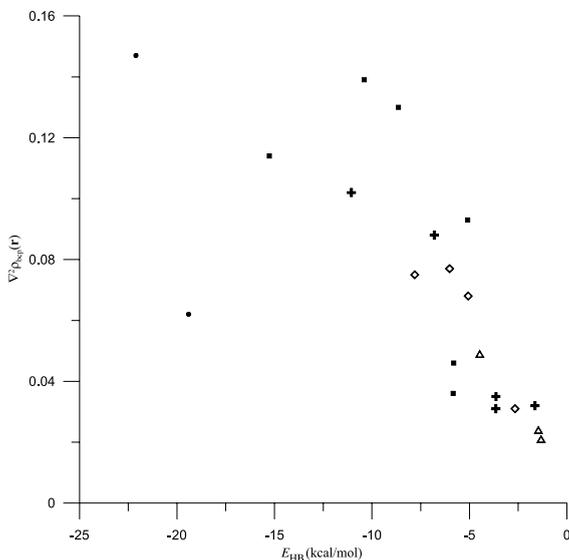

Fig. 3. Laplacian at the bond critical point versus ΔE_{HB}. ■, HF as a donor; ♦, H_2O as a donor, +, HCl as a donor, △, H_2S as a donor; and ●, charged systems.

Fig. 4. $\delta(H, X)$ versus ΔE_{HB}. ■, HF as a donor; ♦, H_2O as a donor; +, HCl as a donor; △, H_2S as a donor; and ●, charged systems.

electrostatic and the orbital interactions are higher for HCl–NH$_3$, compared to HF–H$_2$O. In fact, it is the Pauli repulsion term (not included in Table 1)
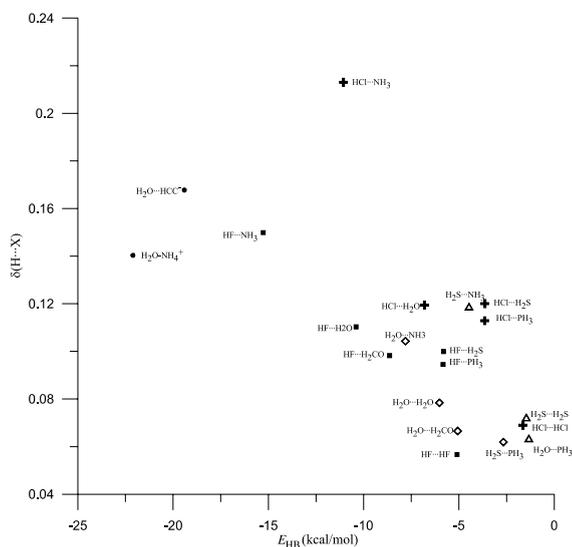
that makes the HB stronger in HF–H$_2$O as compared to HCl–NH$_3$. The electrostatic term accounts for ca. 52% and 59% of the attractive interactions in HCl–NH$_3$ and HF–H$_2$O, respectively. From this point of view, one could consider the HB in the first complex more covalent than the second one, in agreement to the higher degree of intermolecular electron sharing in HCl–NH$_3$.

Fig. 5 plots $\delta(X, H)$ versus ΔE_{oi} for all the complexes. Interestingly, there is quite a good relationship between the two terms. In the conceptual Kohn–Sham framework, the ΔE_{oi} term accounts basically for charge-transfer and donor–acceptor orbital interactions between the two fragments, and can be considered as a measure of the covalent character of the intermolecular bond [7–10]. Thus, the relationship between $\delta(X, H)$ and ΔE_{oi} reveals that the covalent contribution to the interaction energy is directly proportional to the number of electrons shared between the X and H atoms. It is worth noting that, at variance with widespread belief, the HB in most systems is not an essentially electrostatic phenomenon. The charge transfer and donor–acceptor interactions are of the same order of magnitude as the electrostatic term [7–10].
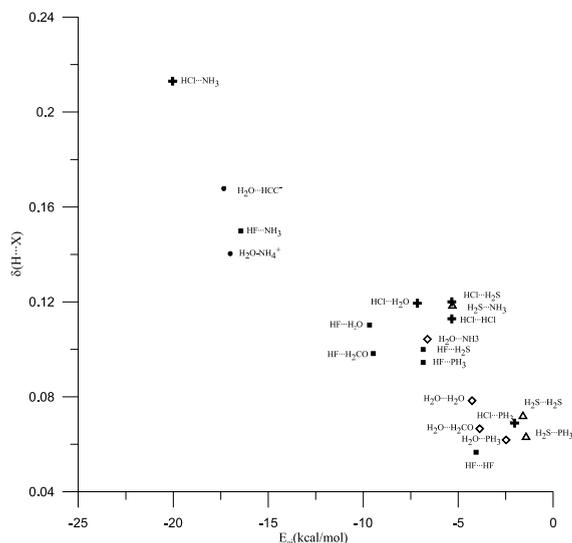
Fig. 5. $\delta(H,X)$ versus orbital interaction energy (ΔE_{OI}). $\blacksquare$, HF as a donor, $\blacklozenge$, H_2O as a donor, $+$, HCl as a donor; $\triangle$, H_2S as a donor; and $\bullet$, charged systems.

These preliminary results point out that an electron-pair analysis in the framework of the AIM theory can be used to characterize hydrogen bonding in terms of the number of electrons shared between the atoms involved in the HB. Further information could be obtained by analyzing the charge transfer between these atoms. It is worth to remark that the results of the AIM analysis and the energy decomposition analysis, which are based on very different theoretical backgrounds, are mutually consistent, at least at a qualitative level.

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