

## Bulk properties from finite-cluster calculations

### IV. Linear chains of hydrogen fluoride [1]

Jerzy Cioslowski

Department of Chemistry and Supercomputer Computations, Research Institute,  
Florida State University, Tallahassee, FL 32306-3006, USA

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**Summary.** Geometries of linear hydrogen fluoride clusters with 1–10 unit cells are optimized at the HF/6-31G\*\* level. MP2/6-31G\*\* energies at the HF/6-31G\*\* optimized geometries are calculated for clusters with 1–6 unit cells. Application of Padé approximants to the electronic properties of finite clusters results in the following estimated bulk properties: dipole moment per unit cell:  $2.66 \pm 0.01$  [D], bond lengths:  $0.913 \pm 0.001/1.686 \pm 0.001$  [Å], stabilization energy per unit cell relative to the HF molecule:  $-7.44 \pm 0.01$  [kcal/mol] (HF),  $-8.66 \pm 0.02$  [kcal/mol] (MP2). The extrapolated atomic charges based on the generalized atomic polar tensors (GAPT) are  $0.61 \pm 0.01$  as compared to the value of 0.42 for the monomer.

**Key words:** Polymers — Bulk properties of — Finite cluster MO calculations — Hydrogen fluoride

### Introduction

The oligomers of hydrogen fluoride have been a subject of several recent *ab initio* calculations [5–8]. The potential surface of the (HF)<sub>2</sub> dimer has been studied by Bunker et al. [5]. Loushin et al. [6] and Schwenke and Truhlar [7] have discussed the basis set superposition error in the (HF)<sub>2</sub> molecule. Finally, Schaefer's group reported the results of SCF and CI calculations on both the (HF)<sub>2</sub> and (HF)<sub>3</sub> oligomers [8].

Although in the gas phase cyclic structures of (HF)<sub>M</sub> are believed to be more stable than their linear counterparts for  $M \geq 3$  [9], solid hydrogen fluoride is composed of zig-zag chains of the HF molecules [10]. It is therefore of interest to investigate the electronic structure of linear polymers of hydrogen fluoride. This can be done by employing the crystal orbital method (CO) [11]. In their early paper [12], Karpfen and Schuster studied linear HF chains using a [8s4p/4s] basis set contracted to [4s3p/3s]. They observed rather slow convergence of the total energy with respect to the number of interacting neighbors included in the CO calculations unless the multipole corrections were added.

As it has been discussed elsewhere [4], the finite cluster calculations followed by extrapolation to the bulk limit appear to be an attractive alternative to the CO calculations on polymers. It is especially true for the post-SCF calculations since the approximate electron correlation methods such as MP2 are now becoming practical

even for quite large systems [13]. In this paper we study the extrapolation of various properties of linear hydrogen fluoride chains to the bulk limit. Three factors can obscure direct comparison of our results with the experimental data: First of all, we use a  $D_{\infty h}$  symmetry in our calculations, whereas the real HF chains possess a zig-zag conformation. Taking into account the recent study on the potential energy surface of the  $(\text{HF})_2$  molecule, we estimate that this assumption causes underestimation of the stabilization energy per unit cell by ca. 1 [kcal/mole]. The basis set superposition error results in probable overestimation of a similar magnitude. The third source of error in the computed properties is a neglect of interaction between the HF chains.

The main goal of this paper is to assess the efficacy of extrapolation based on the Padé approximants to the electronic properties of finite clusters composed of weakly interacting, highly polar molecules. A similar study on carbon clusters [4] has already shown that one can expect a fast convergence of the extrapolated properties to the bulk limit in the case of strong nonpolar (through bond) interactions.

## Theory

Let  $P(M)$  denote a size extensive property of an oligomer composed of  $M$  identical subunits, with or without terminal groups present. Examples of such properties are the total energy, the dipole moment, or the *sum* of respective bond distances or atomic charges. The average value of  $P(M)$  per unit cell is assumed to be a smooth function of the argument  $\nu = M^{-1}$

$$p(\nu) = P(M)/M. \quad (1)$$

This assumption is valid only if the polymer does not have a metallic character [2]. The function  $p(\nu)$  is defined only at  $\nu = 1, 1/2, \dots$  etc.; some of these points corresponding to the computed properties. In order to obtain the bulk properties, one has to extrapolate  $p(\nu)$  to the limit of  $\nu \rightarrow 0$ . Since, even for simple structures and model Hamiltonians,  $p(\nu)$  possesses poles at some values of  $\nu$  (although outside the region  $0 \leq \nu \leq 1$ ) [4], the Padé approximants [14] are expected to be an efficient tool for extracting the values of  $p(0)$  from the computed properties of finite clusters. In general, calculation of the  $[K/L]$  Padé approximant to  $p(\nu)$  requires the computed properties for  $M = 1, \dots, K + L + 1$ . The extrapolations of the dipole moment, the bond length of the "strong" bond and the GAPT atomic charges were performed this way. However, we found that much better convergence is achieved for the stabilization energies and the bond length of the "weak" bond when the computed properties for  $M = 2, \dots, K + L + 2$  are used in conjunction with the  $[K/L]$  Padé approximant to the function  $p(\nu')$ , where  $\nu' = (M - 1)^{-1}$ .

The atomic charges were calculated using the recently proposed GAPT scheme [15, 16]. In this approach, the atomic charge of atom  $A$  is given as one third of the trace of the respective atomic polar tensor

$$Q_A = (1/3) \left( \frac{\partial \mu_x}{\partial x_A} + \frac{\partial \mu_y}{\partial y_A} + \frac{\partial \mu_z}{\partial z_A} \right), \quad (2)$$

where  $\mu$  is the dipole moment and  $x_A, y_A$  and  $z_A$  are the coordinates of  $A$ . Although so defined atomic charges are computationally more expensive (they require solution of the CPHF equations), they are very insensitive to the basis sets used in calculations and provide much better insight into the charge distribution than traditional Mulliken analysis.

All calculations were performed using the 6-31G\*\* basis set [17]. The GAUSSIAN-82 package [18] running on a CRAY X-MP supercomputer located at Los

Alamos National Laboratory was used for both the HF and MP2 calculations. In the latter ones all electrons were correlated. All geometries were fully optimized at the HF/6-31G\*\* level assuming the  $D_{\infty h}$  symmetry. For the sake of minimizing the numerical noise in Padé approximants, all energies were converged to  $10^{-10}$  [au] and the geometries were optimized within  $10^{-5}$  [Å]. In the following,  $R_1$  denote lengths of the (strong) H—F bonds and  $R_2$  those of the F...H hydrogen bonds.

### Results and discussion

The raw data obtained from *ab initio* HF calculations on clusters with 1–10 unit cells and MP2 calculations on clusters with 1–6 unit cells are presented in Table 1. In Table 2 we display the computed GAPT atomic charges.

**Table 1.** Results of computations on  $(\text{HF})_M$ ,  $M = 1, 10$ , clusters

$E_{\text{HF}}$ [au]	$E_{\text{MP2}}$ [au]	$\mu_{\text{HF}}$ [D]	$R_1$ [Å]	$R_2$ [Å]
−100.01169084	−0.18450896	1.9439	0.9005	
−200.03084372	−0.37002962	4.2825	0.9018	1.9189
			0.9031	
−300.05234319	−0.55590069	6.7706	0.9024	1.8414
			0.9058	1.8609
			0.9043	
−400.07479142	−0.74196362	9.3295	0.9027	1.8177
			0.9069	1.7797
			0.9076	1.8426
			0.9049	
−500.09768083	−0.92813572	11.9258	0.9029	1.8083
			0.9074	1.7542
			0.9091	1.7595
			0.9084	1.8351
			0.9051	
−600.12079922	−1.11436572	14.5429	0.9029	1.8040
			0.9077	1.7438
			0.9097	1.7330
			0.9100	1.7512
			0.9088	1.8316
			0.9052	

Table 1 (continued)

$E_{\text{HF}}$ [au]	$E_{\text{MP2}}$ [au]	$\mu_{\text{HF}}$ [D]	$R_1$ [Å]	$R_2$ [Å]
-700.14404732	n/a	17.1725	0.9030	1.8019
			0.9078	1.7391
			0.9100	1.7221
			0.9107	1.7241
			0.9104	1.7472
			0.9090	1.8300
			0.9053	
-800.16737434	n/a	19.8099	0.9030	1.8006
			0.9079	1.7367
			0.9102	1.7172
			0.9111	1.7129
			0.9112	1.7198
			0.9107	1.7451
			0.9091	1.8289
			0.9053	
-900.19075230	n/a	22.4524	0.9030	1.7999
			0.9080	1.7352
			0.9103	1.7145
			0.9112	1.7078
			0.9115	1.7084
			0.9114	1.7176
			0.9108	1.7439
			0.9092	1.8283
			0.9054	

**Table 1** (continued)

$E_{\text{HF}}$ [au]	$E_{\text{MP2}}$ [au]	$\mu_{\text{HF}}$ [D]	$R_1$ [Å]	$R_2$ [Å]
-1000.21416480	n/a	25.0981	0.9030	
			0.9080	1.7994
			0.9104	1.7344
			0.9113	1.7130
			0.9117	1.7050
			0.9118	1.7031
			0.9116	1.7062
			0.9109	1.7163
			0.9092	1.7433
			0.9054	1.8279

**Table 2.** GAPT atomic charges in  $(\text{HF})_M$ ,  $M = 1, 6$ , clusters

$M$	$Q_H$	$Q_F$
1	0.41990	-0.41990
2	0.45800	-0.47289
	0.48131	-0.46643
3	0.46985	-0.48985
	0.53661	-0.53512
	0.49952	-0.48102
4	0.47444	-0.49629
	0.55466	-0.55841
	0.56117	-0.55529
	0.50637	-0.48665
5	0.47652	-0.49915
	0.56186	-0.56751
	0.58182	-0.58116
	0.57068	-0.56329
	0.50942	-0.48920
6	0.47758	-0.50057
	0.56518	-0.57160
	0.59020	-0.59142
	0.59249	-0.59033
	0.57495	-0.56693
	0.51094	-0.49048

With increasing  $M$ , the “strong” bond elongates, whereas the “weak” hydrogen bond shortens as reflected by the values of  $R_1$  and  $R_2$ . As expected, the GAPT atomic charges increase in magnitude with  $M$ . This is due to polarization of the HF molecules caused by the electric field generated by their neighbors. The observation that the charges have the largest magnitudes at the centers of clusters is also consistent with this explanation.

The HF and MP2 stabilization energies are defined as

$$\Delta E_{\text{HF}}(M) = E_{\text{HF}}(M) - ME_{\text{HF}}(1), \quad \Delta E_{\text{MP2}}(M) = E_{\text{MP2}}(M) - ME_{\text{MP2}}(1). \quad (3)$$

The total stabilization energy at the MP2 level is a sum of  $\Delta E_{\text{HF}}(M)$  and  $\Delta E_{\text{MP2}}(M)$ . The simplest method of extrapolating the data from Table 1 to the bulk limit is to use the first-order finite differences

$$p(0) \approx P(M) - P(M - 1). \quad (4)$$

The values of  $R_1$ ,  $R_2$ ,  $Q_H$  and  $Q_F$  reported in Table 3 are calculated from the respective sums of bond lengths and atomic charges, the energies  $\Delta E_{\text{HF}}$  and  $\Delta E_{\text{MP2}}$  are extrapolated from the respective stabilization energies, Eq. (3), and  $\mu_{\text{HF}}$  is computed directly from the HF dipole moments. As revealed in Table 3, this produces estimates that converge only very slowly.

In Tables 4–10 we present the estimates of bulk properties obtained from Padé approximants. Without use of any multipole corrections, one arrives at the HF

Table 3. First-order difference bulk properties (Eq. (4))

$M$	$\Delta E_{\text{HF}}$ [kcal/mol]	$\Delta H_{\text{MP2}}$ [kcal/mol]	$\mu_{\text{HF}}$ [D]	$R_1$ [Å]	$R_2$ [Å]	$Q_H$	$Q_F$
2	-4.68	-0.63	2.339	0.904	1.919	0.5194	-0.5194
3	-6.16	-0.85	2.488	0.908	1.783	0.5667	-0.5667
4	-6.75	-0.98	2.559	0.910	1.738	0.5907	-0.5907
5	-7.03	-1.04	2.596	0.911	1.717	0.6037	-0.6037
6	-7.17	-1.08	2.617	0.911	1.707	0.6110	-0.6110
7	-7.25	n/a	2.630	0.912	1.701	n/a	n/a
8	-7.30	n/a	2.637	0.912	1.697	n/a	n/a
9	-7.33	n/a	2.643	0.912	1.694	n/a	n/a
10	-7.36	n/a	2.646	0.912	1.693	n/a	n/a

Table 4. Padé approximants to  $\Delta E_{\text{HF}}(0)$ . All entries in kcal/mol

$I$	Padé approximants $[I - J/J]$								
$J$	0	1	2	3	4	5	6	7	8
1	-4.88	-7.90							
2	-6.51	-7.71	-7.71						
3	-7.21	-7.55	-7.28	-7.55					
4	-7.41	-7.47	-7.40	-7.40	-7.46				
5	-7.44	-7.44	-7.42	-7.42	-7.42	-7.43			
6	-7.43	-7.43	-7.43	-7.44	-7.44	-7.43	-7.43		
7	-7.43	-7.43	-7.43	-7.44	-7.44	-7.44	-7.43	-7.43	
8	-7.43	-7.43	-7.43	-7.44	-7.44	-7.44	-7.44	-7.50	-7.43

**Table 5.** Padé approximants to  $\Delta E_{\text{MP2}}(0)$ . All entries in kcal/mol

<i>I</i>	Padé approximants [ <i>I</i> - <i>J</i> / <i>J</i> ]				
	<i>J</i>				
	0	1	2	3	4
1	-0.68	-1.14			
2	-0.95	-1.22	-1.22		
3	-1.10	-1.21	-1.21	-1.21	
4	-1.14	-1.16	-1.22	-1.22	-1.15

**Table 6.** Padé approximants to  $\mu_{\text{HF}}(0)$ . All entries in debye

<i>I</i>	Padé approximants [ <i>I</i> - <i>J</i> / <i>J</i> ]									
	<i>J</i>									
	0	1	2	3	4	5	6	7	8	9
1	2.339	2.383								
2	2.563	2.700	2.611							
3	2.652	2.690	2.690	2.675						
4	2.671	2.676	2.744	2.676	2.676					
5	2.662	2.665	5.766	5.841	2.674	2.660				
6	2.662	2.662	2.663	2.722	2.663	2.662	2.662			
7	2.651	2.662	1.666	2.652	2.653	2.590	2.660	2.649		
8	2.663	2.657	2.655	2.657	2.659	2.657	2.656	2.657	2.665	
9	2.578	2.651	2.664	2.669	2.652	2.652	2.652	2.661	2.650	2.571

**Table 7.** Padé approximants to  $R_1(0)$ . All entries in Å

<i>I</i>	Padé approximants [ <i>I</i> - <i>J</i> / <i>J</i> ]									
	<i>J</i>									
	0	1	2	3	4	5	6	7	8	9
1	0.904	0.904								
2	0.909	0.931	0.909							
3	0.912	0.916	0.916	0.912						
4	0.913	0.914	0.913	0.914	0.914					
5	0.912	0.913	0.922	0.922	0.913	0.912				
6	0.917	0.913	0.913	0.913	0.913	0.913	0.917			
7	0.913	0.914	0.910	0.914	0.914	0.910	0.914	0.913		
8	0.877	0.918	0.913	0.913	0.913	0.913	0.913	0.918	0.879	
9	1.063	0.910	0.913	0.913	0.913	0.913	0.913	0.913	0.910	1.095

**Table 8.** Padé approximants to  $R_2(0)$ . All entries in Å

$I$	Padé approximants $[I - J/J]$								
	$J$								
	0	1	2	3	4	5	6	7	8
1	1.509	1.729							
2	1.663	1.699	1.699						
3	1.685	1.688	1.682	1.687					
4	1.686	1.686	1.685	1.685	1.685				
5	1.689	1.685	1.687	1.668	1.687	1.690			
6	1.676	1.686	1.686	1.686	1.686	1.686	1.673		
7	1.709	1.686	1.686	1.686	1.686	1.686	1.686	1.716	
8	1.682	1.693	1.686	1.686	1.686	1.686	1.686	1.694	1.678

**Table 9.** Padé approximants to  $Q_H(0)$ 

$I$	Padé approximants $[I - J/J]$					
	$J$					
	0	1	2	3	4	5
1	0.5194	0.5328				
2	0.5903	0.6544	0.6105			
3	0.6228	0.6398	0.6399	0.6340		
4	0.6303	0.6321	0.6230	0.6328	0.6328	
5	0.6278	0.6284	0.6179	0.6179	0.6348	0.6269

**Table 10.** Padé approximants to  $Q_F(0)$ 

$I$	Padé approximants $[I - J/J]$					
	$J$					
	0	1	2	3	4	5
1	-0.5194	-0.5328				
2	-0.5903	-0.6544	-0.6104			
3	-0.6227	-0.6397	-0.6398	-0.6340		
4	-0.6305	-0.6323	-0.6240	-0.6330	-0.6329	
5	-0.6274	-0.6282	-0.6093	-0.6094	-0.6345	-0.6264

stabilization energy converged within less than 0.01 [kcal/mol]. The MP2 stabilization energy has similar convergence characteristics. The dipole moment per unit cell converges much slower. There are some irregularities in the approximants to  $\mu_{HF}(0)$  for small values of  $M$ . The bond lengths  $R_1$  and  $R_2$  can be estimated within 0.001 [Å]. The convergence of the GAPT atomic charges on the hydrogen and fluorine atoms is similar to that of dipole moment.



## Conclusions

The present system under examination differs from the previously studied carbon clusters [4] in the character of intercell interactions. The individual unit cells in  $X-(\text{—C}\equiv\text{C—})_M\text{—Y}$  interact strongly through bonds, while the relatively weak interaction in  $(\text{HF})_M$  is mainly of electrostatic character and propagates through space. This has important consequences in the behavior of different extrapolation procedures. In the case of carbon clusters it was found that the Padé approximants are superior to the simple finite difference scheme only for small values of  $M$ . In the present case, the Padé approximants perform uniformly better. Even if the computed bond length in finite clusters exhibit much larger variations in  $(\text{HF})_M$  than in  $X-(\text{—C}\equiv\text{C—})_M\text{—Y}$ , the extrapolated values converge much faster in the former case. We therefore conclude that the Padé approximants are expected to be especially effective in extracting the bulk properties of systems with weak ionic interactions, such as hydrogen-bond and charge-transfer complexes.

The present approach complements the multipole expansion technique of Piela and Delhalle [19, 20]. At the Hartree–Fock level, resummation of the electrostatic contributions is certainly less expensive than calculation of the properties of a series of clusters. However, our approach is not limited to the Hartree–Fock energies. As demonstrated in the present paper, it can be successfully applied to calculation of the expectation values and the correlated energies, as well.

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