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Many-Body Energy Decomposition Analysis of Cooperativity in Hydrogen Fluoride Clusters

LUIS RINCÓN,¹ RAFAEL ALMEIDA,^{1,2} DAVID GARCÍA ALDEA^{1,2}

¹*Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, La Hechicera, Mérida 5101, Venezuela*

²*Departamento de Física Fundamental, Universidad Nacional de Educación a Distancia, Apdo. 60141, Madrid 28080, Spain*

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ABSTRACT: This article studies the cooperativity present in hydrogen fluoride clusters, (FH)_n, by means of a many-body decomposition of the binding energy. With the aim of quantifying how the results depend on the calculation level, the partition was performed from dimer to hexamer at the RHF, MP2, and density functional (B3LYP) levels, and for the heptamer and octamer at the RHF and B3LYP levels, using a 6-31++G(d, p) basis set in all cases. We obtain that, for a proper representation of the cooperative effects in hydrogen fluoride, at least the inclusion of the three-body terms is fundamental. The contributions are found to be underestimated at the RHF level and overestimated at the B3LYP level, with respect to the MP2 results. © 2004 Wiley Periodicals, Inc. *Int J Quantum Chem* 102: 443–453, 2005

Key words: hydrogen bond; cooperative effects; many-body expansion; electronic delocalization; nonadditivity

Introduction

One important characteristic of hydrogen bond (HB) clusters is the presence of cooperative effects, which are related to the many-body

nature of the interaction energy [1–11]. Since the equations of classical electrostatic include only pairwise additive interactions of localized monomers, the existence of these effects can be considered a departure from the classical electrostatic model of hydrogen bonding, indicating the inadequacy of considering its electrostatic picture alone, and, perhaps even more important, suggesting the presence of significant electronic delocalization. Employing *ab initio* and density functional theory (DFT) methods, our group [9] has found evidence of this kind of effect. Large cooperative effects for the binding energy per HB in hydrogen fluoride clusters were

Correspondence to: R. Almeida; e-mail: mata@ula.ve

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found, as reflected in the geometric parameters of the clusters and the topological properties of the electron charge density.

In the present study, looking for some additional insights on the cooperative effects, rather than interpreting the HB binding energy in terms of electronic contributions, such as exchange, polarization, and charge transfer, we have chosen instead to perform an analysis of their many-body nature. Thus, the objective of this study is first to explore further the root of the cooperative effects by a decomposition of the binding energy using the contributions of their n -body subclusters [12–16]; second, to assess the effect of electron correlation in the individual n -body contributions; and, by comparing *ab initio* and DFT methodologies, to examine how the manner in which the correlation is introduced affects the results of these contributions. Since the cluster geometries are a signature of the cooperativity present in each case [9], from dimer to octamer we have carried out a full geometry optimization of the molecular clusters at each level of calculation; only after this was done was the partition energy performed.

The decomposition scheme employed in this study was used by Hankins et al. [12], Xantheas [13], and Pedulla et al. [14] for water clusters, and by Quack and colleagues [15, 16], to compute the dissociation energy of hydrogen fluoride oligomers, from dimer to pentamer. In this last study, different *ab initio* levels (CCSD and MP2) together with very large basis sets were employed to compute the individual many-body terms at fixed geometries. These benchmark calculations proved very meaningful when determining how the method chosen to include the electron correlation and the basis set affects the computed binding energy; however, they are probably not as useful if the aim is to perform a comparison among different possible approaches for the description of cooperative effects. This is so because, as mentioned above, the nonadditive effects translate strongly in changes in geometry parameters. Thus, for this last type of comparison, it is important to obtain the optimal geometry for each of the calculation levels employed.

It is a well-known fact that due to the smallness of the binding energy of HB clusters, this energy is particularly sensitive to the basis set superposition error (BSSE). Nevertheless, in our previous study on cooperativity and electronic delocalization in HF clusters [9], we found that the percentage of cooperative enhancement in the RHF binding energies were quite similar for corrected and uncorrected

BSSE values and, therefore, that the obtained behavior of the cooperative effects was broadly representative of what would be found if a much larger basis set were employed. Since these conclusions are applicable to the present study, the cooperative energy properties are described neglecting the BSSE. Finally, it is important to mention that several methods for partitioning the energy of interacting systems have been proposed in the literature [17–27]. They are based on perturbational expansions [17–20], molecular fragment partition [21], or the use of reduced density or pair density matrices [22–27]. However, most of these expansions rely on monoconfigurational Hartree–Fock (HF) formalism and, in general, the associated energy partition scheme, cannot be interpreted as a many-body expansion as in the present approach.

In this work, the geometry optimization and the energy calculations were performed at the Restricted Hartree–Fock (RHF), second-order Møller–Plesset perturbation theory (MP2), and B3LYP DFT levels, using the Gaussian 98 suite of programs [28]. In the case of the heptamer and octamer only RHF and B3LYP levels have been used. The basis set is of a split valence type and includes diffuse and polarization functions in hydrogen and fluoride atoms, 6-31++G(d, p).

Methodology

We employ a many-body partition scheme that has been presented elsewhere [12–16]. This section presents a brief review of the method; otherwise, the discussion of the results will prove difficult. We begin by considering a dimer cluster, denoted AB , in its ground-state geometry, where A and B are two molecular units. Conceptually, the formation of the dimer is ideally divided into two steps involving distortion energy and resonance energy. In the first step, the monomers are distorted from their equilibrium geometry to that of the dimer. This distortion energy is denoted by $DE_2(A)$, or $DE_2(B)$, and can easily be calculated as the difference between the energy of the monomer with the geometry of the dimer, $E(A)_{AB}$, and the same energy with its equilibrium geometry, $E(A)_0$:

$$DE_2(A) = E(A)_{AB} - E(A)_0. \quad (1)$$

Clearly, the distortion energy is always destabilizing and grows with the strength of the hydrogen

bond. In the second step, the monomers are allowed to interact, and the dimer is formed, due to electrostatic, polarization, exchange, and charge transfer interactions between the distorted monomers. All the previous interactions are jointly recorded as the resonance energy of the dimer, denoted $\beta_2(AB)$. Thus, for the dimer, the binding energy, $\Delta E(AB)$ can be written as

$$\Delta E(AB) = DE_2(A) + DE_2(B) + \beta_2(AB), \quad (2)$$

where the binding energy is calculated from

$$\Delta E(AB) = E(A)_0 + E(B)_0 - E(AB). \quad (3)$$

In the spirit of the previous decomposition, the trimer binding energy, $\Delta E(ABC)$, can be written as

$$\Delta E(ABC) = DE_3(A) + DE_3(B) + DE_3(C) + \beta_3(AB) + \beta_3(AC) + \beta_3(BC) + \beta_3(ABC). \quad (4)$$

Note that the notation DE_n and β_n indicates the distortion or resonance energy of the subcluster, shown within the parentheses, which belongs to a cluster of n members. In the case of a symmetric cluster, as the hydrogen fluoride trimer $(FH)_3$, in which all the monomers and hydrogen bond distances are equivalent, the distortion energies are identical for the three monomers, $DE_3(A) = DE_3(B) = DE_3(C)$, and the two-body resonance energies are the same for the three hydrogen bonds, $\beta_3(AB) = \beta_3(AC) = \beta_3(BC)$. Thus, for this case, Eq. (4) becomes

$$\Delta E(ABC) = 3DE_3(A) + 3\beta_3(AB) + \beta_3(ABC). \quad (5)$$

The two-body resonance energy is calculated by means of a generalization of Eq. (2), where the dimer interaction energy, $\Delta E_3(AB)$, is calculated with the monomers having the geometry of the trimer. Thus,

$$\beta_3(AB) = \Delta E_3(AB) - 2DE_3(A). \quad (6)$$

Here, ΔE_n denotes the stabilization energy of the subcluster appearing within the parentheses, belonging to an n -member cluster. Once this is done, the three-body resonance energy, $\beta_3(ABC)$, can be calculated from Eq. (4).

For the $ABCD$ tetramer, the full decomposition result is

$$\begin{aligned} \Delta E(ABCD) = & DE_4(A) + DE_4(B) + DE_4(C) \\ & + DE_4(D) + \beta_4(AB) + \beta_4(AC) + \beta_4(AD) \\ & + \beta_4(BC) + \beta_4(BD) + \beta_4(CD) + \beta_4(ABC) \\ & + \beta_4(ABD) + \beta_4(ACD) + \beta_4(BCD) + \beta_4(ABCD). \end{aligned} \quad (7)$$

Again, because of the symmetry of the $(FH)_4$, the binding energy becomes

$$\Delta E(ABCD) = 4DE_4(A) + 4\beta_4(AB) + 2\beta_4(AC) + 4\beta_4(ABC) + \beta_4(ABCD), \quad (8)$$

where AB means first neighbors and AC second neighbors. For this case, all the equivalent three-body resonance energies are calculated from an extension of Eq. (4):

$$\begin{aligned} \beta_4(ABC) = & \Delta E_4(ABC) - 2\beta_4(AB) \\ & - \beta_4(AC) - 3DE_4(A), \end{aligned} \quad (9)$$

and the four-body resonance energy is computed from Eq. (7). At this point, it is clear that this decomposition scheme of the binding energy permits separation and quantification of the additive (up to second-order terms) and nonadditive (higher-order terms) contributions to the stabilization of the cluster.

In what follows, the expressions for ΔE in the case of symmetric $(FH)_n$ clusters, from the pentamer to the octamer, are presented:

$$n = 5: \Delta E(ABCDE)$$

$$\begin{aligned} \Delta E(ABCDE) = & 5DE_5(A) + 5\beta_5(AB) \\ & + 5\beta_5(AC) + 5\beta_5(ABC) + 5\beta_5(ABD) \\ & + 5\beta_5(ABCD) + \beta_5(ABCDE). \end{aligned} \quad (10)$$

$$n = 6: \Delta E(ABCDEF)$$

$$\begin{aligned} \Delta E(ABCDEF) = & 6DE_6(A) + 6\beta_6(AB) + 6\beta_6(AC) \\ & + 6\beta_6(AD) + 6\beta_6(ABC) + 6\beta_6(ABD) \\ & + 6\beta_6(ABE) + 2\beta_6(ACE) + 6\beta_6(ABCD) \\ & + 6\beta_6(ABCE) + 3\beta_6(ABDE) \\ & + 6\beta_6(ABCDE) + \beta_6(ABCDEF). \end{aligned} \quad (11)$$

$$n = 7: \Delta E(ABCDEFG)$$

$$\begin{aligned}
\Delta E(ABCDEFGG) = & 7DE_7(A) + 7\beta_7(AB) \\
& + 7\beta_7(AC) + 7\beta_7(AD) + 7\beta_7(ABC) + 7\beta_7(ABD) \\
& + 7\beta_7(ABE) + 7\beta_7(ABF) + 7\beta_7(ACE) \\
& + 7\beta_7(ABCD) + 7\beta_7(ABCE) + 7\beta_7(ABCF) \\
& + 7\beta_7(ABDE) + 7\beta_7(ABDF) + 7\beta_7(ABCDE) \\
& + 7\beta_7(ABCDF) + 7\beta_7(ABCEF) \\
& + 7\beta_7(ABCDEF) + \beta_7(ABCDEFGG). \quad (12)
\end{aligned}$$

$$n = 8: \Delta E(ABCDEFGH)$$

$$\begin{aligned}
\Delta E(ABCDEFGH) = & 8DE_8(A) + 8\beta_8(AB) \\
& + 8\beta_8(AC) + 8\beta_8(AD) + 8\beta_8(AE) + 8\beta_8(ABC) \\
& + 8\beta_8(ABD) + 8\beta_8(ABE) + 8\beta_8(ABF) \\
& + 8\beta_8(ABG) + 8\beta_8(ACE) + 8\beta_8(ACF) \\
& + 8\beta_9(ABCD) + 8\beta_8(ABCE) + 8\beta_8(ABCF) \\
& + 8\beta_8(ABCG) + 8\beta_8(ABDE) + 8\beta_8(ABDF) \\
& + 8\beta_8(ABDG) + 4\beta_4(ABEF) + 8\beta_8(ABEG) \\
& + 2\beta_8(ACEG) + 8\beta_8(ABCDE) + 8\beta_8(ABCDF) \\
& + 8\beta_8(ABCDG) + 8\beta_8(ABCEF) + 8\beta_8(ABCEG) \\
& + 8\beta_8(ABCDFG) + 8\beta_8(ABDEG) \\
& + 8\beta_8(ABCDEF) + 8\beta_8(ABCDEG) \\
& + 8\beta_8(ABCDFG) + 4\beta_8(ABCEFG) \\
& + 8\beta_8(ABCDEF) + \beta_8(ABCDEFGH). \quad (13)
\end{aligned}$$

Detailed expressions for each of the β_n terms involved in these n -body expansions are available (by request to the authors) in the Supporting Information (Table A-I). Before continuing to the next section, let us emphasize two points. First, this decomposition scheme demands calculation of all smaller subclusters. Second, within the frame of this work, we think that the main advantage of this energy separation lies on its interpretative character, which facilitates to evidence the many-body nature, i.e., electron density delocalization, of the cooperative effects.

Many-Body Energy Partition of Hydrogen Fluoride Cluster

It is well known that HF is perhaps one of the molecular systems with the largest detectable ef-

fects of cooperativity [10]; therefore, it would be interesting to apply the methodology explained above to gas phase HF clusters, $(HF)_n$ with $n = 2-8$. Within this range, most of the ground-state structures are symmetric cyclic aggregates [9], a fact that simplifies the equations in the manner previously described. Thus, it is found that from dimer to hexamer, these clusters are planar, while for heptamers and octamers, nonplanar symmetric stable structures are found. For these structures, only RHF and B3LYP level results are presented.

Table I shows the computed total m -body cluster contributions to the binding energy. Also given are the partial binding energies obtained when only contributions up to m -order are considered. For each case, Table II displays the values of the resonance energy contributions to the binding energies. Because of the large number of clusters and subclusters involved in the present treatment, the detailed n -body binding energy partitions are presented in the Supporting Information (Table A-II). Note that from Eq. (3) (and its generalizations), the binding energies are negative for destabilization and positive for stabilization. Next, as a reference, Figure 1(a) shows the binding energy per HB for the clusters presented in this study. This energy corresponds to the total binding energy, shown in parentheses at the bottom of each column in Table I, divided by the number of hydrogen bonds. For the cyclic clusters, the number of hydrogen bonds is assumed to be the number of monomers, while for the dimer there is only one HB. For all levels, a sigmoidal shape is shown whose values remain nearly constant from dimer to trimer and then grow with the cluster size, to become approximately constant after the hexamer is reached. For a simpler pairwise electrostatic model (no polarization), the result would remain approximately constant with n .

Another signature of the cooperativity in HB systems is the enhancement of the HB energy, depicted in Figure 1(b). The energy increment resulting from the addition of one monomer to an $n - 1$ cluster, $(FH)_{n-1} + FH \rightarrow (FH)_n$, is shown. For the dimer, the cooperative increment is their total binding energy. Figure 1(b) shows a peaked shape, with the maximum binding energy enhancement occurring from trimer to tetramer. These enhancements are substantially larger for the cases of correlated levels. Note that if noncooperative effects would be present, this energy increment would be constant and identical to the dimer binding energy.

To gain some clues designed to help us to understand the behavior shown in these figures, let us

TABLE I

Computed total m -body subcluster contributions (m -BE) to the binding energy for each $(\text{FH})_n$ cluster ($n = 2-8$).*

m -BE	Method	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
$m = 1$	RHF	-0.02	-0.22	-0.66	-1.06	-1.36	-1.61	-1.87
	MP2	-0.03	-0.42	-1.68	-2.94	-3.78	—	—
	B3LYP	-0.05	-0.80	-3.21	-5.77	-7.55	-9.12	-10.73
$m = 2$	RHF	4.36 (4.34)	11.70 (11.48)	19.39 (18.73)	25.28 (24.22)	30.40 (29.04)	35.66 (34.05)	40.87 (39.00)
	MP2	4.99 (4.96)	13.47 (13.05)	21.73 (20.05)	27.32 (24.38)	32.01 (28.23)	—	—
	B3LYP	5.13 (5.08)	13.92 (13.12)	22.02 (18.81)	27.13 (21.36)	31.88 (24.33)	37.06 (27.94)	42.53 (31.80)
$m = 3$	RHF	—	1.50 (12.98)	4.32 (23.05)	7.25 (31.47)	9.78 (38.82)	11.77 (45.75)	13.69 (52.59)
	MP2	—	2.36 (15.40)	7.39 (27.44)	12.69 (37.07)	16.90 (45.13)	—	—
	B3LYP	—	3.40 (16.52)	10.88 (29.69)	18.41 (39.77)	24.16 (48.49)	29.01 (56.95)	33.82 (65.62)
$m = 4$	RHF	—	—	0.39 (23.44)	0.81 (32.28)	1.10 (39.92)	1.30 (47.05)	1.52 (54.11)
	MP2	—	—	0.85 (28.29)	1.88 (38.95)	3.42 (48.55)	—	—
	B3LYP	—	—	1.30 (30.99)	2.95 (42.72)	4.03 (52.52)	4.91 (61.86)	5.57 (71.19)
$m = 5$	RHF	—	—	—	0.02 (32.30)	0.08 (40.00)	0.11 (47.16)	0.15 (54.26)
	MP2	—	—	—	0.11 (39.06)	0.10 (48.65)	—	—
	B3LYP	—	—	—	0.19 (42.91)	0.45 (52.97)	0.61 (62.47)	1.20 (72.39)
$m = 6$	RHF	—	—	—	—	0.01 (40.01)	0.03 (47.19)	0.03 (54.29)
	MP2	—	—	—	—	0.02 (48.67)	—	—
	B3LYP	—	—	—	—	0.04 (53.01)	0.13 (62.60)	0.26 (72.65)
$m = 7$	RHF	—	—	—	—	—	-0.01 (47.18)	-0.01 (54.28)
	B3LYP	—	—	—	—	—	-0.03 (62.57)	0.11 (72.76)
$m = 8$	RHF	—	—	—	—	—	—	-0.01 (54.27)
	B3LYP	—	—	—	—	—	—	-0.01 (72.75)

* The results for the binding energies obtained when only the contributions up to m th orders are considered are shown in parentheses. All energies are given in kcal mol⁻¹.

analyze the results of Table I. We first observe that, as should be expected [9], the distortion energy per monomer grows rapidly with size up to $n = 6$, after which only a small increase is noted. It is clear that the larger contributions to the binding energy arise

from the two-body and three-body subclusters, noting that their values follow the order B3LYP > MP2 > RHF. The total four-body contributions are close in magnitude to the destabilizing distortion energies and the higher-order ones are compara-

TABLE II

Distortion and resonance energies for the m -body subclusters involved in the computation of the binding energies of the hydrogen fluoride n -body clusters.

a. One-body contributions								
DE_n	Method	2	3	4	5	6	7	8
A	RHF	−0.02	−0.21	−0.64	−1.05	−1.38	−1.61	−1.84
	MP2	−0.03	−0.42	−1.68	−2.95	−3.78	—	—
	B3LYP	−0.04	−0.81	−3.2	−5.75	−7.56	−9.1	−10.72
b. Two-body contributions								
β_n	Method	2	3	4	5	6	7	8
AB	RHF	4.36	3.9	4.06	3.96	3.84	3.78	3.71
	MP2	4.99	4.49	4.44	4.09	3.12	—	—
	B3LYP	5.13	4.64	4.52	4.05	3.77	3.66	3.59
AC	RHF			1.57	1.09	0.98	0.96	0.93
	MP2			1.98	1.38	1.22	—	—
	B3LYP			1.98	1.38	1.23	1.2	1.15
AD	RHF					0.49	0.41	0.22
	MP2					0.59	—	—
	B3LYP					0.63	0.57	0.46
AE	RHF							0.23
	B3LYP							0.24
c. Three-body contributions								
β_n	Method	3	4	5	6	7	8	
ABC	RHF	1.49	1.08	1.21	1.27	1.26	1.25	
	MP2	2.36	1.85	2.13	2.24	—	—	
	B3LYP	3.39	2.72	3.08	3.15	3.17	3.13	
ABD	RHF			0.24	0.15	0.14	0.11	
	MP2			0.4	0.13	—	—	
	B3LYP			0.6	0.38	0.35	0.32	
ABE	RHF				0.19	0.09	0.07	
	MP2				0.43	—	—	
	B3LYP				0.47	0.23	0.13	
ACE	RHF				0.03	0.02	0.01	
	MP2				0.05	—	—	
	B3LYP				0.07	0.04	0.03	
ABF	RHF					0.17	0.07	
	B3LYP					0.41	0.19	
ABG	RHF						0.17	
	B3LYP						0.41	
ACF	RHF						0.01	
	B3LYP						0.02	
(continued)								

(continued)

TABLE II
(Continued)

d. Four-body contributions

β_n	Method	4	5	6	7	8
<i>ABCD</i>	RHF	0.39	0.16	0.13	0.12	0.11
	MP2	0.85	0.38	0.33	—	—
	B3LYP	1.29	0.59	0.48	0.45	0.41
<i>ABCE</i>	RHF			0.03	0.02	0.01
	MP2			0.09	—	—
	B3LYP			0.11	0.06	0.04
<i>ABDE</i>	RHF			0.04	0.02	0.02
	MP2			0.16	—	—
	B3LYP			0.17	0.12	0.11
<i>ABCF</i>	RHF				0.02	0.01
	B3LYP				0.07	0.03
<i>ABDF</i>	RHF				0.00	0.00
	B3LYP				0.01	0.00
<i>ABCG</i>	RHF					0.01
	B3LYP					0.05
<i>ABDG</i>	RHF					0.00
	B3LYP					0.01
<i>ABEF</i>	RHF					0.02
	B3LYP					0.06
<i>ABEG</i>	RHF					0.00
	B3LYP					0.01
<i>ACEG</i>	RHF					0.00
	B3LYP					0.00

e. Five-body contributions

β_n	Method	5	6	7	8
<i>ABCDE</i>	RHF	0.02	0.01	0.01	0.01
	MP2	0.11	0.01	—	—
	B3LYP	0.19	0.08	0.04	0.05
<i>ABCDF</i>	RHF			0.00	0.00
	B3LYP			0.01	0.02
<i>ABCEF</i>	RHF			0.00	0.00
	B3LYP			0.02	0.02
<i>ABCDG</i>	RHF				0.00
	B3LYP				0.01
<i>ABCEG</i>	RHF				0.00
	B3LYP				0.01
<i>ABCFG</i>	RHF				0.00
	B3LYP				0.02
<i>ABDEG</i>	RHF				0.00
	B3LYP				0.02

(continued)

TABLE II
(Continued)

f. Six-body contributions				
β_n	Method	6	7	8
<i>ABCDEF</i>	RHF	0.01	0.00	0.00
	MP2	0.02	—	—
	B3LYP	0.04	0.03	0.01
<i>ABCDGF</i>	RHF			0.00
	B3LYP			0.01
<i>ABCEFG</i>	RHF			0.00
	B3LYP			0.01
g. Seven-body contributions				
β_n	Method		7	8
<i>ABCDEFGF</i>	RHF		0.00	0.00
	B3LYP		−0.03	0.02
h. Eight-body contributions				
β_n	Method			8
<i>ABCDEFGH</i>	RHF			0.00
	B3LYP			−0.01

tively smaller and only account for about 1% of the total binding energy. Note that our results show that the total 8-body term (and also the 7-body one at the RHF level for $n = 8$) are repulsive but very small. Since the contribution of the two-body terms to the stabilization energy is significant, in an effort to gain some additional insight, it would be interesting to explore what the results would be if only contributions up to second order were considered. Thus, Figure 2(a) and (b) shows, respectively, the variation with cluster size of the binding energy per hydrogen bond and the cooperativity enhancement when they are calculated only taking into account contributions up to the second order, i.e.,

$$\Delta E_2 = \sum_A D E_n(A) + \sum_{A,B} \beta_n(AB).$$

We see that these contributions alone are not sufficient to describe the correct qualitative behavior. Thus, Figure 2(a) shows that, for all levels, a minimum is observed for the trimer, while for the correlated levels a maximum is also displayed at the tetramer; these characteristics are not present in the total results [Fig. 1(a)]. In contrast with the observed total cooperative increment in the binding

energy [Fig. 1(b)], Figure 2(b) shows that the largest change occurs from dimer to the trimer, and the existence of a minimum for the B3LYP (located at $n = 5$) and RHF (at $n = 6$) results. This behavior indicates that the two-body interactions are not the only ones determinant in the cluster formation.

Next, to demonstrate the importance of the non-additive contributions, Figure 3(a) and (b) presents the same results, but this time including terms up to third order, i.e.,

$$\Delta E_3 = \sum_A D E_n(A) + \sum_{A,B} \beta_n(AB) + \sum_{A,B,C} \beta_n(ABC).$$

It is striking to observe how the inclusion of these partial nonadditive contributions is enough to reproduce qualitatively the total behavior of Figure 1. Moreover, the results, at the most (for the B3LYP calculations), differ by only about 10% from those in Figure 1. Thus, for a correct description of the binding of HB aggregates that would include a proper account of cooperative effects, it is essential to go beyond the additive part (i.e., the simple pairwise Coulombic interactions).

From the results presented in Table II, one sees that the two-body stabilizing resonance energies

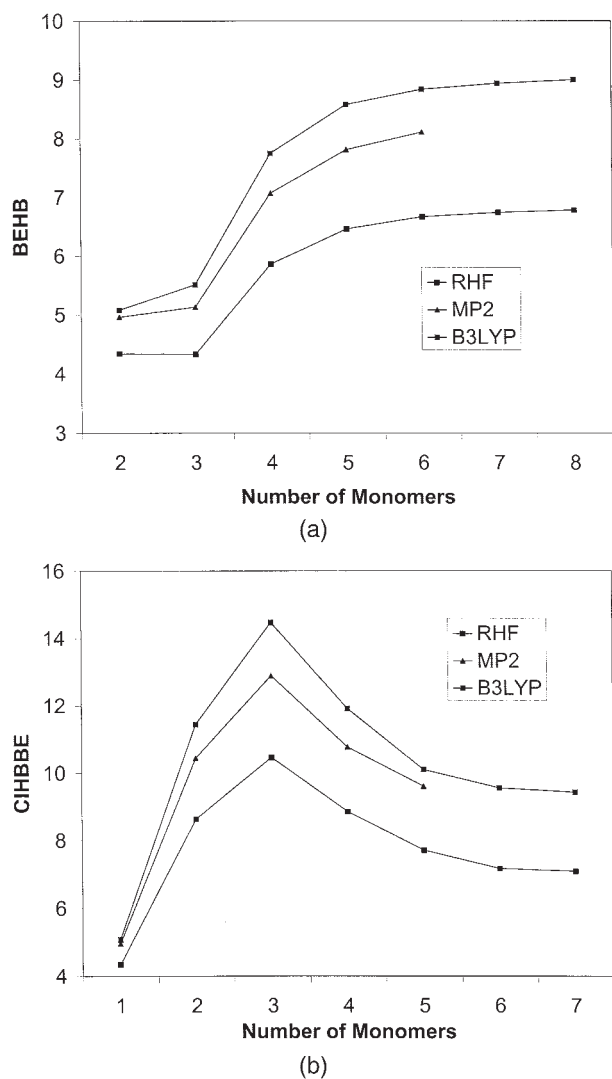


FIGURE 1. (a) Variation of the binding energy per hydrogen bond (BEHB in kcal/mol). (b) Variation of the cooperative increments in hydrogen bond binding energy: $\Delta E_n - \Delta E_{n-1}$ (CIHBBE in kcal/mol).

decrease from first (AB) to second (AC) neighbors (in average about 40%), to third (AD) neighbor (by an approximately additional 45% respect to the AB ones), and so on. This behavior is characteristic of the type of Coulomb interaction involved in these terms [10]. Note as well that, for all levels, $\beta_n(AB)$ diminishes rapidly from dimer to trimer; and, for longer clusters, a slow variation is shown with cluster size. Furthermore, the three-body resonance contributions for consecutive monomers are larger (except for $n = 4$) than those of the two-body AC ones, and, on average, are about 55% of the values of the $\beta_n(AB)$ terms

(at the MP2 level, and 64% for the B3LYP results). Also, the values of the three-body terms, $\beta_n(ABE)$ are close to those of the third-neighbor, two-body contributions, $\beta_n(AD)$. Additionally, the four-body terms $\beta_n(ABCD)$ are approximately one order of magnitude less important than the corresponding $\beta_n(AB)$ ones (except for $n = 4$, where there is a factor of 5), with the other four-body terms showing smaller contributions. All these results emphasize the importance of the higher-order contributions ($n \geq 3$) and, therefore,

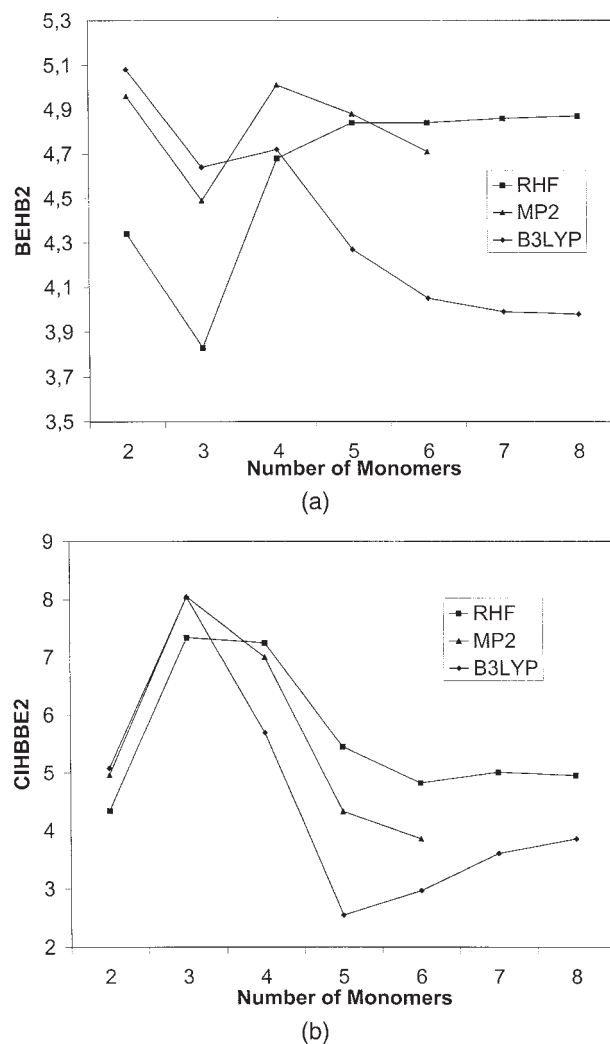


FIGURE 2. (a) Variation of the binding energy per hydrogen bond, including the contribution up to second order (BEHB2 in kcal/mol). (b) Variation of the cooperative increments in hydrogen bond binding energy, including the contribution up to second order (CIHBBE2 in kcal/mol).

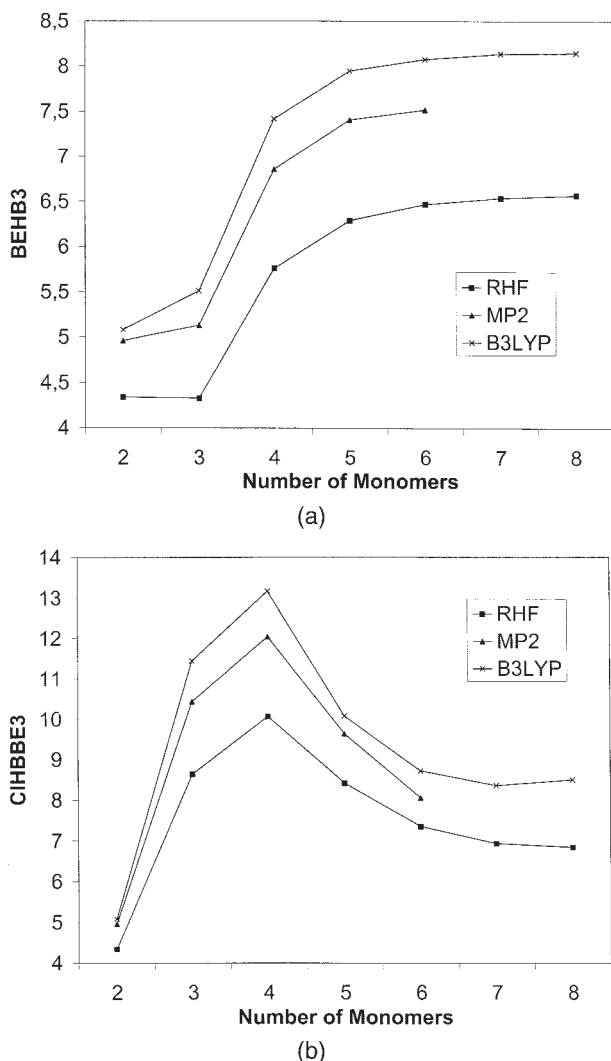


FIGURE 3. (a) Variation of the binding energy per hydrogen bond, including the contribution up to third order (BEHB3 in kcal/mol). (b) Variation of the cooperative increments in hydrogen bond binding energy, including the contribution up to third order (CIHBBE3 in kcal/mol).

of the electron density delocalization in the description of the cooperativity.

From Table II, it is also observed that for $n \geq 6$, the values obtained for the different resonance energies remain approximately unchanged, which would account for the leveling off observed in Figure 1(a). It is interesting to note that the extrapolated value for large n values (at the MP2 level) is close to 8.6 kcal/mol, which has been reported for an HF molecule embedded in an infinitely extended chain [10] and the calculated geometrical properties

characterizing clusters with $n \geq 6$ [9] are very similar to each other and to those obtained from measurements on molecular crystals [29, 30]. Next, looking for some hints that would allow us to explain the maximum observed in Figure 1(b), we have analyzed the difference between the cooperativity increments corresponding to $n = 4$ and $n = 3$, $\Delta(\text{CIHBBE})_{43}$, and to $n = 4$ and $n = 5$, $\Delta(\text{CIHBBE})_{45}$:

$$\begin{aligned} \Delta(\text{CIHBBE})_{43} = & [4DE_4(A) + 2DE_2(A) - 6DE_3(A)] \\ & + [4\beta_4(AB) + \beta_2(AB) - 6\beta_3(AB)] + 2\beta_4(AC) \\ & + [4\beta_4(ABC) - 2\beta_3(ABC)] + \beta_4(ABCD) \quad (14) \end{aligned}$$

$$\begin{aligned} \Delta(\text{CIHBBE})_{45} = & [8DE_4(A) - 3DE_3(A) - 5DE_5(A)] \\ & + [8\beta_4(AB) - 3\beta_3(AB) - 5\beta_5(AB)] + [4\beta_4(AC) \\ & - 5\beta_5(AC)] + [8\beta_4(ABC) - \beta_3(ABC) - 5\beta_5(ABC)] \\ & - 5\beta_5(ABD) + [2\beta_4(ABCD) - 5\beta_5(ABCD)] \\ & - \beta_5(ABCDE). \quad (15) \end{aligned}$$

For the first case, the enhancement of the cooperativity comes mainly from the two-body AC term and the three-body terms. In the second one, in addition to these terms, the distortion energy, which is a consequence of the geometric changes characteristic of the cooperative effects, contributes to the enhancement. These results reaffirm the importance of the charge redistribution responsible for those resonance contributions.

Finally, Table II shows that at the RHF level, the contributions to the resonance energies are generally underestimated. This is even true of the two-body ones, with the exception of $\beta_n(AB)$, for $n \geq 6$, where one might naively expect the correlation effects not to be quite so important; this can lead to underbinding in the aggregates and to results at the upper bound of the real interaction energies, once again demonstrating the need to include correlation to properly account for the polarization and dispersion contributions determinant in the cooperativity. In contrast, if the correlation is included via the LYP functional, the DFT results overestimate the resonance energies, except for $\beta_n(AB)$, for $n \geq 7$, leading to overbinding in the aggregates examined in the present study. Similar results have been reported for the atomization energies of molecules [31].

Summary

The method employed in this study allows us to show the many-body nature of the cooperativity, i.e., to show the significance of electronic density delocalization. It also permits quantification of the relative importance of the different order contributions involved, that is, the extension of the delocalization. The results demonstrate the need to include higher-order contributions for a proper description of the energetic of HB clusters.

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Supporting Information

Tables with detailed many-body decomposition of the total energy for $(\text{HF})_n$ ($n = 2-8$) clusters (Table A-I), many-body binding energy (Table A-II) for all clusters, and subclusters are available upon request to authors.

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