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Minimal basis set MINI-1 – powerful tool for calculating of molecular interactions. I. Neutral complexes

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The Huzinaga MINI-1 minimal basis set was applied to the following complexes: $H_3N\cdots HF$, $H_2O\cdots HF$, $(HF)_2$, $(H_2O)_2$, $HCN\cdots HF$, $OCO\cdots HF$, $HF\cdots HNH_2$, $(HCl)_2$, $CH_4\cdots OH_2$ and $(H_3Si)_2O\cdots H_2O$. The optimized geometries and stabilization energies agree well with the 6-31G* values, while the computing time is reduced considerably. The MINI-1 basis set was further tested for the stacking structure of the ethylene dimer and the cyclic structure of the formamide···formamidine complex, where fair agreement with the 4-31G results was obtained. The normal vibrational frequencies calculated for some complexes are comparable to those evaluated at the 4-31G (6-31G) level.

Key words: Intermolecular interactions—hydrogen-bonded complexes—basis sets

1. Introduction

The interaction energy (ΔE) of molecular complexes can be determined very accurately using the *ab initio* SCF method[1] if the extended basis sets of atomic orbitals including polarization functions are employed. Increasing the size of

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[1] This paper does not take into account the post SCF methods leading, among other things, to dispersion stabilization.

subsystems renders the use of such basis sets prohibitively expensive. This is also true for calculation of the interaction energy for hundreds of relative orientations of the subsystems, e.g. for fitting parameters in analytical potential functions. It is therefore necessary to work with smaller basis sets, most frequently with contracted gaussian type functions (GTF).

Two types of errors are inherently encountered [1] in calculation of the interaction energy with medium or small basis sets. The physical error is connected with an incorrect estimate of subsystem multipole moments; the electrostatic energy forms the most important part of the total interaction energy at distances larger than or comparable to the van der Waals (vdW) minimum. The mathematical error originates in the unbalanced description of the subsystems and the supersystem. More basis functions are available in the supersystem for the subsystems (compared with the isolated subsystems) resulting in a lower supersystem energy and, consequently, in a larger interaction energy. This artificial stabilization (called the basis set superposition error – BSSE) can be eliminated by the function counterpoise method introduced by Boys and Bernardi [2].

In our laboratories [3–11] as well as elsewhere [12–14], an extended body of evidence has been accumulated that the 4-31G basis set [15] yields reasonable relative values of the interaction energies for different types of molecular complexes, from weak to moderately strong ones. The absolute value of the interaction energy is overestimated (sometimes by as much as a factor of 2), due to the overestimated dipole moments of the subsystems. On the other hand, the BSSE is rather small for this basis set and usually does not exceed 10% of the interaction energy. The main drawbacks of this basis set, preventing its general use are: i) it is defined only for some elements of the second and third period, which causes difficulties especially if ionic complexes are considered; ii) because hydrogen and atoms of the second and third period contribute 2, 9 and 13 AO, respectively, the total number of AO even for not too extended complexes becomes rather large, making the SCF part time-consuming. It is therefore clear that a minimal basis set, defined for all the elements of the second and third periods and beyond, should be employed. One of the most widely used sets is the STO-3G basis set developed by Hehre et al. [16, 17].

As a result of the constraints, such as that the exponents of the s and p functions are equal, integral computation with STO-3G is very fast and, furthermore, it often gives the charge distribution and dipole moments of isolated systems close to those obtained using extended basis sets. However, the calculation for molecular complexes is different. The interaction energy attains quite reasonable values for different types of complexes but only at the price of a very large BSSE value, frequently comparable to (and sometimes even larger than) the respective interaction energy.

In 1980 Kołos [18] tested the standard (7, 3/3) minimal basis set proposed by van Duijneveldt [19] for different types of molecular complexes $X \cdots Y$; X, $Y = H_2O$, NH_3, HF; $CH_4 \cdots CH_4$ and $CH_4 \cdots H_2O$. The ΔE values are roughly comparable to the ΔE (4-31G) values; a considerable improvement was achieved after modifying the hydrogen 1*s* orbital. After correcting for the BSSE, the ΔE values were comparable to the uncorrected 6-31G* values.

The (7, 3/3) minimal basis set [20] was used by Clementi et al. for $CH_4\cdots OH_2$, $CH_3OH\cdots OH_2$ [21] and $CO_2\cdots H_2O$ [22] complexes.

Recently, new contracted basis sets were developed in the Huzinaga laboratory [23–30]. Among them, the minimal (6, 3/3) basis set MINI-1 evaluated for the elements H–Ca, Sc–Zn and Ga–Cd is of special interest. The authors analyzed the reasons why the STO-3G succeeds in producing a positive atomization energy for F_2 (contrary to the extended basis sets). It was shown that, among other reasons, this is caused by the poor description of the atomic 1*s* orbital. This orbital "lowers" its energy by borrowing orbitals from other centers. This effect is, of course, analogous to the intermolecular BSSE. The MINI basis sets, [23–30] of which the MINI-1 set has the same (3, 3/3) contraction scheme as STO-3G, were prepared in such a way [23] that the atomic BSSE was as small as possible. At first the orbital exponents and contraction coefficients are obtained from a least-square fit to the accurate Hartree–Fock atomic orbitals. Retaining the contraction scheme, the parameters of the basis set are further optimized to give the lowest atomic energy. Using this procedure, Huzinaga et al. employ on a middle-of-the-road solution between the two extreme types of minimal basis sets, both of which are connected with a large BSSE. i) Energy optimized functions (e.g. van Duijneveldt's set [19] which was adopted by Kołos [18]). The orbital exponents of the uncontracted set are obtained by minimizing the atomic energy. The large BSSE is due to poor description of the valence orbitals as too many functions are used for the best description of the 1*s* orbital, which is the most efficient way of lowering the atomic energy. ii) Basis sets obtained by a least-square fitting to Slater orbitals, e.g. Pople's STO-NG basis sets [16, 17]. Here, the large BSSE is, in turn, due to the poor description of the 1*s* orbitals, which will try to use the orbitals of other surrounding atoms to improve their atomic energies. Therefore, it has been very tempting to test the MINI-1 basis set for molecular interactions. In the first paper, neutral complexes will be investigated; the second one deals with ionic complexes.

2. Calculations

If not mentioned otherwise, the geometries of both subsystems *A* and *B* and supersystem *AB* were completely optimized by the HONDO 76 gradient program [31]. To accelerate the convergence of the optimization, the Pulay's force relaxation method [32] incorporated in the program by Čársky [33] was used for some complexes. The interaction energy was determined as the difference between the energies of these optimized structures $\boldsymbol{R}_{AB}^0$, $\boldsymbol{R}_A^0$ and $\boldsymbol{R}_B^0$:

$$\Delta E = E_{AB}(\boldsymbol{R}_{AB}^0) - E_A(\boldsymbol{R}_A^0) - E_B(\boldsymbol{R}_B^0). \tag{1}$$

The corrected interaction energy (ΔE_c) is determined according to Eq. (2)

$$\Delta E_c = \Delta E - \Delta_A - \Delta_B, \tag{2}$$

where the BSSE for subsystem A, Δ_A, is the extra stabilization which subsystem A gains in the complex. Hence, the evaluation of Δ_A requires knowledge of: i) the energy of subsystem A employing all the basis functions of the whole complex in the optimized complex geometry $[E_A^{AB}(\boldsymbol{R}_{AB}^0)]$, and, ii) the energy of the subsystem using the subsystem basis functions only for the same geometry $\boldsymbol{R}_A^{AB}$ as that of A atoms in the optimized complex structure $[E_A(\boldsymbol{R}_A^{AB})]$

$$\Delta_A = E_A^{AB}(\boldsymbol{R}_{AB}^0) - E_A(\boldsymbol{R}_A^{AB}). \tag{3}$$

For some calculations, the GAUSSIAN 70 program [34] was employed.

3. Subsystems

The geometry and dipole moments of all the subsystems considered in this and the subsequent paper are listed in Table 1. It is evident that the MINI-1 basis set is successful in predicting the subsystem dipole moments; the respective values are comparable with those obtained by the 6-31G* basis set. The MINI-1 bond distances are overestimated by 4.5–7.5% for A–H and by 5–10% for A–B bonds; the valence angles are, on the other hand, close to the 6-31G* values.

Table 1. Equilibrium geometries (in pm and degrees) and dipole moments μ (in 10^{-30} Cm)

Subsystem		MINI-1	STO-3G[a,b]	4-31G[b]	6-31G*[a]
CH_4 (T_d)	r(CH)	113.4	108.3	108.1	108.4
NH_3 (C_{3v})	r(NH)	105.0	103.3	99.1	100.2
	∡(HNH)	110.4	104.2	115.8	107.1
	μ	6.7	5.7	4.7	6.4
H_2O (C_{2v})	r(OH)	101.1	99.0	95.1	94.7
	∡(HOH)	104.2	100.0	111.2	105.5
	μ	7.5	6.2	8.3	7.3
HF ($C_{\infty v}$)	r(HF)	97.9	95.6	92.2	91.1
	μ	6.6	4.2	7.6	6.6
HCN ($C_{\infty v}$)	r(CH)	114.0	107.0	105.1	105.9
	r(CN)	121.4	115.3	114.0	115.3
	μ	9.7	8.2	10.7	10.7
C_2H_4 (D_{2h})	r(CC)	138.3	130.6	131.6	131.7
	r(CH)	113.4	108.2	107.3	107.6
	∡(HCH)	118.1	115.6	116.0	116.4
CO ($C_{\infty v}$)	r(CO)	122.5	114.6	112.8	111.4
	μ[c]	1.3	0.40	2.0	0.93
CO_2 ($C_{\infty v}$)	r(CO)	126.7	119.1	115.8	114.3
H_2S (C_{2v})	r(SH)	141.3	132.9	135.4	—
	∡(HSH)	94.7	92.5	95.5	—
	μ	6.7	3.4	5.9	—
HCl ($C_{\infty v}$)	r(HCl)	136.3	131.3	129.9	—
	μ	6.1	5.9	6.2	—

[a] Geometry of all the subsystems not containing elements of the third period were taken from Ref. [35].
[b] Ref. [36].
[c] A positive sign indicates the polarity C^+O^-.

Minimal basis sets are known to yield better results for dipole moments than split-valence (4-31G) or double-zeta sets. The MINI-1 results (Table 1) are not as close to the experimental values as are the STO-3G values but they are definitely closer than the 4-31G values. It is also evident that MINI-1 and 6-31G* results are very similar.

4. Complexes

The geometries of the complexes investigated are summarized in Table 2 and Fig. 1. The MINI-1 intermolecular distances for all the complexes are in good

Table 2. Geometries of the studied complexes (in pm and degrees)

Complex	Basis Set	R	r_1	r_2	r_3	α	β	γ	Ref.
$H_3N\cdots HF$	MINI-1	273.3	99.6	105.3	—	110.4	—	—	[a]
	STO-3G	277	95.6	103.1	—	113.6	—	—	37
	4-31G[b]	269	—	—	—	—	—	—	38
	6-31G*	276	93	100.2	—	111.3	—	—	39
$H_2O\cdots HF$	MINI-1	266.8	99.0	101.1	—	106.0	122.5	0.0	[a]
	STO-3G	263	95.6	98.7	—	101.3	128.2	3.0	37
	6-31G[c]	262	94	95	—	113	180	0.0	40
	6-31G*	273	92	95	—	106.6	139	0.0	39
$(HF)_2$	MINI-1	270.3	98.4	98.2	—	128.1	0	—	[a]
	STO-3G	257.0	95.4	95.3	—	109.1	4.0	—	37
	4-31G	269	92.7	92.5	—	124	8.0	—	41
	6-31G*	274	91.5	91.4	—	106	10.0	—	39
$(H_2O)_2$	MINI-1	288.4	100.8	101.7	101.1	104.4	132.2	104.9	[a]
	STO-3G	273.4	98.8	99.0	98.7	100.9	121.3	100.4	37
	4-31G	283	95.0	95.8	95.0	111	148.6	112	42
	6-31G*	298	94.7	95.2	94.8	104	120.3	106	39
$HCN\cdots HF$	MINI-1	303.7	114.3	121.2	98.3	—	—	—	[a]
	STO-3G	303.2	107.1	115.2	95.3	—	—	—	39
	4-31G	283	105	114	93	—	—	—	43
$OCO\cdots HF$	MINI-1	421.5	126.5	126.6	98.1	—	—	—	[a]
	STO-3G	413.7	118.6	118.9	95.3	—	—	—	39
	4-31G	399.6	115.3	116.1	92.4	—	—	—	8
	6-31G*[b]	408.8	—	—	—	—	—	—	8
$HF\cdots HNH_2$	MINI-1[d]	319.8	98.1	105.4	105.1	106.0	3.0	107.9	[a]
	STO-3G[e]	280.9	95.4	103.4	103.2	104.9	2.8	103.9	37
	4-31G[f]	326	—	—	—	100	—	—	38
	6-31G*[f]	338	—	—	—	97.2	—	—	12
$(HCl)_2$	MINI-1	398.4	136.4	136.5	—	104.3	7.1	—	[a]
	STO-3G	374.6	131.4	131.7	—	106.3	4.9	—	39
	4-31G	399	130	130	—	102	7	—	3
	DZ+P	395.8	127.7	127.4	—	97	2.6	—	44

[a] This paper.

[b] Intrasystem coordinates were not optimized.

[c] The 6-31G optimized structure corresponds to the planar C_{2v} one.

[d] Angle δ equal to 122.5°.

[e] Angle δ equal to 116.8°.

[f] Only R and α were optimized, β was set equal zero; r_1, r_2, r_3, γ and δ were taken from the subsystems.

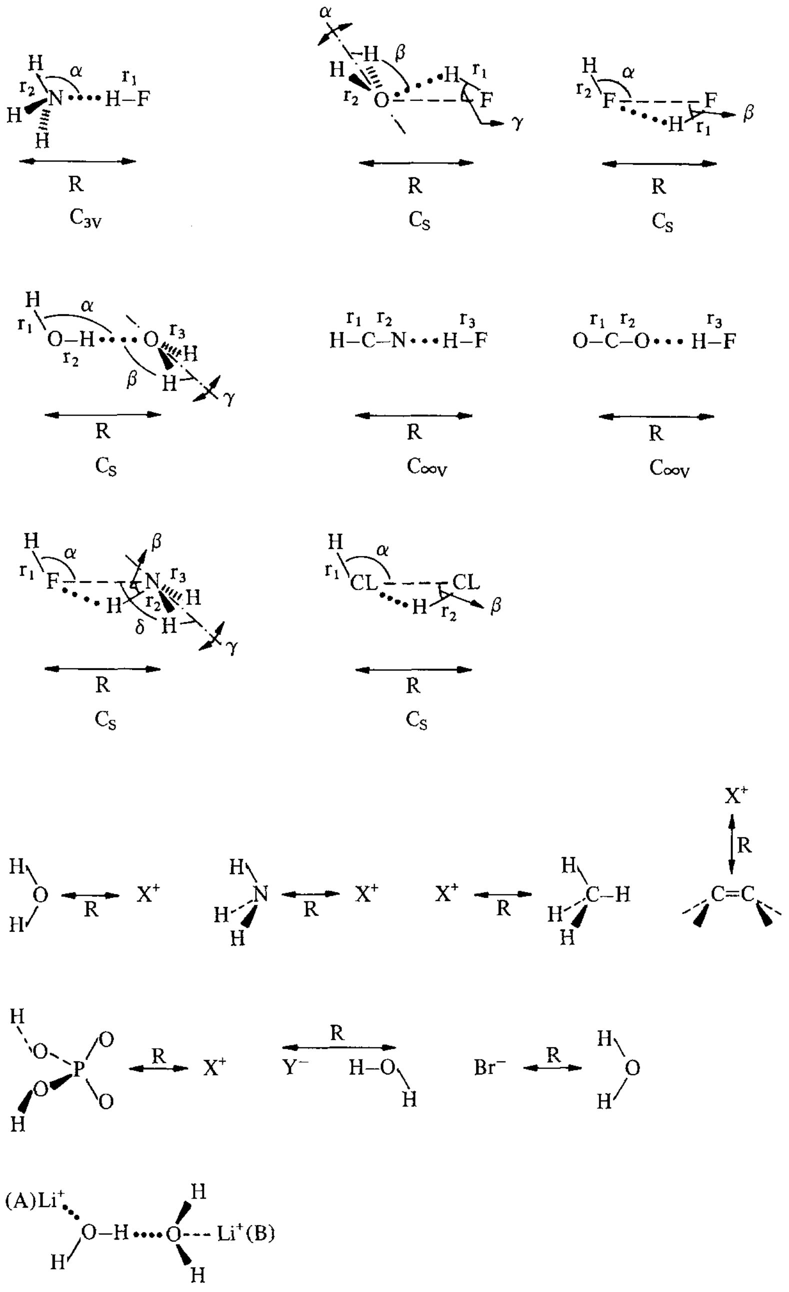

Fig. 1. Structures of complexes investigated

agreement with the 6-31G* values. As expected, the 4-31G values are too short, while the STO-3G values are sometimes comparable to the 6-31G* ones, and are sometimes smaller. Intrasystem distances are overestimated with the MINI-1 set (see above). The relative changes in the subsystem geometry upon complex

Table 3. Interaction energies (ΔE) and interaction energies corrected for the BSSE (ΔE_c) of the complexes studied (in kJ/mol)

	MINI-1		STO-3G			4-31G			6-31G*		
Complex	$-\Delta E$	$-\Delta E_c$	$-\Delta E$	$-\Delta E_c$	Ref.	$-\Delta E$	$-\Delta E_c$	Ref.	$-\Delta E$	$-\Delta E_c$	Ref.
$H_3N \cdots HF$	59.5	53.0	34.7	13.99	12, 45	68.2	—	38	51.0	47.3	12, 39
$H_2O \cdots HF$	48.2	39.6	31.4[a]	—	12	65.5[b]	—	40	38.5	—	12
$(HF)_2$	29.2	17.9	23.0	−14.5	12, 45	33.5	25.6	41, 39	25.1	18.4	39
$(H_2O)_2$	28.1	20.1	25.0	−3.13	12, 39	34.3	31.4	42, 39	23.4	19.7	39
$HCN \cdots HF$	24.5	22.6	15.0	8.08	39	38.4	23.2	43, 39	—	—	
$OCO \cdots HF$	12.6	10.3	9.9	1.5	39	22.3	18.5	8	12.5[c]	10.7	8
$HF \cdots HNH_2$	10.1	5.1	13.8	—	12	14.6	—	38	10.9	—	12
$(HCl)_2$	6.3	4.7	8.1	3.3	39	8.8	5.8	3	8.0	3.6	44

[a] For the planar structure, the following values of ΔE and ΔE_c result: −28.7 and −3.4 kJ/mol (Ref. [39]).

[b] 6-31G calculation for the planar structure.

[c] CO_2 and HF geometries were kept fixed and taken from 4-31G calculations

formation are, however, more important. The prolongation of HF on formation of $H_3N\cdots HF$, $H_2O\cdots HF$ and $HF\cdots HF$ amounts to 1.7, 1.1 and 0.5 pm, in very good agreement with the respective 6-31G* values (1.9, 0.9 and 0.4 pm). It should be noted that STO-3G fails completely in this respect, the respective values being 0.0, 0.0 and −0.2 pm.

The energy characteristics are collected in Table 3. The ΔE(MINI-1) values are larger than the 6-31G* ones, but not by as much as ΔE(4-31G) values. On the other hand the ΔE(STO-3G) values are too small. After correcting the ΔE value for the BSSE, the agreement between MINI-1 and 6-31G* (also corrected) becomes excellent. The MINI-1 characteristics for the $CH_4\cdots OH_2$ (linear $C—H\cdots O$ structure; point by point optimization) ($\Delta E = -3.0$ kJ/mol, $R = 356$ pm) agree well with the Clementi results [21] ($\Delta E = -2.9$ kJ/mol, $R = 370$ pm). It is important to mention that MINI-1 succeeds with strong, medium and weak complexes.

The corrected ΔE value was determined by adding the BSSE to ΔE at the potential energy minimum. Rigorously, the whole potential energy surface should be corrected for the BSSE which can result in a different position and depth of the minimum. However, this happens only for very large BSSE corrections. The disiloxane···water complex proved to be a very sensitive case (Table 4). Only intermolecular degrees of freedom R and β (cf. Fig. 1, the same coordinates as for $(H_2O)_2$) were optimized neglecting a possible deviation of the hydrogen bond from linearity (cf. Refs. [5] and [9]). The experimental geometries of the subsystems were adopted. The table shows that the STO-3G and 4-31G basis sets yield stabilization energies that are twice as large as for the 6-31G* basis set, and equilibrium distances that are 47 and 24 pm resp., shorter. Even the 6-31G* results are connected, however, with a BSSE as large as one half of the stabilization energy [46]. If the equilibrium distance is determined from the corrected potential curve, the 6-31G* and MINI-1 results are virtually identical: the deviation of the distance is only 5 pm (1.5%) and that of the interaction energy is 0.6 kJ/mol (10%).

Table 4. Disiloxane···water complex: Equilibrium distances and interaction energies before (R, ΔE) and after (R_c, ΔE_c) correcting for the BSSE for the linear hydrogen-bonded structure[a]

Basis set	$\beta^{a,c}$	R	$-\Delta E(R)$	$-\Delta E_c(R)$	R_c	$-\Delta E_c(R_c)$	ref.	Time[e]
MINI-1	155°	289	17.0	3.3	322	6.2	[b]	1.0[f]
STO-3G	163°	268	22.7	−11.5	—	—	5	0.8[f]
4-31G	163°	291	22.5	16.8	300	17.4	9	4.0[f]
6-31G*	(145°)[d]	315	11.5	5.2	327	5.6	46	9.9[g]

[a] Cf. Fig. 1, the same coordinates as with $(H_2O)_2$.

[b] This paper.

[c] Values obtained from the uncorrected interaction energies.

[d] Not varied.

[e] Relative values for one complete calculation including the BSSE (EC 1040 computer).

[f] GAUSSIAN 70 program [34], 38 iterations.

[g] HONDO 76 program [31], 18 iterations.

Table 5. Interaction energies (ΔE) and interaction energies corrected for the BSSE (ΔE_c) of some complexes (in kJ/mol)[a]

	MINI-1		(7, 3/3; OLD)[b]		(7, 3/3; NEW)[b]	
Complex	$-\Delta E$	$-\Delta E_c$	$-\Delta E$	$-\Delta E_c$	$-\Delta E$	$-\Delta E_c$
$H_3N\cdots HF$	52.7	46.1	59.5	49.7	50.4	42.0
$H_2O\cdots HF$	42.4	34.1	52.5	37.8	41.6	31.3
$(HF)_2$	24.1	13.9	33.2	15.9	22.2	12.2
$(H_2O)_2$	25.1	18.7	31.2	20.4	25.4	18.6
$HF\cdots HNH_2$	8.6	5.4	11.6	5.9	7.3	5.4

[a] The geometries of complexes are taken from the 6-31G* calculations (Ref. [12]), only for $(HF)_2$ the experimental geometry (Ref. [47]) was used.
[b] Ref. [18].

Table 5 contains ΔE and ΔE_c for some complexes obtained with MINI-1 and the two basis sets used by Kołos [18]. The geometry used by Kołos is maintained in all the complexes. The table indicates that the MINI-1 values are comparable to the "NEW" ones (a basis set with a reoptimized hydrogen 1*s* orbital).

All the complexes investigated so far are characterized by the presence of one hydrogen bond. Two other types of complexes – stacking and cyclic (with more hydrogen bonds) play a vital role in biology. Stacking complexes are represented by the ethylene dimer; the subsystems whose geometry was optimized (cf. Table 1) are located in the parallel planes separated by distance R. For $R = 265$, 318 and 370 pm, ΔE amounts to 91.1, 22.2 and 6.38 kJ/mol, in fair agreement with the sum of the perturbation coulombic and exchange-repulsion terms [48] evaluated with the 4-31G basis set (80.4, 11.8 and 3.0 kJ/mol).

Complexes with more hydrogen bonds are represented by the formamide···formamidine complex (Fig. 2) with the same hydrogen bonds as the adenine···thymine pair. The MINI-1 values of R, α, β (cf. Fig. 2) and ΔE (obtained by step by step optimization) 289 pm, 118 and 120 degrees and −61 kJ/mol, respectively, agree fairly well with the respective 4-31G values [49] (218 pm, 117 and 120 degrees, −66 kJ/mol). Only the intermolecular distance differs more. Unfortunately, no data are available for this and similar complexes, originating in extended basis set calculations. It is believed, however, that the MINI-1 distance is sound.

Moreover, we have tested the capability of the MINI-1 basis set to cope with weak interactions occurring in the complexes of water with closed shell and

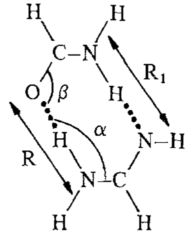

Fig. 2. Structure of formamide···formamidine complex

transition metal atoms such as $H_2O\cdots Mg$ [50] and $H_2O\cdots Ni$ [51]. Results obtained using extended basis sets [50–52] reveal that, at the SCF level, the potential surface is purely repulsive. MINI-1 reproduces this behavior qualitatively for both complexes although numerically it exaggerates the repulsion.

The normal vibrational modes represent rather important characteristics of *vdW* complexes, especially because of the importance of the vibrational contribution to the entropy. Table 6 lists these frequencies for the $H_2O\cdots HF$, $(H_2O)_2$ and $(HF)_2$ complexes. The table indicates that the MINI-1 frequencies are roughly comparable to the 4-31G (6-31G) values. Let us further compare the changes in the subsystem frequency ($\Delta\nu$) upon formation of a hydrogen bond (this value can play a role in determining the zero-point energy). The $\Delta\nu$ values for HF (proton donor) in $(HF)_2$ and $H_2O\cdots HF$ amount to 72 and 190 cm^{-1}, respectively, which

Table 6. Vibrational frequencies (in cm^{-1}) for $(H_2O)_2$, $H_2O\cdots HF$ and $(HF)_2$[a]

$(H_2O)_2$		$H_2O\cdots HF$			$(HF)_2$		
MINI-1	4-31G[b]	MINI-1	6-31G[c]	exp.[d]	MINI-1	4-31G[e]	extended[f]
109	81	199	250	94	230	171	148
197	118	294	265	180	326	226	185
217	185	327	276	198	554	519	436
261	204	745	740	666	626	588	491
403	452	683	913	696	4083	4038	4366
683	536	1719	1755	1600	4135	4081	4418
1806	1771	3900	3747	3608			
1852	1813	3965	3974				
3843	3907	4113	4112				
3900	3979						
4071	4085						
4115	4121						

[a] MINI-1 vibrational frequencies for H_2O and HF equal 1816, 3897, 4127 and 4155 cm^{-1}.
[b] Ref. [42].
[c] Ref. [40].
[d] Ref. [53].
[e] Ref. [41].
[f] Ref. [54].

Table 7. CPU time (EC 1040) in minutes for evaluation of the two-electron integrals, SCF part, gradient and total time for 1 gradient cycle of $(H_2O)_2$

Basis set	Two-el. integr.	SCF[a]	Grad.	Total 1 grad. cycle
STO-3G	1.60	0.42	6.51	9.43
MINI-1	2.60	0.43	10.12	14.21
4-31G	4.67	4.96	22.75	33.97

[a] Convergence criterion was reached with STO-3G, MINI-1 and 4-31G after 8, 8 and 21 iterations, respectively.

can be compared with the 4-31G (6-31G) values of 79 and 423 cm^{-1}. The 6-31G $\Delta\nu$ for $H_2O\cdots HF$ is too high and probably originates in too strong 6-31G ΔE value for this complex. We would like finally to point out that the interaction entropy is not very sensitive to the quality of the calculated vibrational frequencies [55]; hence, we can expect that the $T\Delta S$ term evaluated by MINI-1 will not be too different from that evaluated using the 4-31G basis set (the $T\Delta S$ term calculated on the basis of the 4-31G characteristics is satisfactory [55]).

Table 7 gives the CPU time (EC 1040) for evaluation of all the integrals, calculation of the energy as well as of the gradient (HONDO – 76, Ref. [31]) using MINI-1, STO-3G and 4-31G basis sets for $(H_2O)_2$. It is evident from the table that MINI-1 is about 2–3 times faster than 4-31G and about 50% slower than STO-3G. With more extended complexes, the MINI-1 becomes even more efficient, which can be demonstrated with the disiloxane$\cdots$water complex. The time for complete SCF calculation with additional evaluation of BSSE by STO-3G is only 20% shorter than for MINI-1 and, furthermore, the 4-31G calculation takes four times longer. For this complex, the 6-31G* calculation is approximately ten times longer than the MINI-1 calculation.

5. Conclusion

The MINI-1 basis set predicts equilibrium geometries and stabilization energies for a broad set of complexes, from strong to weak ones, in accordance with the extended 6-31G* basis set. The BSSE for all the complexes is rather small. Satisfactory results were also obtained for stacking complexes and for complexes with more than one hydrogen bond. The basis set also succeeds with vibrational frequencies. Taking into account i) the above mentioned conclusions, ii) the fact that the basis set is defined for 47 elements and iii) the very favorable time economy, the MINI-1 basis set can be strongly recommended for general use in the field of molecular interactions.

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