

# An Intermolecular Potential Function for the Hydrogen Fluoride Dimer from ab Initio 6-31G Computations<sup>1</sup>

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**Abstract:** An intermolecular potential function for the hydrogen fluoride dimer has been determined from ab initio molecular orbital calculations with the extended 6-31G basis set. Interaction energies for 250 configurations of (HF)<sub>2</sub> were fit via a statistical procedure to a simple analytic expression that contains 9 adjustable parameters and 16 terms in  $r^{-1}$ ,  $r^{-3}$ ,  $r^{-6}$ , and  $r^{-12}$ , where  $r$  represents internuclear distances. The standard deviations between the 12-6-3-1 potential and the 6-31G interaction energies ( $\Delta E$ ) are 0.49 kcal/mol for the 233 points in the range  $-7.5 < \Delta E < 10$  kcal/mol and 0.38 kcal/mol for the 131 points with  $\Delta E < 0$ . The high quality of the fit and the simplicity of the potential are a great improvement over earlier work in this area. The potential is suitable for use in Monte Carlo simulations of liquid HF and superacid solutions, and in molecular dynamics calculations.

The water and hydrogen fluoride dimers have been widely studied using ab initio molecular orbital techniques owing to their importance as key examples of hydrogen bonding.<sup>2</sup> The analysis of the water dimer has proceeded to the point where accurate intermolecular potential functions are now available for the system.<sup>3</sup> The functions were obtained by Clementi and co-workers using interaction energies computed by ab initio methods at several levels of sophistication including single determinant and configuration interaction calculations.<sup>3</sup> Several investigators subsequently applied the potential functions in Monte Carlo simulations of liquid water with great success in both reproducing experimental properties of the liquid and in providing a fascinating description of the liquid's structure.<sup>4</sup> Attempts have also been made at obtaining an intermolecular potential function for the hydrogen fluoride dimer.<sup>5</sup> The most intensive effort was that of Schaefer et al.,<sup>5b</sup> who performed ab initio calculations at 294 points on the (HF)<sub>2</sub> surface. However, Schaefer and Alexander both found it difficult to fit the computed interaction energies to a functional form.<sup>5b,c</sup> The conclusions were that the angle variation of 45° in the grid used by Schaefer et al. was too crude and that the cost of a fine enough grid might be prohibitive.<sup>5b,c</sup>

It is reported here that an easily evaluated function for (HF)<sub>2</sub> has been determined from 250 ab initio calculations employing the extended, split 6-31G basis set of Pople et al.<sup>6</sup> Although the computed geometry of the dimer and dimerization energy are in good agreement with experiment, evidence is discussed which indicates that these values for the dimerization energy are ca. 30% too negative. Inclusion of polarization functions in the basis set would improve the results; however, this has not been attempted at present because it was found that a large number of points on the (HF)<sub>2</sub> potential surface need to be considered to obtain a reasonable potential function. Further enhancement of the computations by estimating correlation energy corrections does not appear to be essential owing to the fortuitous cancellation of inter- and intramolecular correlation effects for the HF dimer.<sup>7</sup> The simplicity of the potential function reported here and the high quality of the fit to the 6-31G energies render the function or a scaled version suitable for initial use in Monte Carlo simulations of liquid HF and superacid solutions and in molecular dynamics calculations.

## Computational Procedure

The potential function was generated by a statistical procedure that has been used previously by Beveridge et al. for water-formaldehyde and water-methane.<sup>8</sup> Briefly, the method consists of fitting a potential function to the computed energies of a randomly generated, initial set of dimer configurations.

The function's predictive ability is then tested for a new sample of computed configurations. A new fit is made to the expanded data base and the process is repeated until the predictive ability converges.

The geometries for (HF)<sub>2</sub> were randomly selected based on the coordinate system shown in Figure 1. The FF distance,  $R$ , was permitted to range from 2.0 to 4.5 Å while  $\theta$  and  $\phi$  varied from  $-90$  to  $90^\circ$  and  $\Psi$  could have values  $0-180^\circ$ . The limits on  $R$  avoid the high-energy inner region of the surface and the uninteresting flat area as  $R \rightarrow \infty$ , while the first and second solvation sheaths are still sampled. The angular limits are sufficient to permit all possible orientations of the dimer. The covalent H-F distance was held fixed at the experimental value for the monomer (0.917 Å).<sup>9</sup> All configurations were produced with a random number generator. The interaction energies were determined using the 6-31G basis and the GAUSSIAN/74 computer program<sup>10</sup> on the CDC/6500 system at Purdue.

The function selected to fit the 6-31G energies is a 12-6-3-1 potential which contains terms in  $r^{-1}$ ,  $r^{-3}$ ,  $r^{-6}$ , and  $r^{-12}$  where  $r$  represents the FF, FH, HF, and HH distances in the dimer. The function is given in eq 1 and contains nine adjustable parameters,  $Q^2$  and the  $b$ ,  $c$ , and  $d$  sets for FF, FH, and HH interactions. Although little physical significance should be attached to the functional form and computed parameters, the power series suggests that Coulomb, dipole, and short-range interactions are taken into account.

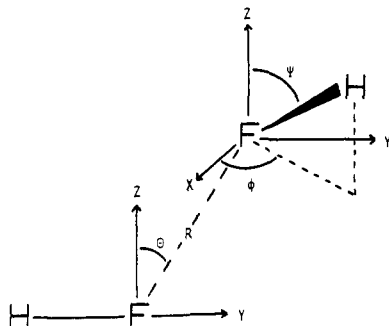
$$\begin{aligned} \Delta E (12-6-3-1) = & Q^2 \left( \frac{1}{r_{FF}} - \frac{1}{r_{FH}} - \frac{1}{r_{HF}} + \frac{1}{r_{HH}} \right) \\ & + \frac{b_{FF}}{r_{FF}^3} - \frac{1}{2}(b_{FF} + b_{HH}) \left( \frac{1}{r_{FH}^3} + \frac{1}{r_{HF}^3} \right) + \frac{b_{HH}}{r_{HH}^3} \\ & + \frac{c_{FF}}{r_{FF}^6} + c_{FH} \left( \frac{1}{r_{FH}^6} + \frac{1}{r_{HF}^6} \right) + \frac{c_{HH}}{r_{HH}^6} \\ & + \frac{d_{FF}}{r_{FF}^{12}} + d_{FH} \left( \frac{1}{r_{FH}^{12}} + \frac{1}{r_{HF}^{12}} \right) + \frac{d_{HH}}{r_{HH}^{12}} \quad (1) \end{aligned}$$

A few comments need to be made concerning the choice and form of the 12-6-3-1 function. First, pseudo-lone-pairs were not placed on fluorine in contrast to the treatment of oxygen in the methane-water and formaldehyde-water potentials.<sup>8</sup> The higher symmetry of HF than water or formaldehyde causes problems with rotational invariance if three lone pairs are assigned to fluorine. For the oxygen compounds, the lone pairs do not create or destroy any symmetry elements, while for HF the  $C_\infty$  axis is reduced to  $C_3$ . Thus, once one HF is fixed, the energy would vary with rotation about the  $C_3$  axis of the second HF, which is physically improper. Second, for modeling liquids it is crucial that the contributions to the en-

Table I. Standard Deviations for Fitting the ab Initio 6-31G Energies of (HF)<sub>2</sub> to the 12-6-3-1 Potential

cycle	points in data base	standard deviations, kcal/mol					
		$\sigma_{<10}$		$\sigma_{<0}$		$\sigma_{<-2}$	
		initial	test	initial	test	initial	test
1	150	0.48	0.41	0.43	0.51	0.56	0.62
2	175	0.46	0.55	0.44	0.13	0.56	0.01 <sup>a</sup>
3	200 <sup>b</sup>	0.47	0.57	0.42	0.57	0.57	0.74
4	225 <sup>c</sup>	0.47	0.54	0.42	0.54	0.56	0.54
5	250	0.49		0.38		0.48	

<sup>a</sup> Only one point in sample. <sup>b</sup> Points 201–225 all have  $\Delta E < 0$ . <sup>c</sup> Points 226–250 all have  $\Delta E < -2$ .

Figure 1. Coordinate system used for 6-31G calculations on (HF)<sub>2</sub>.

ergy from distant molecules average out to zero; otherwise the energy will be dependent on the sample size and will tend to  $\pm\infty$ . This condition requires that the integral of  $4\pi r^2 \Delta E(r)$  must be zero as  $r$  goes to  $\infty$ . Thus, there is no difficulty with terms in  $r^{-n}$  for  $n \geq 4$ ; however, the terms with  $n = 1-3$  must be balanced to cancel for large  $r$ . This is achieved in eq 1 for the  $r^{-1}$  terms by only using the one parameter,  $Q^2$ , and by requiring that  $b_{FF} + b_{HH} + 2b_{FH} = 0$  for the  $r^{-3}$  terms.

Other considerations are also critical in selecting a potential function. No extraneous minima are permissible and for (HF)<sub>2</sub> it is important that acyclic structures have lower energy than cyclic forms. Furthermore, to facilitate simulations of condensed media, it is desirable to avoid exponential terms in the potential. As a consequence of these restraints, dozens of functions were considered before the final potential was accepted.

### Minimum Energy Form of (HF)<sub>2</sub>

The most obvious tests of the soundness of the 6-31G calculations are their prediction of the geometry and dimerization energy of (HF)<sub>2</sub>. Allen et al.<sup>12a</sup> and Kollman<sup>12b</sup> have recently reviewed theoretical studies of hydrogen-bonded systems. The variation in dimerization energies for (HF)<sub>2</sub> that they note is substantial, ranging from  $-3$  to  $-8$  kcal/mol. As a general trend, the more sophisticated ab initio calculations give the higher dimerization energies. Thus, Lischka's calculations including various treatments for the correlation energy predict the dimerization energy to be  $-3.3$  to  $-3.5$  kcal/mol.<sup>7</sup> In contrast, the experimental results are in better agreement with the less sophisticated calculations. A variety of experiments have been performed on gaseous HF, as reviewed by Vanderzee and Rodenburg,<sup>13</sup> with the conclusion that the enthalpy of dimerization is  $-6.8 \pm 1$  kcal/mol.<sup>13</sup> Theoreticians have, however, been in the habit of reporting the value as  $-6 \pm 1.5$  kcal/mol. The only support for the lower limit comes from Smith's IR study,<sup>14</sup> which yields  $-6 \pm 1$  kcal/mol, while most experimental determinations have been near  $-7$  kcal/mol.<sup>13,15</sup> The dichotomy between refined theory and experiment is disturbing. There are no obvious explanations, though questions can be raised concerning the reliability of the experiments due to complications from HF tetramer formation in the gas

phase. The theoretical treatments of the correlation energy and geometry optimizations are also suspect.

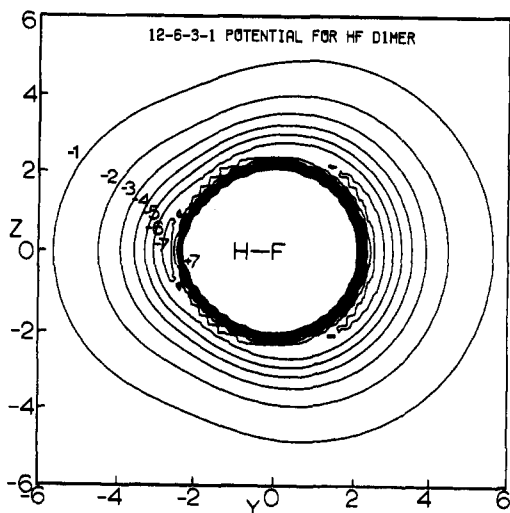
The minimum energy of (HF)<sub>2</sub> was determined with 6-31G calculations assuming that the experimental H-F bond length for the monomer<sup>9</sup> is retained in the dimer and the hydrogen bond, i.e. F-H...F fragment, is linear. The optimized F-F distance is then 2.714 Å and the H...F-H angle is 138°. These values compare well with the experimental estimates of 2.79 Å and 110–120°.<sup>17</sup> The computed dimerization energy is  $-7.3$  kcal/mol. Following Kollman's example,<sup>12b</sup> the energy can be converted to an enthalpy change of ca.  $-6.9$  kcal/mol, which is in excellent agreement with the experimental results. It may be argued that the accord indicates that the experimental value is too high because 6-31G and 4-31G calculations are known to overemphasize the polarity of molecules<sup>18</sup> and this would presumably cause dipole-dipole interactions to be too attractive. However, the same logic would claim that 4-31G calculations should poorly estimate rotational barriers, which is not true.<sup>20</sup>

At this time, the 6-31G calculations which are the basis for the potential function reported here are in good agreement with the available experimental data for the geometry and dimerization energy of the HF dimer. More definitive work in this area is highly desirable. This is emphasized by the fact that Monte Carlo simulations of liquid HF with the unscaled 12-6-3-1 potential yield energies of vaporization that are too high by ca. 40% (vide infra).<sup>21</sup>

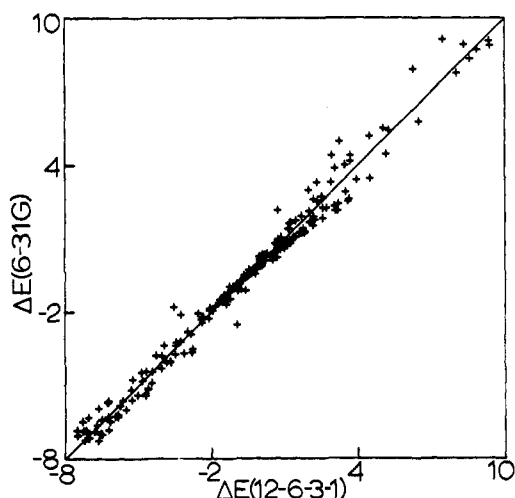
### Results for the Potential Function

The parameters for the potential were obtained from a standard nonlinear least-squares program. For Monte Carlo simulations, it is particularly important to have the low-energy regions of the surface well represented. To help achieve this goal, all points with  $\Delta E$  (6-31G) greater than 10 kcal/mol were discarded in the fitting. This amounted to less than 10% of the configurations. Furthermore, a weighting function,  $w_i = 1 + \alpha \exp(-(\Delta E_i - \Delta E_0)/kT)$ , was used in the least-squares procedure to enhance the fit for the low-energy points. The same function was used by Beveridge et al.<sup>8</sup> For the present purposes,  $\Delta E_0$  and  $kT$  were set at  $-8.0$  and  $0.6$  kcal/mol, respectively. The adjustable parameter,  $\alpha$ , was chosen to be 130. Increasing  $\alpha$  beyond this value yielded little benefit for the low-energy points and considerable deterioration in the fit for points with  $\Delta E > 0$ . The statistics for the fitting are shown in Table I. The standard deviations,  $\sigma_{<\chi}$ , refer to all configurations with interaction energies (6-31G) less than  $\chi$  kcal/mol.

After the first set of parameters was determined for an initial group of 150 points, test sets of 25 points each were treated. The predictive ability of the function for the first test set is respectable, i.e., the test and initial  $\sigma$ 's are similar. Increasing the size of the data base to 175 points enhanced the predictive ability of the function to the point where the size of the test sample appears statistically too small because two  $\sigma$ 's for the test set are smaller than the  $\sigma$ 's for the initial function. The  $\sigma_{<-2}$  for the test set of 0.01 is similarly too optimistic because



**Figure 2.** Energy surface for planar  $(\text{HF})_2$  constructed from the 12-6-3-1 potential including points with 6-31G interaction energies less than 10 kcal/mol. The orientation for the second hydrogen is chosen to minimize the energy for each positioning of the second fluorine in the plane. The outermost contour is at  $-1$  kcal/mol and the contour increment is  $\pm 1$  kcal/mol. Innermost contours (at high energy) have been removed for clarity. Distances are in ångströms.

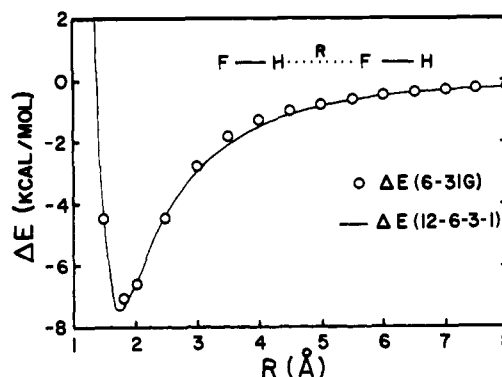


**Figure 3.** Comparison of the dimerization energies from the 6-31G calculations and the 12-6-3-1 potential for configurations with  $\Delta E < 10$  kcal/mol.

there was only one point in the set in the  $\Delta E < -2$  range. The overall statistics for the first 200 points are, however, clearly acceptable. The  $\sigma_{<10}$  of 0.5 for the 9-parameter, 12-6-3-1 function can be compared with the  $\sigma$ 's of 1.2–2.5 kcal/mol for the ca. 30-parameter functions of Schaefer and Alexander.<sup>5b,c</sup>

Analysis of the function after 200 points showed, however, that cyclic dimers were being favored over acyclic forms. To rectify this problem, 10 randomly chosen cyclic structures and 15 dimers with linear hydrogen bonds were used in the next test set (201–225). To further ensure that the function was representing the low-energy regions well, 25 final points (226–250) with bent geometries were randomly generated in this area with  $2.5 \text{ \AA} < R < 3.0 \text{ \AA}$ ,  $30^\circ < \theta < 90^\circ$ ,  $210^\circ < \psi < 270^\circ$ , and  $\phi = 90^\circ$ . In view of the convergence of the  $\sigma$ 's and the constancy of the parameter values between interactions ( $\pm 5\%$ ), further computation was not called for. The final parameter values are given in Table II as derived from the 250 points.

The 12-6-3-1 function is illustrated by the contour map in Figure 2. The map is for planar configurations of  $(\text{HF})_2$ . The



**Figure 4.** Comparison of dimerization energies from 6-31G calculations and the 12-6-3-1 potential for linear  $(\text{HF})_2$ .

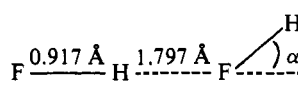
**Table II.** Final Values for Parameters in the 12-6-3-1 Potential Function for  $(\text{HF})_2$  Fit to ab Initio 6-31G Energies

	parameter		
	FF	FH	HH
$Q^2$	104.025		
$b$	13.8785		-41.4783
$c$	-563.463	42.3605	59.3664
$d$	114169.	408.745	381.556

indicated HF is held fixed and for each location of the second F, the orientation of its H was then optimized to yield the lowest energy. The figure may be interpreted to yield a hard sphere radius of ca. 1.8 Å for HF as a point dipole. However, the asymmetry of the dipole is clear from the potential map. The value of  $Q^2$  for the 12-6-3-1 function, 104.025, can be translated to a charge of  $\pm 0.56$  electron for hydrogen and fluorine. The consequent estimate of the dipole moment for HF from the point charges is 2.45 D. The coupling between the  $r^{-1}$  and  $r^{-3}$  terms in the potential makes such calculations far from rigorous; however, the accord with the 6-31G value for the dipole moment (2.30 D) is reasonable.<sup>18</sup>

Further indications of the quality of the fit for the 12-6-3-1 function can be obtained from Figures 3 and 4. The first illustration compares the computed energies for the dimer configurations with  $\Delta E < 10$  kcal/mol using the 6-31G basis and the 12-6-3-1 potential. The figure also indicates the distribution of energies for the dimer configurations. The distribution is fairly uniform, though it would appear much less so if the final 50 points with low energy had not been included. The region between  $\pm 2$  kcal/mol is the most heavily represented. Figure 4 reveals the variation of energy with distance for linear configurations of  $(\text{HF})_2$  as computed with the 6-31G basis and the 12-6-3-1 function. The agreement is excellent. In addition, the long-range nature of the dipole-dipole interaction is apparent in Figure 4.

One aspect of the 12-6-3-1 function that was initially disturbing is its prediction that the minimum energy form for  $(\text{HF})_2$  is linear. As noted above, ab initio calculations<sup>5,12</sup> and experiment<sup>17</sup> predict a geometry bent  $40$ – $70^\circ$ . Since the  $\sigma$ 's for the function are small, it is clear that the distortion in question has a low force constant. This is verified by the 6-31G results in Table III which were performed at the 6-31G optimized value of  $R$ , 2.714 Å (experiment, 2.79 Å<sup>17</sup>), assuming a linear F-H...F fragment. It is found that varying  $\alpha$  from  $0^\circ$  (fully linear geometry) to the minimum value at  $42.1^\circ$  requires less than 0.3 kcal/mol which is within  $\sigma_{<-2}$ . It is unlikely that this subtle effect<sup>20</sup> can be reproduced by simple models like the 12-6-3-1 potential. Furthermore, since it is such an energetically small effect, it is not anticipated to have significant consequences for dynamics and Monte Carlo studies at normal temperatures.

**Table III.** Ab Initio 6-31G and Empirical Dimerization Energies (kcal/mol) vs.  $\alpha$  for (HF)<sub>2</sub>


$\alpha$ , deg	$-\Delta E$ (6-31G)	$-\Delta E$ (12-6-3-1)
0.0	7.0462	7.5006
15.0	7.1178	7.4258
30.0	7.2714	7.1944
39.1	7.3354	6.9686
41.1	7.3403	6.9093
42.1	7.3408 <sup>a</sup>	6.8783
43.1	7.3404	6.8462
45.0	7.3355	6.7829
60.0	7.0620	6.1444
75.0	6.1722	5.1903
90.0	4.3764	3.7351

<sup>a</sup>  $E_{\text{TOT}} = -199.978\ 512$  au. Dimerization energies ( $\Delta E$ ) in kcal/mol.

In summary, the potential function that is presented here is suitable for preliminary studies of liquid HF using Monte Carlo and molecular dynamics techniques. The bases of this conclusion are the facts that (1) the function has a simple form and is well behaved; (2) the ab initio 6-31G calculations upon which the potential are based yield a geometry and dimerization energy for (HF)<sub>2</sub> that are in agreement with the available experimental data; (3) correlation energy effects are reported to be relatively unimportant on the HF dimer surface;<sup>7</sup> and, (4) the standard deviations of the fit for the potential to the 6-31G energies are small. A series of Monte Carlo simulations of liquid HF using the 12-6-3-1 potential has recently been completed in this laboratory.<sup>21</sup> For a sample size of 64 HF<sub>s</sub>, the computed energy of vaporization for liquid HF going to the ideal gas at 20 °C is 9.7 kcal/mol. This result is considerably larger than the experimental value, 6.7 kcal/mol,<sup>13</sup> which confirms the concern for the experimental dimerization energy. Scaling the 12-6-3-1 potential by 0.75 yields a computed  $\Delta E_{\text{vap}}$  in good agreement with experiment for samples of 64 or 108 HF<sub>s</sub>. After consideration of three-body effects, these initial results suggest a value of 5.0–5.5 kcal/mol for the true dimerization energy of (HF)<sub>2</sub>.<sup>21</sup> Furthermore, the scaled potential is recommended for additional studies of liquid HF. Such empirical adjustment of a quantum mechanical potential finds precedent in Clementi's work on the water dimer in which the intramolecular correlation energy was neglected post facto.<sup>3a,4a</sup>

**Note Added in Proof.** Professor McDonald has kindly provided a preprint of a paper (M. L. Klein, I. R. McDonald, and

S. F. O'Shea, *J. Chem. Phys.*, in press) describing the successful development of an intermolecular potential function for (HF)<sub>2</sub> from the ab initio results of Schaefer et al.<sup>5b</sup> The quality of the fit is similar to the results reported here; however, the functional form employed by McDonald et al. is substantially more complex than eq 1.

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