

# Further Applications of Molecular Orbital Calculations for Solid HF According to Pseudolattice Method

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The molecular orbital calculations for solid HF are performed by using the pseudolattice method considering the coulomb lattice sum. In order to obtain the reliable net atomic charges and lattice energy of one dimensional chains, the limited counting of interactions terms up to second neighbours for zig-zag chain and third neighbours for linear chain are sufficient in this calculation. In three dimensional solid HF, the contribution of interaction energy between non-hydrogen bonded neighbours to lattice energy is about 3.5% and the lattice energy of nonpolar structure is stabilized by 2.05 kcal/mole compared with that of polar structure. And, this method is further tested and compared with the other methods.

## Introduction

Molecular orbital (MO) calculation of solid hydrogen fluoride gives many interesting results, since it is a typical example of molecular crystals held together by strong hydrogen bonds. As the molecules in molecular crystal are arranged infinitely, the MO calculations using the truncated cluster model can not predict the reasonable wavefunction and quantum chemical properties of solid. Accordingly, following methods were proposed by several workers in order to represent the characteristic properties of the solid. The perturbation method for hydrogen bonded molecular crystals was proposed by Bacon and Santry,<sup>1,2</sup> and a self-consistent tight-binding calculation (crystal orbital method) originally formulated by Del Re *et al.*<sup>3</sup> was practiced in CNDO/2<sup>4,5</sup> and *ab initio*<sup>6-8</sup> version to calculate the energy band of one and two dimensional aggregates of hydrogen bonded molecules. Small periodic cluster method (SPC) which is based on the periodic boundary condition was proposed by Zunger and was applied to perfect and defect crystals.<sup>9,10</sup> Recently, the pseudolattice (PL) method was proposed by No and Jhon in order to perform the MO calculation of three dimensional molecular crystals.<sup>11</sup> For one dimensional molecular crystal model, both SPC and PL methods give same results if PL method does not involve coulomb lattice sum, since the translational symmetry of unit cell and that of molecule become identical in perfect one dimensional crystals.

Among the above methods, the PL method may be appropriate for describing the feature of solid because it contains both the interaction due to the overlap of atomic orbitals and the interaction through the bond. We have practiced this method by including the coulomb interactions between the long distant molecules and the periodic cluster molecules. This coulomb lattice sum was previously included in the per-

turbation,<sup>2</sup> crystal orbital<sup>5</sup> and PL MO calculations.<sup>11</sup>

In this paper, the justification of PL method is investigated by the MO calculation of one dimensional (HF)<sub>n</sub> chains. And then, this method is extended to three dimensional HF crystals. The lattice energy and the charge distribution of HF crystals are obtained and compared with the other methods.

## Method of Calculations

HF crystal provides very useful system for the study of hydrogen bond and one of good testing model for the MO calculation of solid. Previously, MO calculations of one dimensional linear and zig-zag chains containing up to 15 HF molecules are performed by using CNDO/2 method<sup>12-14</sup> to obtain the approximated lattice energy of infinite one dimensional HF chains. Here, we use the CNDO/2 PL method<sup>11</sup> including the coulomb lattice sum for one dimensional infinite HF chains in the various interaction order.<sup>10</sup> In the coulomb lattice sum, all the HF molecules within the range of 200 Å distance are included.

Next, this method is applied for three dimensional HF crystal in order to investigate the effects of nonhydrogen bonded neighbours. For two structures, polar and nonpolar, the calculations are performed. And, MO calculations are performed for each structure in two cases; one with overlap interaction of only the first nearest neighbours, (HF)<sub>4</sub>, and the other with overlap interaction up to 10 HF neighbours, (HF)<sub>16</sub>. All the HF molecules, in 25 × 19 × 15 (a × b × c) unit cells are included in the coulomb lattice sum.

The models of one dimensional zig-zag chain (Figure 1b) and three dimensional polar structure (Figure 2) are constructed with the data from the neutron diffraction study at 4.2K,<sup>15</sup> and the bond lengths of one dimensional linear chain (Figure 1a) are obtained from the CNDO/2 minimized data of HF dimer.<sup>16</sup> The structure of three dimensional nonpolar HF crystal in the same as that of polar HF crystal except the

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reversed HF directions in the unit cell chain. All the geometric data are listed in Table 1.

## Results and Discussion

In Table 2, the lattice energies for one dimensional (HF)<sub>n</sub> chains are shown as a function of the number of monomers. The nonadditivity in lattice energies of clusters is demonstrated clearly in Table 2. It is shown that the lattice energy increases considerably with the number of monomers. Same

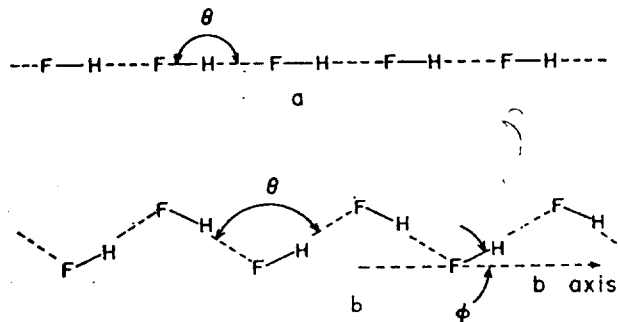


Figure 1. One-dimensional (HF)<sub>n</sub>-chain a. linear arrangement  $\theta=180^\circ$ ; b. zig-zag arrangement  $\theta=116.6^\circ$ ;  $\phi=29.6^\circ$ .

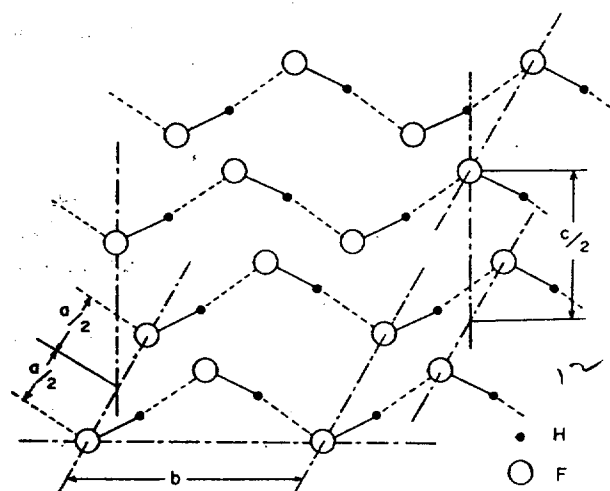


Figure 2. Three-dimensional HF polar structure ( $a=3.31 \text{ \AA}$ ,  $b=4.26 \text{ \AA}$ ,  $c=5.22 \text{ \AA}$ ).

TABLE 1: Molecular Geometries for (HF)<sub>n</sub>

Geometry		Bond distances (Å)	Intermolecular angle (degree)
One dimensional chain	Linear	$R_{\text{HF}}=1.01$	180
	CNDO/2-minimum <sup>a</sup>	$R_{\text{FF}}=2.44$	
	Zig-zag Chain <sup>b</sup>	$R_{\text{HF}}=0.97$ $R_{\text{FF}}=2.50$	116.6 $\angle \text{FHb}=29.6$
Three dimensional molecular crystal	Polar	$R_{\text{HF}}=0.97$ $R_{\text{FF}}=2.50$	116.6 $\angle \text{FHb}=29.6$
	Nonpolar	$R_{\text{HF}}=0.97$ $R_{\text{FF}}=2.50$	116.6 $\angle \text{FHb}=29.6$

<sup>a</sup> Ref. (16); <sup>b</sup> Ref. (15).

results was obtained by ab initio calculations,<sup>17</sup> which were restricted to the first few members of the series. The  $\Delta E_{n-1,n}$ , which describes the stabilized energy by insertion of a monomer into an already existing chain, converges much faster than the average hydrogen bond energy,  $\Delta \bar{E}$ .<sup>5</sup> In the case of infinite chains, of course,  $\Delta \bar{E}$  and  $\Delta E_{n-1,n}$  have to become identical ( $\Delta E_\infty$ ).

In order to obtain the lattice energy of the infinite chain ( $\Delta E_\infty$ ), the lattice energies in Table 2 are extrapolated. Table 3 shows this extrapolated lattice energy,  $E_\infty$ , and the results of the PL. MO calculations for one dimensional chains. For the linear HF chain, the calculated results of lattice energy for (HF)<sub>5</sub> model is within the error of 0.2 % compared with  $\Delta E_\infty$ , and for (HF)<sub>7</sub> model, the error is negligible. In the case of (HF)<sub>9</sub> model, the lattice energy is the same with that of (HF)<sub>7</sub> model. This results show that the interaction terms, except electrostatic term, within third nearest neighbours are sufficient to obtain the reliable lattice energy of HF linear infinite chain. For the zig-zag chain, the calculated results of

TABLE 2: Lattice Energies of (HF)<sub>n</sub>, One Dimensional Chains

Geometry	Number of monomer: $n$	$\Delta \bar{E}^a$ (kcal/mole)	$\Delta E_{n-1,n}^b$ (Kcal/mole)	
linear chain	3	10.88	12.25	
	5	12.08	13.45	
	(CNDO/2 minimized structure) <sup>c</sup>	7	12.60	13.68
		8	12.76	13.72
		9	12.89	13.75
14		13.23	13.79	
Zig-zag chain <sup>d</sup>	5	13.27	13.80	
	3	8.69	9.50	
	5	9.39	10.18	
	7	9.69	10.32	
	5	9.86	10.37	
	11	9.96	10.39	
	13	10.04	10.40	
	14	10.07	10.41	
	15	10.09	10.41	

$$^a \Delta \bar{E}_G = \frac{E((\text{HF})_n) - n \cdot E(\text{HF})}{m} \quad (m: \text{number of hydrogen bonds})$$

$$^b \Delta E_{n-1,n} = E((\text{HF})_n) - (E(\text{HF})_{n-1}) + E(\text{HF}). \quad ^c \text{Ref. (16)}. \quad ^d \text{Ref. (15)}$$

TABLE 3: Lattice Energies for Infinite HF Chains Calculated by Direct MO and the PL method Including Coulomb Lattice Sums<sup>a</sup>

Case	Interaction order ( $\eta$ ) <sup>b</sup>	Extrapolated <sup>c</sup> value (kcal/mole)	Our method (Kcal/mole)
Linear chain	(HF) <sub>3</sub>		12.89
	(HF) <sub>5</sub>		13.80
	(HF) <sub>7</sub>	13.83	13.83
	(HF) <sub>9</sub>		13.83
Zig-zag chain	(HF) <sub>4</sub>		10.41
	(HF) <sub>6</sub>	10.43	10.43
	(HF) <sub>8</sub>		10.43

<sup>a</sup> All molecules within the range of 200Å distance are included in coulomb lattice sum; <sup>b</sup> The  $\eta$  denotes the maximal interaction order;<sup>10</sup> <sup>c</sup> The lattice energies in Table 2 are used to obtain the extrapolated lattice energy for the infinite chain.

lattice energy for (HF)<sub>4</sub> model is also within the error of 0.2 % compared with  $\Delta E_{\infty}$ , and for (HF)<sub>6</sub> and (HF)<sub>8</sub> models, the errors are negligible.

Figure 3 shows the rapid convergency of net atomic charges versus numbers of neighbours in this work. In order to obtain the reliable net atomic charges, the interaction terms within third nearest neighbours and those within second neighbours are sufficient for MO calculation of linear and zig-zag HF chain, respectively. As shown in Table 3 and Figure 3, the slow convergency of HF linear chain in the lattice energy and net atomic charges indicate that the 2p-orbital parallel to bond axis contribute considerably to the interaction through the bond.

As shown previously, the method used in this work is appropriate for the MO calculation of solid HF and gives rapid convergency for the reasonable lattice energy and net atomic charges of solid HF.

Table 4 and 5 show the intramolecular and nearest neighbour intermolecular density submatrices obtained from the center of the density matrix of (HF)<sub>5</sub> chain and from our (HF)<sub>6</sub> model for the zig-zag chain. The agreement between two sets of results is within 0.3 %. This provides one measure of the accuracy of the method used in this work.

In table 6, this method is compared with the other methods applied to the one dimensional HF chain. Both the perturbation method and the crystal-orbital method, give considerable difference in the lattice energy compared with the estimated lattice energy ( $E_{\infty}$ ), and the SPC method without coulomb lattice sum<sup>10</sup> needs a relatively large cluster to obtain reliable values for the infinite chain, however, our PL method gives reasonable results in the lattice energy, net atomic charges and convergency. The satisfactory results in this work might be ascribed to the fact that the interaction through bond is well represented by the PL model.

In Table 7, the results for three dimensional polar and non-polar HF crystals are given. The lattice energy of (HF)<sub>16</sub> PL model which include the interaction of the HF neighbours are stabilized by 0.38 kcal/mole for polar structure and 0.39

kcal/mole for nonpolar structure compared with that of (HF)<sub>4</sub> models which include the interactions of hydrogen bonded neighbours only. Those stabilization energies have their origin in the interaction through the space (the overlap of electron cloud) between nonhydrogen bonded neighbours. The influence of nonhydrogen bonded neighbours on net atomic charges is relatively small although the electrons are distributed between nonhydrogen bonded neighbours due to the overlap of electron cloud. According to the results of Table 7, the nonpolar structure is stable about 2.05 kcal/mole compared with the results of the perturbation method.<sup>2,18</sup> But the neutron diffraction study shows that the proton arrangement in HF crystal is polar.<sup>15</sup> Above disagreement between

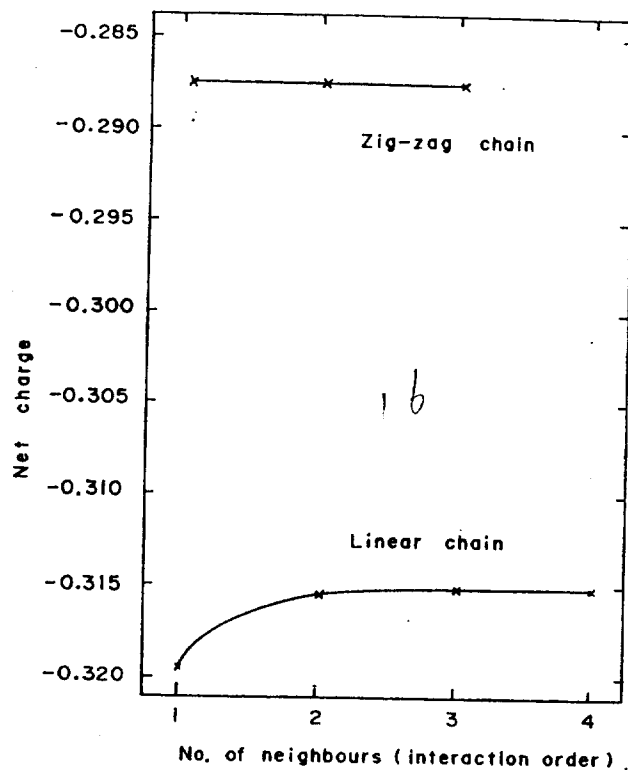


Figure 3. Dependence of the fluorine net charge on the interaction order.

TABLE 4: Intra- and Intermolecular Density Submatrices for HF Zig-Zag Chain Calculated Directly. The  $x$  Axis Lies Perpendicular to the Plane of the Chain and  $y$  Axis Along the Chain

Molecule I	Molecule I					Molecule II				
	2S	2P <sub>x</sub>	2P <sub>y</sub>	2P <sub>z</sub>	1S	2S	2P <sub>x</sub>	2P <sub>y</sub>	2P <sub>z</sub>	1S
2S	1.8711	0.0	-0.2100	0.1371	0.3910	-0.0375	0.0	0.0417	-0.0367	0.0091
2P <sub>x</sub>		2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2P <sub>y</sub>			1.5617	0.2263	0.7347	-0.0723	0.0	0.0718	-0.0711	0.0259
2P <sub>z</sub>				1.8541	-0.4187	0.0415	0.0	-0.0422	0.0407	-0.0140
1S					0.7131	0.1116	0.0	-0.1565	0.1082	0.0065

TABLE 5: Intra- and Intermolecular Density Submatrices for HF Zig-Zag Chain Using Our Method. The Axes Are the Same as Those in Table 4

Molecule I	Molecule I					Molecule II				
	2S	2P <sub>x</sub>	2P <sub>y</sub>	2P <sub>z</sub>	1S	2S	2P <sub>x</sub>	2P <sub>y</sub>	2P <sub>z</sub>	1S
2S	1.8711	0.0	-0.2098	0.1370	0.3910	-0.0376	0.0	0.0418	-0.0368	0.0091
2P <sub>x</sub>		2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2P <sub>y</sub>			1.5622	0.2260	0.7344	-0.0723	0.0	0.0719	-0.0712	0.0259
2P <sub>z</sub>				1.8542	-0.4186	0.0415	0.0	-0.0423	0.0407	-0.0140
1S					0.7125	0.1117	0.0	-0.1569	0.1085	0.0065

TABLE 6: Comparison the Pseudo Lattice Method Including Coulomb Lattice Sums with Other Methods

Method	Geometry	Estimated value <sup>a</sup> (kcal/mole)	Calculated value <sup>b</sup> (kcal/mole)	Ref.
Perturbation	<i>c</i>	13.0	11.9	[ 2 ]
Crystal-orbital	CNDO/2-min. zig-zag	14.2	15.95	[ 5 ]
Small-periodic-cluster	(HF) <sub>9</sub> <sup>d</sup>	12.05	12.00	[10]
This work	CNDO/2min. linear (HF) <sub>5</sub>	13.83	13.80	
	Experimental zig-zag (HF) <sub>5</sub>	10.43	10.41	

<sup>a</sup> The lattice energy estimated from direct calculation for the same geometry, respectively; <sup>b</sup> The lattice energy calculated by the given method, respectively; <sup>c</sup>  $R_{\text{HF}}=0.99975\text{\AA}$ ,  $R_{\text{FF}}=2.44275\text{\AA}$ ,  $\angle\text{HFH}=136^\circ$ ; <sup>d</sup>  $R_{\text{HF}}=0.92\text{\AA}$ ,  $R_{\text{FF}}=2.49\text{\AA}$ ,  $\angle\text{HFH}=180^\circ$ ; <sup>e</sup> Neutron diffraction study at 4K [Ref. 15].

TABLE 7: Lattice Energies and Charges for Three-dimensional HF Crystal Calculated by Pseudo-Lattice Method Including Coulomb Lattice Sum<sup>e</sup>

Model		Lattice energy (kcal/mol)	Net charge for atom F (e)
Polar structure	(HF) <sub>4</sub> -zig-zag chain <sup>b</sup>	8.76	-0.2696
	(HF) <sub>16</sub> -three-dimensional pseudo-lattice <sup>c</sup>	9.14	-0.2701
Nonpolar	(HF) <sub>4</sub> -zig-zag chain <sup>b</sup>	10.80	-0.2918
	(HF) <sub>16</sub> -three-dimensional pseudo-lattice <sup>c</sup>	11.19	-0.2923

<sup>a</sup> Coulomb lattice sum is calculated up to  $25 \times 19 \times 15$  (a×b×c) unit cell (about 80Å sphere); <sup>b</sup> Only nearest neighbour are included in the calculation; <sup>c</sup> Calculation of interactions up to 10 members of surrounding neighbours.

theoretical and experimental proton arrangement has been discussed by crowe and Santry.<sup>18</sup>

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