Theoretical research of multipolymers with hydrogen bonds (I)

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It is a kind of work about how the properties of multipolymers with hydrogen bonds changed. In this article, applying the different number of HF molecules, a series of characters of multipolymers, such as ESP, ELF, AIM, etc. have been observed. There are several results after calculations.

Computational details:

Geometry and frequency: M06-2X/6-311G** with "int=ultrafine" in Gaussian 09 D.01 program package

Wavefunction analysis: Multiwfn 3.6 (dev)

Isosurface plot: VMD 1.9.2

Results:

What should I say before discuss the results is that, the system with five HF molecules is unstable after geometry optimization. So, in the results display in below, the $(HF)_5$ has been passed.

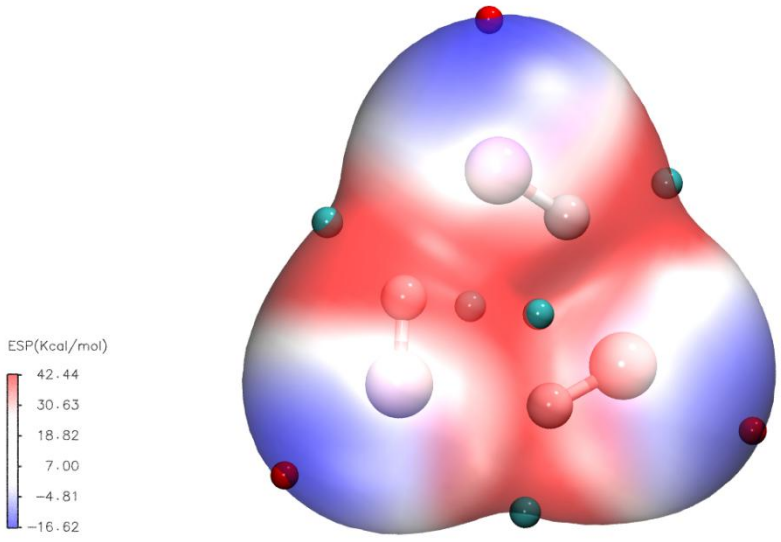
1. Average Interaction Energy

	$(HF)_3$	$(HF)_4$	$(HF)_6$
E_int(Kcal/mol)	8.07	9.83	10.58
Symmetry	C_{3h}	C_{4h}	S_6

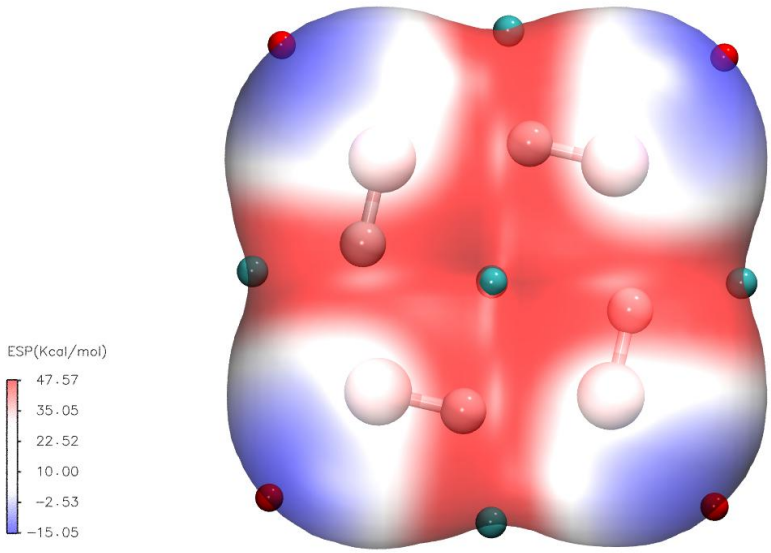
2. ESP: Electrostatic Potential

PS: a novel method of plotting ESP with .cub files can be seen in the appendix (in Chinese).

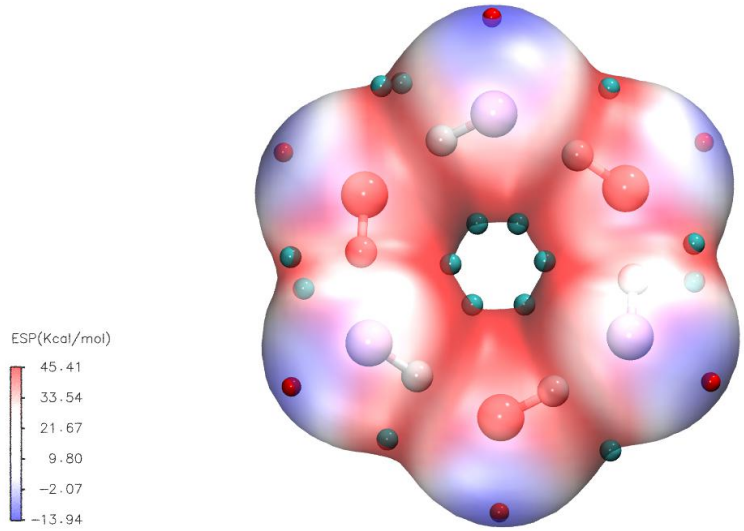
(1). ESP of $(HF)_3$



(2). ESP of $(HF)_4$

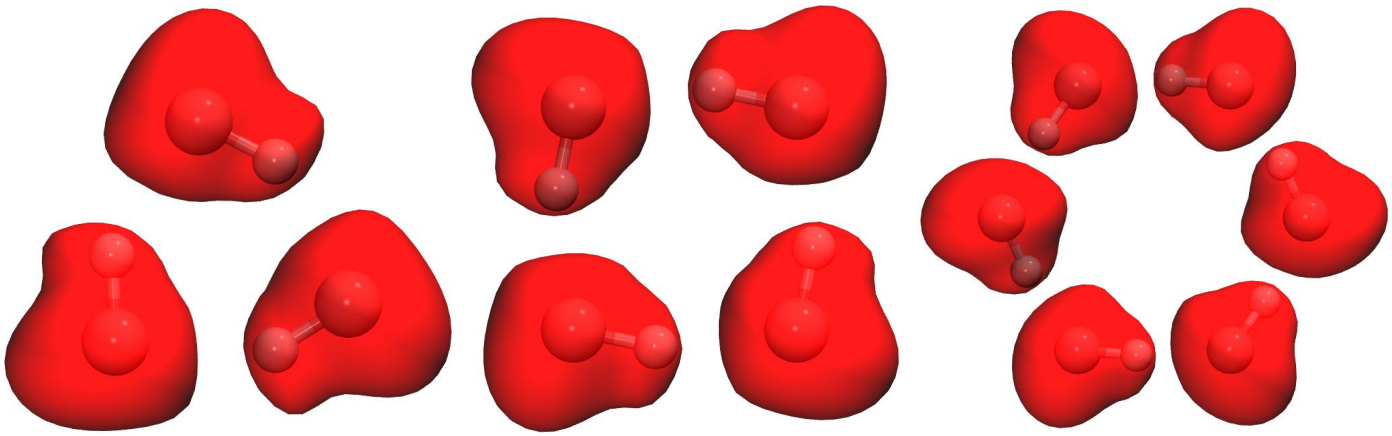


(3). ESP of $(HF)_6$



3. ELF: Electron Localization Function

ELF of $(HF)_3$ (left), ELF of $(HF)_4$ (middle) and ELF of $(HF)_6$ (right)



4. Mayer bond order and Multicenter bond order

Mayer	$(HF)_3$	$(HF)_4$	$(HF)_6$
H-F…H	0.091	0.115	0.130
Multicenter	$(HF)_3$	$(HF)_4$	$(HF)_6$
F-F-F(-F-F-F)	0.020	0.070	0.057

5. AIM topology analysis

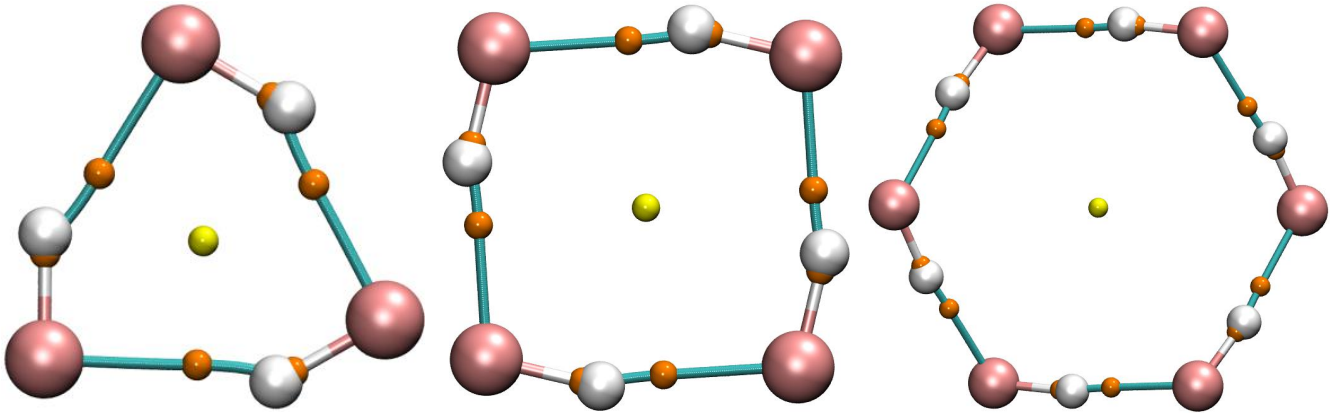
(1). Several properties of CPs are listed in the table below.

Tripolymers	$(HF)_3$		$(HF)_4$		$(HF)_6$	
Kind of Critical Point (CP)	BCP	RCP	BCP	RCP	BCP	RCP
Lagrangian kinetic energy G(r)	3.51E-02	1.32E-02	4.79E-02	3.49E-03	5.76E-02	6.38E-05
Hamiltonian kinetic energy K(r)	3.59E-04	-2.45E-03	2.59E-03	-1.53E-03	5.37E-03	-7.28E-05
Potential energy density V(r)	-3.54E-02	-1.07E-02	-5.04E-02	-1.96E-03	-6.30E-02	8.94E-06
Energy density E(r) or H(r)	-3.59E-04	2.45E-03	-2.59E-03	1.53E-03	-5.37E-03	7.28E-05
Laplacian of electron density	1.39E-01	6.25E-02	1.81E-01	2.01E-02	2.09E-01	5.46E-04
Electron localization function (ELF)	7.80E-02	1.09E-02	1.06E-01	1.07E-03	1.27E-01	1.50E-05
Localized orbital locator (LOL)	2.25E-01	9.52E-02	2.56E-01	3.18E-02	2.76E-01	4.46E-03
Local information entropy	7.67E-03	2.72E-03	7.66E-03	5.60E-04	6.29E-03	1.44E-05
Reduced density gradient (RDG)	1.34E-16	1.48E-14	1.77E-16	1.42E-15	1.00E+02	1.61E-15
Sign(lambda2)*rho	-3.39E-02	1.02E-02	-4.52E-02	2.29E-03	-5.38E-02	6.29E-05
Average local ionization energy	7.24E-01	7.46E-01	7.48E-01	7.02E-01	7.66E-01	6.00E-01
Delta_g	7.72E-02	3.44E-02	1.01E-01	1.33E-02	1.20E-01	1.52E-03
Total ESP	2.94E-01	1.26E-01	4.00E-01	9.94E-02	4.70E-01	6.32E-02
Ellipticity of electron density	9.91E-03	-1.32E+00	3.68E-02	-1.22E+00	3.56E-02	-1.12E+00
eta index	2.18E-01	3.16E-01	2.42E-01	2.16E-01	2.58E-01	1.17E-01

*BCP = Bond Critical Point; RCP = Ring Critical Point

(2). plots of AIM topology analysis

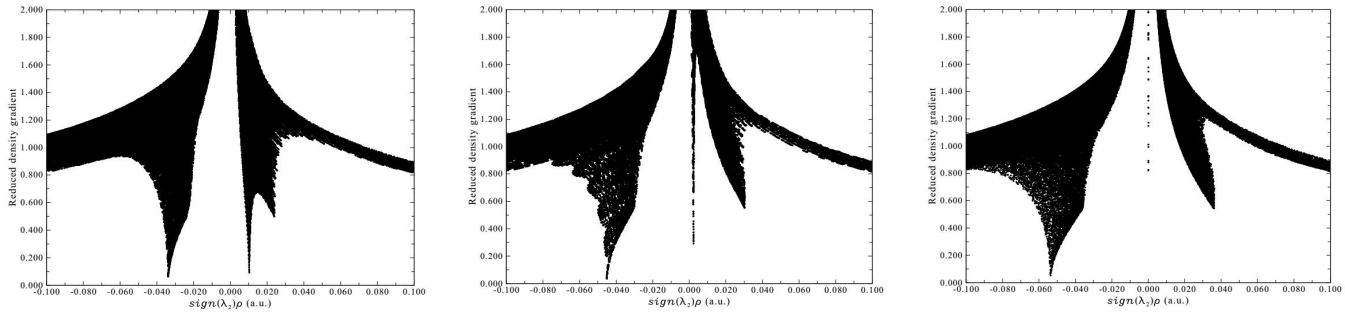
A. plots of $(HF)_3$; B. plots of $(HF)_4$; C.plots of $(HF)_6$



6. RDG: Reduced density gradient

(1). Scatter plots

A. plots of $(HF)_3$; B. plots of $(HF)_4$; C.plots of $(HF)_6$

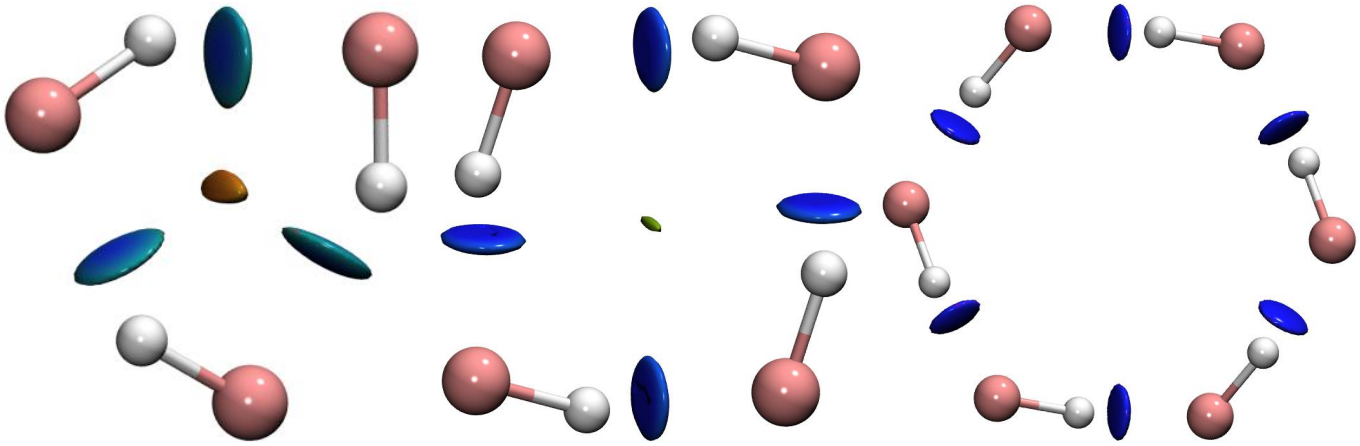


The marked scales of two cusps on the X axis are

A: -0.035(left); 0.010(right); B: -0.043(left); 0.005(right); C: -0.058(left); doesn't exist (right);

(2). Isosurface plots of RDG

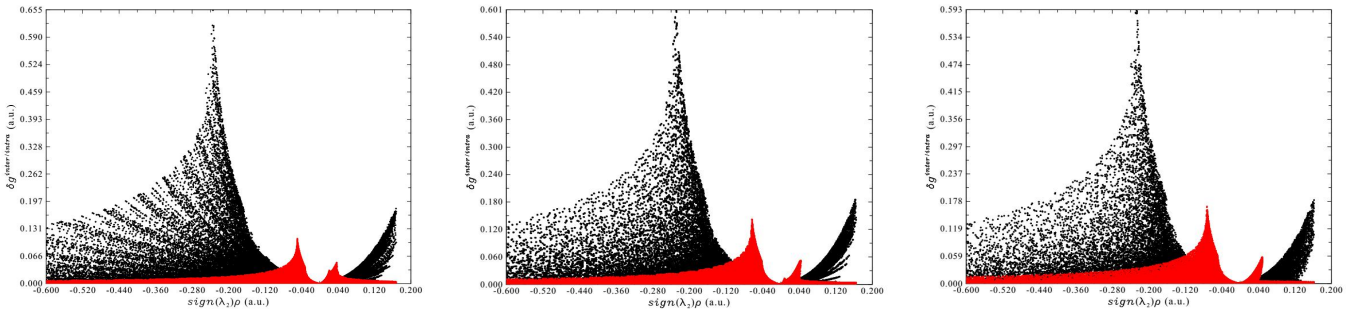
A. plots of $(HF)_3$; B. plots of $(HF)_4$; C.plots of $(HF)_6$



7. IGM: Independent Gradient Model

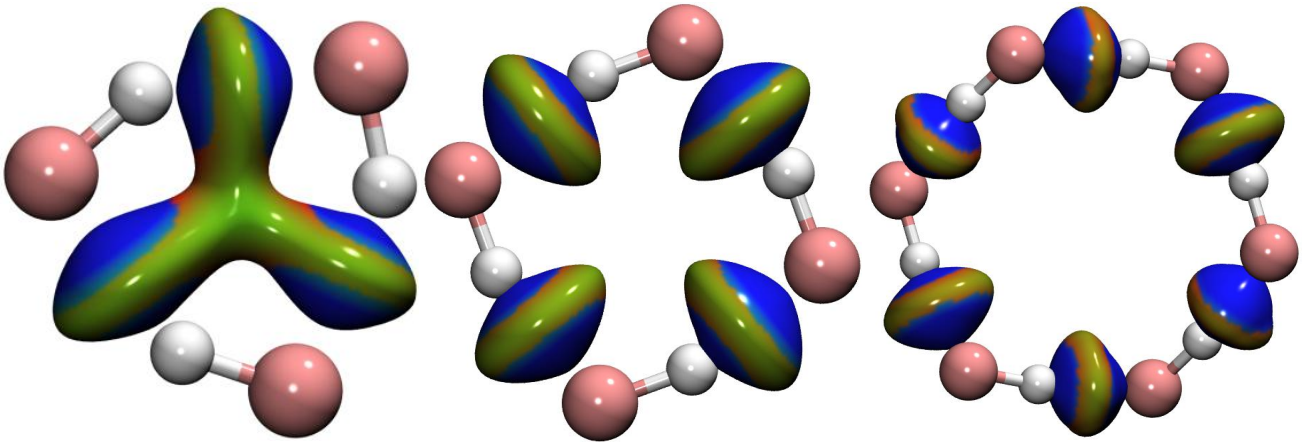
(1). Scatter plots

A. plots of $(HF)_3$; B. plots of $(HF)_4$; C.plots of $(HF)_6$



(2). Isosurface plots of IGM

A. plots of $(HF)_3$; B. plots of $(HF)_4$; C.plots of $(HF)_6$



*all of isovalue of isosurfaces are 0.015.

Conclusion

According with the original idea, the weak interaction of the system increased with the arising of number of HF molecules.