

# Ab Initio Calculations on Intermolecular Forces. III. Effect of Electron Correlation on the Hydrogen Bond in the HF Dimer

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**Abstract:** The influence of electron correlation on the linear hydrogen bond in F-H...F-H is studied in the frameworks of the IEPA-, CEPA-, and PNO-CI approaches. Due to compensating effects of the intrasystem and the intersystem correlation energy we find a relatively small net effect of the total correlation energy on the interaction energy, the F-F distance, and the intermolecular vibration. The following  $R_{FF}$  and  $\Delta E$  values (in au) result in the SCF-, IEPA-, CEPA-, and PNO-CI approach respectively: 5.48, -0.0055; 5.47, -0.0054; 5.46, -0.0056; 5.43, -0.0056. The intermolecular stretching vibration of the H-F bond involved in the hydrogen bond is hardly affected in comparison with the isolated HF molecule. The experimentally observed shifts of 10-15% in the absorption frequencies of infrared spectra are thus attributed to higher polymers, in agreement with previous theoretical and experimental works.

In the last few years *ab initio* SCF calculations with large basis sets have been reported for several types of intermolecular potentials and relatively large systems. For a recent review of these works, see, e.g., Kollman and Allen<sup>2a</sup> and Schuster.<sup>2b</sup> A substantially larger computational effort, however, is necessary to properly take into account the electron correlation. The first successful applications of CI methods were achieved for van der Waals interactions between neutral atoms.<sup>3,4</sup> Improvement of the techniques for the computation of electron correlation energies as well as the existence of high-speed computers made it possible to treat larger systems, including systems of polar molecules.<sup>5-8</sup> Because of the importance of hydrogen bonding in chemical processes a detailed calculation of electron correlation effects is desirable. In the present work we chose the HF dimer as a model system for our studies.

## (1) Method of Calculation

The method of calculation for the correlation energy is based on the electron pair approach.<sup>9-11</sup> The essential features of the procedure used in this work were developed by Kutzelnigg, Ahlrichs, and coworkers.<sup>12-14</sup>

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(2) (a) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972); (b) P. Schuster, "The Hydrogen Bond," P. Schuster, G. Zundel, and C. Sandorfy, Ed., North-Holland Publishing Co., Amsterdam, in press.

(3) W. Kutzelnigg and M. Gélus, *Chem. Phys. Lett.*, **7**, 296 (1970).

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(5) P. Kollman, C. F. Bender, and St. Rothenberg, *J. Amer. Chem. Soc.*, **94**, 8016 (1972).

(6) A. Meunier, B. Levy, and G. Berthier, *Theor. Chim. Acta*, **29**, 49 (1973).

(7) (a) H. Lischka, *Chem. Phys. Lett.*, **20**, 448 (1973); (b) H. Lischka, *Chem. Phys.*, **2**, 191 (1973).

(8) W. Meyer, W. Jakubetz, and P. Schuster, *Chem. Phys. Lett.*, **21**, 97 (1973).

(9) O. Sinanoglu, *Advan. Chem. Phys.*, **6**, 315 (1964).

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(11) W. Kutzelnigg, "Topics in Current Chemistry," Vol. 41, Springer-Verlag, New York, N. Y., 1973, pp 31-73.

(12) W. Kutzelnigg, *Theor. Chim. Acta*, **1**, 327 (1963).

(13) R. Ahlrichs and W. Kutzelnigg, *J. Chem. Phys.*, **48**, 1819 (1968).

(14) (a) M. Jungen and R. Ahlrichs, *Theor. Chim. Acta*, **17**, 339 (1970); (b) R. Ahlrichs and F. Driessler, in preparation for publication.

We do not intend to present details of the method here, since they will be described elsewhere.<sup>15,16</sup>

The successive steps in the course of our computations follow. (a) A conventional SCF calculation. (b) The canonical orbitals are transformed to localized ones according to the criterion of Boys.<sup>17</sup> We chose three different kinds of localization for the isolated hydrogen fluoride ( $\alpha$ - $\gamma$ ) and one for the dimer: ( $\alpha$ ) the canonical orbitals remain unchanged, ( $\beta$ ) the  $\sigma$  orbitals of the valence shell only are used for localization ("localization A"), ( $\gamma$ ) all orbitals of the valence shell are transformed ("localization B"), ( $\delta$ ) a "left-right" localization is performed in the case of (HF)<sub>2</sub>; i.e., no mixing of  $\sigma$  and  $\pi$  orbitals is allowed during the localization process ("localization C"). (c) For each pair of orbitals  $\phi_R$  and  $\phi_S$  ( $R = S$  and  $R \neq S$ ), pair natural orbitals (PNO's) are determined in the effective field of the remaining electrons. (d) We then calculate the correlation energy in the framework of three different approaches: the independent electron pair approach (IEPA),<sup>9-11</sup> the coupled electron pair approach (CEPA),<sup>18</sup> and the pair natural orbital CI approach (PNO-CI).<sup>18</sup>

The correlation energy is defined in the framework of IEPA and CEPA as the sum of individual electron pair contributions  $\epsilon_{RS}$ .

$$E_{\text{corr}}^{\text{IEPA}} = \sum_{R \leq S} \epsilon_{RS}^{\text{IEPA}} \quad (1)$$

$$E_{\text{corr}}^{\text{CEPA}} = \sum_{R \leq S} \epsilon_{RS}^{\text{CEPA}} \quad (2)$$

The PNO-CI approach furnishes an upper bound to the exact energy, since it represents a conventional CI calculation with optimized doubly excited configurations. Additional "unlinked cluster" type substitutions are taken into account in an approximate way in the IEPA and CEPA methods. In the latter, more

(15) R. Ahlrichs, *Theor. Chim. Acta*, **33**, 157 (1974).

(16) R. Ahlrichs, F. Driessler, W. Kutzelnigg, H. Lischka, and V. Staemmler, in preparation for publication.

(17) S. F. Boys, "Quantum Theory of Atoms, Molecules and the Solid State," P. O. Löwdin, Ed., Interscience, New York, N. Y., 1967, p 253.

(18) W. Meyer, *J. Chem. Phys.*, **58**, 1017 (1973).

Table I. Basis Sets

No.	Fluorine				Hydrogen			
	Primitive set	Contraction	Exponent	Ref	Primitive set	Contraction	Exponent	Ref
1	8s	(41111)		<i>a</i>	4s 1p	(211)	0.75	<i>b</i> 16
	4p	(211)		<i>a</i>				
	1p		0.1					
	1d		1.6					
2	8s	(41111)		<i>a</i>	The same as for basis 1			
	4p	(211)		<i>a</i>				
	1p		0.1					
	2d	(11)	1.6, 0.15					
3	8s	(41111)		<i>a</i>	The same as for basis 1			
	4p	(211)		<i>a</i>				
	1p		0.1					
	3d	(111)	1.6, 0.3, 0.1					
4	11s	(5111111)		<i>c</i>	6s 1p	(3111)	0.75	<i>b</i> 16
	7p	(4111)		<i>c</i>				
	2d	(11)	1.6, 0.15					
	11s	(5111111)		<i>c</i>				
5	7p	(4111)		<i>c</i>	The same as for basis 4			
	3d	(111)	1.6, 0.3, 0.1					

<sup>a</sup> S. Huzinaga, "Approximate atomic functions I," University of Alberta, Canada, 1971. <sup>b</sup> S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).  
<sup>c</sup> C. Salez and A. Veillard, *Theor. Chim. Acta*, **11**, 441 (1968).



Figure 1. The linear arrangement of the HF dimer discussed in this work.

sophisticated approach, coupling terms between substitutions of different pairs, which are neglected in IEPA, are taken into consideration. For all three approaches only the valence shell correlation energy is calculated.

The total energy  $E_{\text{tot}}$  is obtained as the sum of the SCF energy  $E_{\text{SCF}}$  and the respective correlation energies  $E_{\text{corr}}$ . For the calculation of the HF dimer we need some extra definitions which will be used in section 3b. Since  $E_{\text{corr}}^{\text{PNO-CI}}$  has the wrong asymptotic behavior for  $n \rightarrow \infty$  ( $n$  is the number of electrons),<sup>19</sup> we relate the energy differences in the framework of PNO-CI to  $E_{\text{corr}}^{\text{PNO-CI}}(\text{F-H} \cdots \text{F-H})$  at infinite separation. No such problems occur in the IEPA and CEPA treatment.

In addition to the total correlation energy  $E_{\text{corr}}^{\text{tot}}$  we compute separately the intrasystem correlation energy  $E_{\text{corr}}^{\text{ias}}$  and the intersystem correlation energy  $E_{\text{corr}}^{\text{irs}}$ .  $E_{\text{corr}}^{\text{ias}}$  is here defined as the correlation energy due to the intrapair contributions together with those interpair interactions which belong to the same subsystem. For  $E_{\text{corr}}^{\text{irs}}$  only the interpair interaction between the two HF molecules is considered. The sum of  $E_{\text{corr}}^{\text{ias}}$  and  $E_{\text{corr}}^{\text{irs}}$  is not equal to  $E_{\text{corr}}^{\text{tot}}$  for CEPA and PNO-CI because additional coupling terms between the intrasystem and the intersystem pairs change the resultant total correlation energy. The definitions are somewhat arbitrary; for our purpose we could equally well have taken in CEPA the sum of the respective pair energies which add up to  $E_{\text{corr}}^{\text{tot}}$ . The specific choice, however, has no influence on our interpretations in section 3b.

In the discussion of section 3 we interpret the changes of the correlation energy in the HF dimer in terms of the electronic properties of the isolated hydrogen fluo-

ride. Thus our intention is not to calculate very accurate values of properties like the dipole moment or the polarizability of the HF monomer but to obtain a, as much as possible, balanced description of the correlation effects for HF as well as for  $(\text{HF})_2$ . At present a treatment of such a large system as the HF dimer is tractable at the CEPA level with explicit consideration of doubly substituted configurations only. We do not include, therefore, any singly excited functions although single excitations have been important for the calculation of dipole moments.<sup>20</sup>

## (2) Basis Sets and Geometries

The Gaussian basis sets used in this work are collected in Table I. p and d functions were simulated by appropriate linear combinations of lobes which are shifted from the origin in a way described by Ahlrichs and Driessler.<sup>21</sup> We took the exponent 1.6 for the d function of F and that for the p function on H from ref 16. The exponents of the remaining d's on F were optimized with the smaller basis sets 1-3 with respect to the dipole moment and the polarizability of the isolated HF molecule (see also section 3a). We used these values without any change also for the larger basis sets 4 and 5. The calculations of the HF dimer were performed with basis 4 only.

Previous SCF calculations<sup>22,23</sup> have indicated that the most stable geometric arrangement is a bent structure. The difference in energy to the linear arrangement, however, is exceedingly small. Since we wanted to discuss only the general features of the correlation energy, we restricted ourselves to linear structures (Figure 1). Thus the computation time (one point on the energy surface with inclusion of the electron correlation energy took approximately 5 hr CPU time on a Univac 1108) is reduced significantly, because the higher symmetry ( $C_{\infty v}$  vs.  $C_s$ ) of the linear geometry reduces

(20) (a) F. Grimaldi, A. Lecourt, and C. Moser, *Int. J. Quantum Chem., Symp.*, **1**, 153 (1967); (b) C. F. Bender and E. R. Davidson, *J. Chem. Phys.*, **49**, 4222 (1968).

(21) R. Ahlrichs and F. Driessler, *Chem. Phys. Lett.*, **23**, 571 (1973).

(22) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970).

(23) G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.*, **6**, 419 (1970).

(19) See, e.g., H. Primas, "Modern Quantum Chemistry," Vol. 2, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, pp 45-74.

considerably the number of integrals as well as the number of pair interactions which have to be calculated.

### (3) Results and Discussion

The interaction energy between two charge distributions at large distances may be discussed in terms of the Coulomb, the polarization, and the dispersion energies. We therefore present at first the results for the dipole moment  $\mu$  and the polarizability  $\alpha$  of the isolated HF. The effects of electron correlation on  $\mu$  and  $\alpha$  will help us as far as the interpretation of the potential energy curve of the HF dimer is concerned.

**(a) The Dipole Moment and the Polarizability of HF.** In order to obtain the dipole moment and the polarizability we do not perform a perturbation calculation explicitly but compute the total energy of the system in the presence of a small but finite and constant electric field  $F$ . This procedure was developed by Cohen and Roothaan at the SCF level<sup>24</sup> and is here extended to calculations that include correlation energy. The energy difference  $\Delta E = E(F) - E(F = 0)$  is expanded as a power series in  $F$  given by the following expression in the notation of Buckingham.<sup>25</sup>

$$\Delta E = -\sum_{\alpha} \mu_{\alpha} F_{\alpha} - \frac{1}{2} \sum_{\alpha, \beta} \alpha_{\alpha\beta} F_{\alpha} F_{\beta} - \dots \quad (3)$$

$\Sigma_{\alpha}$  and  $\Sigma_{\alpha, \beta}$  indicate summation over the three Cartesian components. The field strength  $|F|$  is chosen so small that higher order terms in eq 3 do not contribute but are large enough to guarantee numerical significance. A typical value is 0.01 au. Different field strengths are used to allow the evaluation of  $\mu$  and  $\alpha$  from eq 3.

It has been noted<sup>16, 18, 26</sup> that the electron correlation treatment employed in this work is not invariant with respect to unitary transformations of the occupied SCF orbitals. We tested possible effects of such an orbital transformation on  $\mu$  and  $\alpha$  by using the differently localized SCF orbitals described in section 1.

In Table II the results obtained with basis 2 are col-

Table II. The Effect of Localization on the Dipole Moment  $\mu$  and the Polarizability  $\alpha$  in Calculations That Include Electron Correlation<sup>a</sup>

	Canonical SCF orbitals	Localization A	Localization B
$\mu$ IEPA	0.682	0.703	0.701
CEPA	0.718	0.719	0.721
PNO-CI	0.727	0.726	0.728
$\alpha_{  }$ IEPA	6.34	6.14	6.17
CEPA	5.93	5.88	5.82
PNO-CI	5.83	5.79	5.74

<sup>a</sup> Basis set no. 2 is used and all values are given in au.

lected. The difference between the IEPA values for the canonical orbitals and those for localization A are reduced significantly by the CEPA and PNO-CI treatment and agree with the latter two methods satisfactorily for all three choices of the localization.

Table III shows several properties of HF at  $R_{\text{HF}} = 1.733$  au calculated with different basis sets. With the

(24) H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.*, **43**, S34 (1965).

(25) A. D. Buckingham, *Discuss. Faraday Soc.*, **40**, 232 (1965).

(26) C. F. Bender and E. R. Davidson, *Chem. Phys. Lett.*, **3**, 33 (1970).

largest basis sets 4 and 5 our computed  $E_{\text{SCF}}$  is near the Hartree-Fock limit ( $-100.0703$  au<sup>27</sup>) and we obtain in CEPA approximately 65–70% of the valence shell correlation energy. More important for the calculation of interaction energies than the absolute energy values is, however, the fact that we need sufficient flexibility in the basis to reproduce as well as possible the charge distribution and its changes due to polarization effects. We take for a test of our basis the dipole moment and the polarizability as representatives.

The dipole moment is lowered significantly at the SCF level by passing from basis 1 to basis 2. The Hartree-Fock limit of  $\mu$  is 0.764 au.<sup>28</sup> The electron correlation shifts the dipole moment in the correct direction. The effect due to double excitations is much larger here than it was found *e.g.*, for CO<sup>20a</sup> and LiH.<sup>20b</sup> As already observed in other cases,<sup>18, 29</sup> IEPA tends to overcompensate the SCF error; the dipole moment in CEPA happens to be very close to the experimental result for the basis sets 2–5.

There is a distinct jump between the values of the polarizability between basis 1 and 2. The additional d function with exponent 0.15 improves drastically  $\alpha_{\perp}$  and to a somewhat smaller extent  $\alpha_{||}$ . Our SCF values for the largest basis 5 agree well with the coupled Hartree-Fock results obtained by Stevens and Lipscomb<sup>30</sup> ( $\alpha_{||} = 5.80$  au,  $\alpha_{\perp} = 4.20$  au). Again IEPA overestimates the changes due to electron correlation. The experimental values for the polarizability are certainly less reliable than those for the dipole moment, thus making a comparison of our calculation with experiment more difficult.

The  $d_{\delta}$  functions with exponent 0.15 were found to contribute insignificantly to the correlation corrections of  $\mu$  and  $\alpha$  and were, therefore, omitted in the calculations on the HF dimer.

**(b) The HF Dimer.** From the experience with the calculations on the hydrogen fluoride molecule we chose basis set 4 for the calculation of  $(\text{HF})_2$ . In addition to the electrostatic effects at large distances, overlap contributions become important at intermediate separations. We believe that our basis has sufficient flexibility to also take into account these effects. The localization procedure C (see section 1) is employed for all calculations concerning the HF dimer.

The results of our computations are presented in Tables IV and V. Table V shows that for the intermolecular vibration the interaction energy, the equilibrium distance, and the harmonic force constant are not changed significantly by the inclusion of the correlation energy. We obtain a somewhat smaller  $|\Delta E_{\text{SCF}}|$  for the formation of the HF dimer than Diercksen and Kraemer<sup>23</sup> ( $-0.0070$  au). This is due to the larger basis set employed in the present paper.

Experimental estimates of  $\Delta H$  for the reaction  $2\text{HF} = (\text{HF})_2$  by Franck and Meyer<sup>31a</sup> and by Smith<sup>3b</sup> yield values in the range of  $-5$  to  $-7$  kcal/mol. The contributions of the translational, rotational, and vibrational modes to  $\Delta H$  are roughly evaluated from the equi-

(27) P. E. Cade and W. H. Huo, *J. Chem. Phys.*, **47**, 614 (1967).

(28) P. E. Cade and W. H. Huo, *J. Chem. Phys.*, **45**, 1063 (1966).

(29) H. Lischka, *Theor. Chim. Acta*, **31**, 39 (1973).

(30) P. M. Stevens and W. N. Lipscomb, *J. Chem. Phys.*, **41**, 184 (1964).

(31) (a) E. U. Franck and F. Meyer, *Z. Elektrochem.*, **63**, 571 (1959);

(b) D. F. Smith, *J. Mol. Spectrosc.*, **3**, 473 (1959).

Table III. Calculated and Experimental Data for the HF Monomer<sup>a</sup>

		Basis no.				
		1	2	3	4	5
$-E_{\text{SCF}}$		100.026040	100.027874	100.028196	100.062611	100.063044
$-E_{\text{corr}}^b$	IEPA	0.275942	0.280047	0.287205	0.274395	0.281322
	CEPA	0.228114	0.231319	0.237516	0.225222	0.231243
	PNO-CI	0.219223	0.221999	0.227514	0.216383	0.221769
$-E_{\text{tot}}$	IEPA	100.301983	100.307922	100.315401	100.337006	100.344366
	CEPA	100.254154	100.259194	100.265712	100.287832	100.294287
	PNO-CI	100.245264	100.249873	100.255710	100.278994	100.284813
$\mu$	SCF	0.821	0.767	0.758	0.767	0.759
	IEPA	0.765	0.682	0.677	0.702	0.701
	CEPA	0.784	0.718	0.713	0.717	0.715
	PNO-CI	0.792	0.727	0.721	0.725	0.723
	Exptl	0.716 <sup>c</sup>				
$\alpha_{\parallel}$	SCF	4.41	5.48	5.55	5.64	5.72
	IEPA	4.82	6.34	6.54	6.43	6.41
	CEPA	4.62	5.93	6.22	6.20	6.12
	PNO-CI	4.55	5.83	6.11	6.10	6.03
	Exptl	6.48 <sup>d</sup>				
$\alpha_{\perp}$	SCF	1.76	4.11	4.33	4.25	4.47
	IEPA	2.00	5.14	5.46	5.33	5.56
	CEPA	1.80	4.55	4.85	4.71	4.89
	PNO-CI	1.77	4.46	4.75	4.60	4.79
	Exptl	4.86 <sup>d</sup>				
$R_e$	SCF				1.700	
	IEPA				1.752	
	CEPA				1.732	
	PNO-CI				1.726	
	Exptl				1.733 <sup>27</sup>	
$k_e$	SCF				11.20	
	IEPA				9.27	
	CEPA				9.92	
	PNO-CI				10.20	
	Exptl				9.66 <sup>27</sup>	

<sup>a</sup> The force constant  $k_e$  is given in mdyn/Å; all other values are in au. <sup>b</sup> The pair correlation functions were determined in the field of the canonical SCF orbitals for the basis sets 1-3. In contrast to that, the SCF orbitals were transformed in the case of the basis sets 4 and 5 by the localization procedure A before calculating the PNO's. <sup>c</sup> R. Weiss, *Phys. Rev.*, **131**, 659 (1963). <sup>d</sup> Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," Vol. 1, Part 3, A. Eucken and K. H. Hellwege, Ed., Springer-Verlag, Berlin, 1951, p 511.

Table IV. SCF, Correlation, and Total Energies for Different Linear Arrangements<sup>a</sup>

$R_{F_1F_2}$	$R_{F_1H_1}$	$R_{F_2H_2}$	$-E_{\text{SCF}}$	$-E_{\text{corr}}^{\text{tot}}$			$-E_{\text{tot}}$		
				IEPA	CEPA	PNO-CI	IEPA	CEPA	PNO-CI
4.25	1.733	1.733	200.113177	0.544339	0.447013	0.414524	200.657515	200.560190	200.527701
4.75	1.733	1.733	200.127227	0.544529	0.446881	0.414099	200.671757	200.574108	200.541326
5.0	1.733	1.733	200.129564	0.544583	0.446858	0.413985	200.674147	200.576422	200.543548
5.25	1.733	1.733	200.130523	0.544627	0.446853	0.413912	200.675151	200.577376	200.544435
5.50	1.733	1.733	200.130735	0.544673	0.446870	0.413880	200.675409	200.577605	200.544615
5.75	1.733	1.733	200.130564	0.544687	0.446866	0.413841	200.675252	200.577430	200.544405
6.0	1.733	1.733	200.130219	0.544697	0.446854	0.413805	200.674915	200.577073	200.544024
6.5	1.733	1.733	200.129392	0.544712	0.446847	0.413765	200.674104	200.576239	200.543157
8.0	1.733	1.733	200.127510	0.544741	0.446830	0.413705	200.672251	200.574340	200.541215
10.0	1.733	1.733	200.126388	0.544820	0.446884	0.413727	200.671208	200.573272	200.540115
12.0	1.733	1.733	200.125897	0.544889	0.446933	0.413760	200.670786	200.572830	200.539658
100.0	1.733	1.733	200.125222	0.545005	0.447021	0.413823	200.670227	200.572243	200.539045
5.5	1.50	1.733	200.111499	0.536759	0.442084	0.410521	200.648258	200.553582	200.522019
5.5	1.60	1.733	200.126531	0.540195	0.444141	0.411980	200.666726	200.570671	200.538511
5.5	1.65	1.733	200.129842	0.541893	0.445167	0.412699	200.671734	200.575009	200.542541
5.5	1.69	1.733	200.130910						
5.5	1.80	1.733	200.128208	0.546845	0.448202	0.414782	200.675053	200.576410	200.542990
5.5	1.90	1.733	200.120540	0.549969	0.450147	0.416074	200.670509	200.570687	200.536614
5.5	2.10	1.733	200.096633	0.555769	0.453820	0.418426	200.652402	200.550452	200.515059

<sup>a</sup> All values are given in au. For the definition of the geometry parameters see Figure 1.

**Table V.** Interaction Energies, Geometries, and Force Constants for the HF Dimer<sup>a</sup>

		Variation of $R_{F_1F_2}$ <sup>b</sup>	Variation of $R_{H_1F_1}$ <sup>c</sup>
$-\Delta E_e$	SCF	0.005512	
	IEPA	0.005176	
	CEPA	0.005362	
	PNO-CI	0.005577	
$R_e$	SCF	5.48	1.705
	IEPA	5.47	1.757
	CEPA	5.46	1.736
	PNO-CI	5.43	1.726
$k_e$	SCF	0.0951	11.0
	IEPA	0.101	9.18
	CEPA	0.104	9.83
	PNO-CI	0.109	10.24

<sup>a</sup> The force constants are given in mdyne/Å; all other values are in au. <sup>b</sup>  $R_{H_1F_2} = R_{H_2F_2} = 1.733$  au. <sup>c</sup>  $R_{F_1F_2} = 5.5$  au,  $R_{H_2F_2} = 1.733$  au.

The harmonic force constant of the stretching vibration of the isolated molecule remains practically unchanged by the hydrogen bond. The experimentally observed shifts of the absorption frequencies attributed to dimers are of the order of magnitude of 1–2%.<sup>31b</sup> Neither the SCF method nor the inclusion of electron correlation yield at present sufficient accuracy to predict reliably changes in the force constants of less than 5% for systems as large as (HF)<sub>2</sub>. From recent measurements of the radiofrequency and microwave spectrum of (HF)<sub>2</sub>,<sup>33</sup> a F–F distance of  $\sim 5.26$  au is computed, which is in reasonable agreement with our results.

Table VI presents an analysis of the correlation energy contributions to the total interaction energy  $\Delta E_{\text{tot}}$  for a variation of  $R_{F_1F_2}$ . In the case of the HF monomer we have found (section 3a) that the electron correlation reduces the dipole moment and increases the polarizability. On the basis of the asymptotic  $R^{-1}$

**Table VI.** An Analysis of the Correlation Energy Contributions<sup>a</sup>

		$\Delta E_{\text{SCF}}$	$\Delta E_{\text{corr}}^{\text{ias}}$	$\Delta E_{\text{corr}}^{\text{irs}}$	$\Delta E_{\text{corr}}^{\text{tot}}$	$\Delta E_{\text{tot}}$
5.0	IEPA	-0.004342	+0.002875	-0.002452	+0.000423	-0.003921
	CEPA		+0.001946	-0.002177	+0.000160	-0.004182
	PNO-CI		+0.001338	-0.002176	-0.000162	-0.004503
5.5	IEPA	-0.005513	+0.001614	-0.001282	+0.000333	-0.005183
	CEPA		+0.001071	-0.001133	+0.000148	-0.005365
	PNO-CI		+0.000712	-0.001133	-0.000057	-0.005570
6.0	IEPA	-0.004997	+0.001006	-0.000697	+0.000309	-0.004689
	CEPA		+0.000660	-0.000613	+0.000164	-0.004833
	PNO-CI		+0.000428	-0.000613	+0.000018	-0.004979
8.0	IEPA	-0.002288	+0.000360	-0.000095	+0.000265	-0.002025
	CEPA		+0.000252	-0.000082	+0.000188	-0.002100
	PNO-CI		+0.000166	-0.000082	+0.000118	-0.002170
12.0	IEPA	-0.000675	+0.000124	-0.000007	+0.000117	-0.000560
	CEPA		+0.000089	-0.000006	+0.000085	-0.000590
	PNO-CI		+0.000066	-0.000006	+0.000063	-0.000613

<sup>a</sup> All values are given in au.

partition principle of thermodynamics (see, e.g., ref 32). We take into account intermolecular effects only and calculate the energy changes due to the transformation of ten degrees of freedom (translation and rotation) of the two isolated HF molecules into three translational and three rotational modes of the complex (which is assumed here to be nonlinear) and into four intermolecular vibrations. Depending on the limiting cases  $h\nu \gg kT$  and  $h\nu \ll kT$ , we obtain  $-3RT \leq \Delta H - \Delta E_0 \leq RT$ .  $\Delta E_0$  is the energy difference at 0°K. Our computations yield directly the equilibrium energy  $\Delta E_e$  only (see Table V) which has to be corrected for the zero-point vibration energy of the complex. Assuming a mean value  $\bar{\nu} \approx 100$  cm<sup>-1</sup>, we obtain approximately  $\Delta E_0 \approx \Delta E_e + 0.6$  kcal/mol. We may expect at  $T \sim 300^\circ\text{K}$  considerable contributions of the intermolecular vibration to the partition function and thus also to  $\Delta H$  and put for our purposes  $\Delta H \approx \Delta E_e$ . In spite of the crudeness of the estimate of  $\Delta H - \Delta E_e$  and considering possible errors of our calculated  $\Delta E_e$ , for which it is very difficult to give even approximate bounds, we find that our results are somewhat lower than the experimental values mentioned above.

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expansion of the interaction energy (taking the leading terms only) one would expect that the Coulomb interaction decreases and that the polarization energy is not too much affected, since the increase of the polarizability is compensated at least in part by a reduction of the dipole moment. The dispersion interaction should be attractive and fall off much more rapidly ( $\sim R^{-6}$ ) than the Coulomb energy ( $\sim R^{-3}$ ). This situation is correctly reproduced by our results (Table VI).  $\Delta E_{\text{corr}}^{\text{ias}}$  represents the sum of the changes due to the Coulomb and polarization interactions and is always positive. At  $R = 12$  au  $|E_{\text{corr}}^{\text{irs}}|$  is an order of magnitude smaller than  $\Delta E_{\text{corr}}^{\text{ias}}$ . In the region of the energy minimum  $\Delta E_{\text{corr}}^{\text{ias}}$  and  $E_{\text{corr}}^{\text{irs}}$  compensate each other almost completely.

Because of the breakdown of the  $R^{-1}$  expansion and the importance of overlap and exchange effects the asymptotic considerations cannot be applied strictly at intermediate distances. We find, however, in agreement with previous works<sup>7</sup> that the trends of  $\Delta E_{\text{corr}}^{\text{ias}}$  and  $E_{\text{corr}}^{\text{irs}}$  at large distances do not change essentially as the distance decreases. Therefore, the conclusions drawn from calculations at large separations may be

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useful even for the qualitative interpretation of results obtained at distances near the energy minimum. The situation is certainly different for systems (e.g.,  $(\text{LiH})_2^5$ ) where overlap effects dominate. In such a case it is not possible to discuss the interaction energy near the equilibrium geometry in terms of the asymptotic expansion.

### Conclusion

Equilibrium distances and force constants for the intermolecular stretching vibration and shifts of the intramolecular stretching vibration calculated with the IEPA method agree well with the values obtained with the more sophisticated CEPA and PNO-CI methods. The effect of electron correlation is very small for the geometries treated in this paper. From the discussion in the preceding section it is clear that we do not expect in every case a vanishing influence of the correlation energy. Especially the corrections to the Coulomb interaction may modify the anisotropy of the intermolecular potential considerably.

We find negligible differences between the force constants of the intramolecular stretching vibration in the hydrogen bond and that of the isolated hydrogen fluoride. This fact supports previous experimental<sup>31b,34,35</sup> and theoretical<sup>1,22,36</sup> results that the observed

shifts of infrared absorption frequencies of 10–15% are due to higher polymers in the gas phase as well as in the liquid and that the properties of polymers larger than dimers cannot be explained from calculations of the dimer alone.<sup>37</sup>

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## The Hydration Number of $\text{Li}^+$

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**Abstract:** We present calculations on  $\text{Li}^+$  hydrates that predict that the preferential first coordination sphere of  $\text{Li}^+$  is tetrahedral.

In view of the current interest in ion hydration, we have examined<sup>1</sup> cation monohydrate potential surfaces as well as single points on the potential surfaces for cation di- and trihydrates. An important conclusion of the previous study was that one should be able to represent the energetics of  $\text{Li}^+(\text{H}_2\text{O})_n$  surfaces ( $n > 3$ ) in terms of appropriate  $\text{Li}^+(\text{H}_2\text{O})$  and  $\text{Li}(\text{H}_2\text{O})_2$  surfaces. In this paper we explore this approach for calculation of the relative energies of lithium hexahydrates. Tetra- and pentahydrates are also considered. The general method involves *ab initio* calculations on  $\text{Li}^+\cdots\text{OH}_2$  as a function of  $R(\text{Li}\cdots\text{O})$  and  $\text{Li}^+\cdots(\text{OH}_2)_2$  and  $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$  surfaces as a function of  $R(\text{Li}\cdots\text{O})$  and  $\theta(\text{OLiO})$ . We have used the double  $\zeta$  + polarization basis set previously<sup>1</sup> described. For  $\text{Li}^+\cdots(\text{H}_2\text{O})_2$  and  $(\text{H}_2\text{O})_2$  surfaces, we have done explicit calculations for  $\theta = 90, 109^\circ 28'$ , and  $180^\circ$  (Table I) and interpolated assuming an exponential repulsion which is a function of the O–O separation to find the energy at  $120^\circ$ . We then added up the  $\text{Li}^+\cdots\text{OH}_2$ ,  $\text{Li}^+\cdots(\text{OH}_2)_2$ , and  $\text{OH}_2\cdots\text{OH}_2$  energies as a function of

$R(\text{Li}\cdots\text{O})$  for a particular coordination geometry. For example, the  $\Delta E$  for the reaction  $6\text{H}_2\text{O} + \text{Li}^+ \rightarrow \text{Li}^+(\text{H}_2\text{O})_6$  (octahedral) was determined by the following expression<sup>1</sup> at different  $\text{Li}\cdots\text{O}$  distances:  $\Delta E = 6E^{(2)}(\text{Li}^+\cdots\text{OH}_2) + 3E^{(2)}(\text{H}_2\text{O}\cdots\text{H}_2\text{O}, \theta = 180^\circ) + 12E^{(2)}(\text{H}_2\text{O}\cdots\text{H}_2\text{O}, \theta = 90^\circ) + 3E^{(3)}(\text{Li}^+\cdots(\text{OH}_2)_2, \theta = 180^\circ) + 12E^{(3)}(\text{Li}^+\cdots(\text{OH}_2)_2, \theta = 90^\circ)$ .

The results of such *ab initio* calculations are summarized in Table II and are compared with the experimental gas phase hydration energies.<sup>2</sup> We calculate directly the energy of two-, four-, and six-coordinated  $\text{Li}^+$  hydrates as well as the minimum energy  $\text{Li}^+\cdots\text{O}$  distance. Using our interpolated potential surfaces for  $\theta = 120^\circ$ , we predict  $\Delta E$  for  $n = 3$  (trigonal) and 5 (trigonal bipyramid), assuming the axial  $R(\text{Li}-\text{O})$  equals the equatorial  $R(\text{Li}-\text{O})$ .

What is the optimum coordination geometry for a given number of water molecules around  $\text{Li}^+$ ? To answer this question one must compare the energies for different arrangements of the same number of water molecules and include the possibility that there might be an energetic preference for a water to be in the second

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