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Calculating interaction energies of hydrogen bonded dimers and complexes of HF, H₂O and NH₃: Super-molecular versus AIM Approach

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ABSTRACT

We perform a critical test on two theoretical approaches of calculating inter-molecular interaction energies of Hbonded systems namely, super-molecular and AIM. We choose conventional H-bonds existing in dimers and complexes of H_2O , HF and NH_3 and notice that there are substantial differences in the values calculated by two schemes. AIM approach seems to be better to calculate hydrogen bond strengths. However, a more detailed study with diverse set of molecules is needed in order to compare the reliability of schemes.

Keywords: Hydrogen bond, Density Functional Theory, Atoms in Molecule.

INTRODUCTION

The hydrogen bond (H-bond), discovered more than a century ago, is still a subject of scientific research and investigations due to its universal impact on natural sciences. The latest IUPAC definition recognizes H-bond as an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H, in which X is more electronegative than H, and an atom Y of the same or a different molecule [1] generally symbolised as X–H…Y. H-bonds having X, Y = F, O and N are the most frequently studied. Recently, C–H…O type H-bonds had also received a lot of attention [2] and X–H… π H-bonds were also detected [3].

H-bonds play a key role in determining the shapes, properties and functions of biomolecules [4]. Despite a dominant role of H-bonding in nature, accurate data on the respective stabilization or interaction energies are quite rare. The situation with extended H-bonded complexes is, despite enormous progress in various experimental techniques, even less satisfactory and accurate data on stabilization energies of these complexes are almost unavailable. Reliable and consistent information on the stability of various types of H-bonded complexes, from the very weak to the strongest, comes from high-level correlated quantum chemical ab initio or density functional theory (DFT) calculations and these methods, thus, represent one of the most promising sources of relevant data. Furthermore, DFT has established itself as a universal tool for electronic structure calculations [5] and comparable to or sometimes superior than highly correlated ab initio methods but at reduced computational cost. Quantum chemical calculations offer a direct estimation of Inter-molecular interaction energy as the energy lost by dimerization or complexation of molecules. This is what is known as super-molecular approach.

Another approach based on quantum theory of atoms in molecules [6], abbreviated as AIM, has become very popular for describing various inter- and intra-molecular interactions efficiently. The AIM theory exploits some topological parameters viz. electron density (ρ) and its Laplacian ($\nabla^2 \rho$), kinetic energy density (*G*), potential energy density (*V*) and total electron energy density (*H*) at the bond critical point (BCP) of interaction atoms or fragments.

We wish to present here a comparative study on these two approaches in a specific case of calculating intermolecular hydrogen bonding interaction energies. We have chosen conventional and prototype H-bonds existing between dimers as well as complexes of H_2O , HF and NH_3 .

1. Computational details

DFT calculations are performed on Gaussian 09 program [7]. B3LYP functional [8, 9] is employed to optimize the geometries of dimers of H_2O , HF, NH₃ and their complexes. The basis set used was diffused and polarized spilt valence type, 6-311++G^{**}. The optimization of dimers and complexes was further supported by presence of all real frequencies. We found that global minima of (NH₃) dimer did not correspond to hydrogen bonded structure but all the rest were hydrogen bonded systems. AIM calculations are carried out with AIMAII program [10].

2. Geometry of H-bonded systems

The optimized geometries of H-bonded dimers and complexes are shown in Fig. 1. The geometrical parameters associated with H-bonds are listed in Table 1. The water dimer, $(H_2O)_2$ is a very classic example and considered as prototype for the analysis of hydrogen bonding. We have calculated the O...O distance in water dimer as 2.94 A° against the experimental value of 2.98 A° [11]. Similarly, distances F...H for dimer $(HF)_2$ and O...H for complex $(H_2O)(HF)$ are calculated to be 2.78 and 2.66 A° respectively which are in good agreement with corresponding experimental values of 2.79 and 2.68 A°. Thus the present computational scheme is capable of reproducing the geometries of H-bonded systems, efficiently. Furthermore, these geometries can be utilized to predict relative strengths of interaction at least qualitatively. We may infer that hydrogen bonding interaction is stronger in the complex $(H_2O)(HF)$ and $(HF)(NH_3)$ while the rests are expected to show moderate type of interaction [12].

3. Super-molecular Approach

The energy of interaction between two molecules A and B in dimer or complex AB can be calculated as, $\Delta E = E(AB) - E(A) - E(B)$, where E denotes electronic energies of respective species [13]. ΔE must be corrected to account for basis set super-position errors (BSSE). Boys and Bernadi have suggested a counterpoise (CP) method [14] that ensures the simultaneous optimization of geometries of dimeric complexes along with their components and hence overcome the superposition. Interaction energies for H-bonded dimers and complexes calculated by DFT using CP technique are listed in Table 2.

The calculated H-bond energy in water dimer, 5.08 kcal/mol closely matches with the experimental value of 5.1 kcal/mol [15, 16]. In (HF)₂, the experimental value ranges from 5 to 7 kcal/mol [17, 18] while calculated value is 4.64 kcal/mol, slightly underestimated. Moreover, the reliability of the rest of calculated interaction energy values becomes suspicious for which experimental data are no longer available.

4. The AIM approach

The AIM theory efficiently describes the nature and strength of various types of hydrogen-bonded interactions. The basis set reliability and stability in the values of AIM parameters have been studied and found that they are almost independent of basis set in case of used functional B3LYP in DFT [19]. In AIM theory, the existence of hydrogen bond follows Koch and Popelier criterion [20] which requires (i) The existence of bond critical point (BCP) for the 'proton (H)...acceptor (A)' contact (ii) The value of electron density should lie in the range 0.002–0.040 a.u. (iii) The corresponding Laplacian ($\nabla^2 \rho$) should be within the range 0.024–0.139 a. u. The three types of H-bond are characterized on the basis of topological parameters. According to Rozas et al. [21], the characterization demands at BCP (i) $\nabla^2 \rho < 0$ and H < 0 for strong H-bond of covalent nature (ii) $\nabla^2 \rho > 0$ and H < 0 for medium H-bond of partially covalent nature (iii) $\nabla^2 \rho > 0$ and H > 0 for weak H-bond of electrostatic character. According to Espinosa et al. [22], the interaction energy of A...B contact is defined as, $\Delta E = \frac{1}{2}V$ at BCP.

BSSE corrected geometries are used to calculate various topological parameters listed in Table 3. The values of electron density and its Laplacian support the existence of H-bond. Topological parameters suggest medium strength H-bonding interaction in case of $(H_2O)(HF)$ and $(HF)(NH_3)$ of partially covalent nature while rests are treated as weak interactions. This is what is reflected by interaction energy values, so, the characterization of H-bonds in the framework of AIM theory is well defined and reliable.

The interaction energies calculated for H-bonds in dimers and complexes are also listed in Table 3. Unlike supermolecular approach in DFT, calculated H-bond energies are more close to realizations. The underestimation in energy values is removed to a certain extent hence AIM calculated values are more reliable as compared to that with DFT super-molecular approach in general. However, in case of $(H_2O)(NH_3)$, the energy of N...H bonds are further underestimated. It should be emphasized that inter-molecular energies of N...H type H-bonds needs a further investigation and corresponding calculated values by super-molecular as well as AIM approaches should be handled carefully.



Figure 1. Optimized geometries of dimers/complexes under study. Hydrogen bond is shown by broken lines.

H-bonded systems	X–H	Х–Н НҮ ХҮ Х–НҮ		X–H…Y
(H ₂ O) ₂ [OH]	0.9694	1.9759	2.9406	173.05
(HF) ₂ [FH]	0.9283	1.8694	2.7833	167.62
(H ₂ O) (HF) [OH]	0.9404	1.7257	2.6650	176.46
(NH ₃)(H ₂ O) [NH]	0.9761	1.9891	2.9548	169.80
(HF)(NH ₃) [NH]	0.9594	1.6915	2.6510	179.95

Table 1. Geometries of H-bonds in dimers and complexes at DFT-B3LYP/6-311++G^{**}. The type of existing H-bond is shown in square brackets.

 Table 2. Super-molecular interaction energies of H-bonded dimers and dimeric complexes.

 All energy values (except ΔE in kcal/mol) are in a. u.

Monomer [Energ	y] Dimer	[Energy]	Complex [Energy]	
$E(\mathbf{A})$ or $E(\mathbf{B})$	E(AB)	ΔE	E(AB)	ΔE
H ₂ O [-76.4585]	(H ₂ O) ₂ [-152.9251]	-5.08	(H ₂ O)(HF) [-176.9552]	-9.03
HF [-100.4823]	(HF) ₂ [-200.9720]	-4.64	(HF)(NH ₃) [-157.0861]	-13.24
			(NH ₃)(H ₂ O) [-133.0516]	-6.52

Table 3. Topological parameters calculated by AIM approach. All parameters are in a. u. and ΔE is in kcal/mol.

Dimer/Complex	ρ	$^{2}\rho$	$G \nabla$	V	Н	ΔE
$(H_2O)_2$	0.0224	0.0837	0.0185	-0.0160	0.0025	-5.02
(HF) ₂	0.0219	0.0969	0.0215	-0.0189	0.0026	-5.89
$(H_2O)(HF)$	0.0381	0.1371	0.0346	-0.0350	-0.0004	-10.98
(H ₂ O)(NH ₃)	0.0272	0.0799	0.0191	-0.0182	0.0009	-5.71
$(HF)(NH_3)$	0.0531	0.1103	0.0383	-0.0491	-0.0010	-15.37

CONCLUSION

We have performed a critical study of inter-molecular hydrogen bonding interaction energies calculated by two different approaches viz. super-molecular and AIM. We can possibly infer that the AIM calculated values are comparatively more reliable. However, in case of N...H bond the calculated energies show an appreciable departure from experimental values. Therefore, a more detailed study is required to further compare the reliability of approaches and predict the efficiency of method of calculating the hydrogen bonding energies. Further work in this regard is in progress and shall be reported soon. The present work is supposed to pave a way to assist the theoretical calculations on inter-molecular H-bond interaction energies in biomolecules, where H-bonds affect the structure, properties and functions, appreciably.

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