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The minimal basis set MINI-1—powerful tool for calculating intermolecular interactions. II. Ionic complexes

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Optimum geometries and stabilization energies are determined for complexes of H_2O, NH_3, CH_4, C_2H_4, CO, and N_2 with metal cations including Li^+, Na^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, and Al^{3+}, for the complex $(HO)_2PO_2^- \cdots Mg^{2+}$ and for the complexes of water with F^-, Cl^-, and Br^- by SCF calculations employing the MINI-1 minimal gaussian basis sets. The Boys-Bernardi method was used to evaluate the superposition error. Comparison with the extended basis set results revealed that the MINI-1 set gives uniformly good results for a broad variety of ionic complexes and therefore should be preferred to other small basis sets.

Key words: Intermolecular interactions—cation-molecule complexes—anion-molecule complexes—basis sets

1. Introduction

In the preceding paper [1] we have shown that the recently proposed [2–8] minimal basis set of contracted Gauss-type functions, MINI-1, is the best choice among various small basis sets for studying molecular complexes. This is a result of the following features

(i) as a result of its preparation, the basis set superposition errors (BSSE) are small;

(ii) as is indicated by the values for the dipole moments, it yields reasonable charge distributions leading to small errors in the electrostatic interaction energy; (iii) it is consistently defined for all elements between H and Cd including the first row transition metals.

This paper deals with ionic complexes of the type $X^{+}\cdots M$ where X^{+} is a metal cation (Li^{+}, Na^{+}, K^{+}, Rb^{+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Al^{3+}) and M includes H_2O, NH_3, CH_4, C_2H_4, CO as well as N_2 and $Y^{-}\cdots H_2O$, where Y^{-} is one of the halide ions F^{-}, Cl^{-} and Br^{-}. In addition, the ion pair $(HO)_2PO_2^{-}\cdots Mg^{2+}$, for which accurate SCF calculations became recently available is considered. Since it was our primary aim to explore the capabilities of the MINI-1 basis set we confined ourselves to SCF calculations, although in some complexes correlation effects may contribute substantially to the total binding. All the technical details are given in paper I [1].

There are a number of reasons why the two types of errors mentioned above become particularly important with ionic complexes. The use of small basis sets which were standardly derived for neutral atoms in their ground states for building wavefunctions for cations or anions inevitably leads to seriously unbalanced sets connected with a huge basis set superposition error. With the metal cations (e.g. alkaline, alkaline earth, Al^{3+}), the whole valence set of orbitals is unoccupied. If these orbitals are present in the basis set, they are used by the ligand to improve its energy so that it artificially donates electrons. From the published MINI-1 basis set it can be seen that this problem is diminished by cancelling the *p*-orbitals from the valence shell for alkaline and alkaline earth metal atoms. The *p*-orbitals of the valence shell are considered as polarization functions unless there is some *p*-occupation in the atom. With the halide ions, the problem is complicated by the fact that in a minimal basis set there are no unoccupied orbitals at all. Hence, in the complex they will compete for the unoccupied orbitals of the ligand to improve their energy. This will result in an artificial charge transfer to the ligand and in a substantial BSSE. Moreover, the orbital exponents which are optimal for the neutral atoms are certainly not optimal for the atomic cations or anions. For metal cations Pullman et al. [9] have investigated several ways of improving the STO-3G basis set for cations. Either the *p*-orbitals or all the orbitals were removed from the valence shell and/or the exponents of the inner shell orbitals were reoptimized. It was found that combination of the STO-3G basis set with reoptimized inner shell exponents for the cation and the 4-31G basis set for the ligands permits setting up of a well-balanced basis set for cation···molecule complexes. The BSSE for both the cation and the ligand are of comparable magnitude (see, e.g. [10]). Clementi et al. have described real minimal cation basis sets, i.e. basis sets without any functions for the (unoccupied) valence shell, for Li^{+} [11], Na^{+} [12] and Zn^{2+} [13]. It is common knowledge that the atomic anions need additional flat functions [14]. In a study of several complexes with Cl^{-} [15], the flexibility of the 4-31G basis set was substantially improved by adding a flat *p*-function. Kołos studied the $F^{-}\cdots H_2O$ complex [16] using a minimal basis set which was optimized directly for F^{-}.

In this study we would like to retain the advantage of working with standard basis sets as far as possible. Therefore we first investigate whether or not the MINI-1 basis set without any modification can also be successfully applied to ionic complexes. We find that this is indeed true for cations (*vide infra*). For halide ions, however, some improvement seems desirable. Reoptimized exponents for the outer *p*-shells are recommended as this is only a minor change which has been found to be nearly as efficient as adding a flat *p*-function.

Generally, small basis sets overestimate the strength of the interaction, i.e. they overestimate the interaction energy while the equilibrium distances obtained are too short. With a properly prepared minimal basis set, i.e. one that yields a basically correct charge distribution, after correcting for the BSSE, we should not be surprised to find too small interaction energies (in absolute terms) and too long distances. The insufficient description of polarizabilities by minimal basis sets could account for this effect. Hence, it may be encountered with complexes of small, strongly polarizing ions such as Be^{2+} or F^-, where the polarization energy is a substantial part of the total stabilization energy.

2. Cation-molecule complexes

For the cations investigated, the following total energies in a.u. were obtained: Li^+ (−7.18253), Na^+ (−160.69742), K^+ (−596.25835), Rb^+ (−2926.79277), Be^{2+} (−13.51748), Mg^{2+} (−197.68234), Ca^{2+} (−673.11625), Zn^{2+} (−1769.18744) and Al^{3+} (−238.68634). For ions with occupied *d*-orbitals, the energy refers to six cartesian *d*-functions i.e. an additional *s*-function is effectively included in the basis set with the same exponent as the genuine set of five *d*-functions. This is exactly the energy that is necessary when calculating binding energies (cf. Ref. [5]) or interaction energies. Complete geometry optimizations were performed for the complexes of all the cations with water, as well as for $Li^+\cdots NH_3$ and $K^+\cdots NH_3$. The minimum energy structures (Fig. 1) have C_{2v} and C_{3v} symmetry, respectively. The results are reported in Tables 1–3.

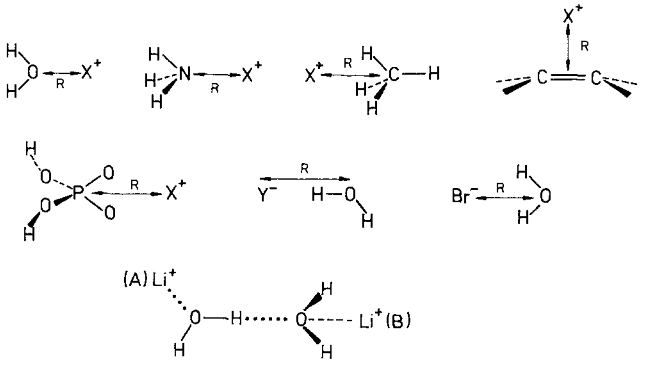

Fig. 1

Table 1. Equilibrium distances, R(pm), and interaction energies, ΔE(kJ/mol), for complexes of water with different cations X^+. ΔE_c are the interaction energies corrected for the basis set superposition error

X^+		MINI-1[a]	STO-3G[b]	4-31G/BASE[c]	Extended[d]
Li^+	R	179	170	178	185
	$-\Delta E$	175	335	190	155
	$-\Delta E_c$	159	196	189	—
Na^+	R	212	200	216	220
	$-\Delta E$	131	178	139	113
	$-\Delta E_c$	117	104	135	—
K^+	R	259	240[f]	260	265
	$-\Delta E$	86[e]	117[f]	101	75
	$-\Delta E_c$	78[e]	—	—	—
Be^{2+}	R	155	—	—	150
	$-\Delta E$	533	—	—	586
	$-\Delta E_c$	512	—	—	—
Mg^{2+}	R	187	180	190	195
	$-\Delta E$	356	490	382	335
	$-\Delta E_c$	335	393	377	—
Ca^{2+}	R	227	—	230	240
	$-\Delta E$	228	—	267	222
	$-\Delta E_c$	214	—	—	—
Zn^{2+}	R	187	—	—	191[g]
	$-\Delta E$	376	—	—	346[g]
	$-\Delta E_c$	343	—	—	—
Al^{3+}	R	176	—	—	175
	$-\Delta E$	832	—	—	753
	$-\Delta E_c$	791	—	—	—

[a] This work.

[b] Ref. [17], exceptions noted; rigid, experimental geometry for water.

[c] 4-31G basis set for water combined with specially prepared basis sets for the cation. Use was made of the STO-3G set with reoptimized valence shell exponents (Ref. [9]). Results for K^+ and Ca^{2+} from Ref. [9], for the other cations from Ref. [17].

[d] Ref. [18]; rigid, experimental geometry for water.

[e] Cf. S. Huzinaga, private communication to the authors of Ref. [19].

[f] Ref. [20].

[g] Ref. [13].

Although not the most accurate results available, the calculations of Kollman and Kuntz [18] were chosen as a reference as this is the most complete study of water···cation complexes using an extended basis set. It can be seen that MINI-1 performs better than STO-3G which produces a huge BSSE and slightly better than even the composed 4-31G (ligand)/STO-3G (cation, reoptimized inner shell exponents) set. The equilibrium distances are somewhat too small, typically by 2–5% ($H_2O\cdots Be^{2+}$, +3.3%, and $H_2O\cdots Al^{3+}$, +0.6% are exceptions). The interaction energy corrected for the BSSE deviates from the extended basis set results by less than 5% for the water complexes and by less than 10% for the ammonia complexes. The stronger binding of cations by ammonia compared to water cannot be understood simply on the basis of ion-dipole interactions as the dipole

Table 2. Equilibrium distances, R(pm), and interaction energies, ΔE(kJ/mol), for complexes of ammonia with different cations. ΔE_c are the interaction energies corrected for the basis set superposition error. In parenthesis are given the differences compared to the corresponding values for complexes with water (cf. Table 1)[a]

Cation		MINI-1[b]	4-31G/BASE[c]	Extended[d]
Li^+	R	191 (12)	195[e] (17)	200 (20)
	$-\Delta E$	194	201[e] (12)	161 (20)
	$-\Delta E_c$	176 (17)	—	—
K^+	R	272 (13)	275[f] (16)	290 (20)
	$-\Delta E$	93	101[f] (4)	77 (5)
	$-\Delta E_c$	83 (5)	—	—

[a] $\Delta R = R(NH_3) - R(H_2O)$; $-\Delta\Delta E = -\Delta E(NH_3) + \Delta E(H_2O)$.
[b] This work.
[c] See footnote [c] in Table 1.
[d] Ref. [21].
[e] Ref. [22].
[f] Ref. [23].

Table 3. Geometry change of the water molecule on complex formation with different cations (distances in pm, angles in degree)

Cation		Li^+	Be^{2+}	Mg^{2+}	Ca^{2+}	Al^{3+}	Zn^{2+}
Δr(OH)	MINI-1	−0.2	0.1	0.7	0.2	4.9	0.9
	Extended[a]	0.5	—	1.7	—	5.3	—
$\Delta\alpha$	MINI-1	0.4	1.0	−0.8	−1.7	−1.0	0.0
	Extended[a]	−0.5	—	−0.01	—	1.13	—

[a] Ref. [24].

moment of water is larger. Table 2 shows that the differences between water and ammonia complexes as predicted by the extended basis sets are almost perfectly reproduced by the MINI-1 calculations. For $H_2O\cdots Li^+$ and $Li^+\cdots NH_3$ the results of complete geometry optimizations at the 6-31G* level are also available ($R = 186$ and 200 pm, $\Delta E = -163$ and -188 kJ/mol) [25]. These are still accompanied by a non-negligible BSSE, which is revealed by comparison with the extended basis set results (Tables 1 and 2). The uncorrected MINI-1 results are only slightly poorer. For the $H_2O\cdots Rb^+$ complex no calculations are available for comparison. However, the experimental value for the enthalpy of formation −66.5 kJ/mol [26] lends confidence to the MINI-1 result, $R = 281$ pm, $\Delta E = -73.4$ and $\Delta E_c = -66.4$ kJ/mol.

In Table 3 are listed the changes in the internal coordinates of the water molecule on complex formation with different cations. The changes for monovalent ions are so small that it is not worthwhile to give the values for all cations investigated. The changes in the bond angle are small (less than one degree except for Ca^{2+}) and no regularity emerges either in the extended basis set or in the MINI-1

Table 4. Harmonic vibrational frequencies (cm^{-1}) and changes in the zero point vibrational energy, $\Delta H_0^{\mathrm{VIB}}$, vibrational part of the enthalpy at 298 K, $\Delta H_{298}^{\mathrm{VIB}}$, (kJ/mol) and vibrational entropy, ΔS^{VIB} (J/mol K) for some water···cation complexes

	$Li^+\cdots OH_2$		$Mg^{2+}\cdots OH_2$		$Al^{3+}\cdots OH_2$	
Vibrational mode[a]	MINI-1	Ext.[a]	MINI-1	Ext.[b]	MINI-1	Ext.[b]
$\nu_1(O \leftrightarrow H, \mathrm{sym.})$	3952	4052	3868	3929	3304	3420
$\nu_2(\delta_{HOH})$	1857	1869	1893	1819	1761	1751
$\nu_3(X^+ \leftrightarrow OH_2)$	636	445	628	572	763	777
$\nu_4(O \leftrightarrow H, \mathrm{antisym.})$	4088	4111	3925	3995	3361	3416
$\nu_5(X^+$ in plane$)$	560	521	753	1047	964	1322
$\nu_6(X^+$ out of plane$)$	572	529	828	571	962	617
$\Delta H_0^{\mathrm{VIB}}$	11.3	10.0	12.9	10.7[c]	7.6	7.0[c]
$\Delta H_{298}^{\mathrm{VIB}}$	12.6	11.8	13.7	11.7[c]	8.1	7.65[c]
ΔS^{VIB} [d]	5.9	8.2	3.5	4.5	1.9	2.9

[a] Ref. [27].

[b] Unpublished results of H. Lischka (1978), cf. Ref. [28].

[c] Ref. [28].

[d] Only intermolecular frequencies (ν_3, ν_5 and ν_6) contribute.

results. The OH bond tends to become longer, particularly with Mg^{2+} and Al^{3+} complexes.

The harmonic vibrational frequencies for $H_2O\cdots Li^+$, $H_2O\cdots Mg^{2+}$ and $H_2O\cdots Al^{3+}$ are given in Table 4. The MINI-1 intramolecular frequencies are 97–104% of the reference values. Larger deviations appear for the intermolecular modes particularly for the difference between the in-plane and out-of-plane motions of the cation. Nevertheless, the results are very satisfactory especially in relation to calculations of thermodynamic functions of complex formation. Table 4 includes MINI-1 and extended basis set results for zero point vibrational energies, vibrational contributions of ΔH at 298 K and vibrational entropy contributions. The deviations between the two levels of calculation will affect the total enthalpy change [28] by only 0.6, 0.6 and 0.1% and the total entropy change [28] by only 2.5, 1.0 and 1.0% for the $H_2O\cdots Li^+$, $H_2O\cdots Mg^{2+}$ and $H_2O\cdots Al^{3+}$ complexes.

So far, only complexes of two subsystems have been considered. In systems consisting of more subsystems, three-body effects will arise. For two different structures of the $Li^+(H_2O)_2$ complex, it was shown [29] that the three-body contributions to the total interaction energies were dominated by polarization forces. Bearing in mind that minimal basis sets in general poorly describe polarizabilities, the three-body interactions in $Li^+(H_2O)_2$ seemed worth studying by MINI-1. The results in Table 5 indeed indicate the anticipated lack of polarizability at the MINI-1 level. The absolute magnitude of the three-body interaction, V_{Liww}, is underestimated by one third and one fourth, respectively. However, the different sign for the different structures and the relative values are correctly reproduced, which is very satisfactory. These statements refer to the

Table 5. Total interaction energy, $\Delta E_{\mathrm{LiWW'}}$, two-body interaction energy, V_{IJ}, and three-body interaction energy, $V_{\mathrm{LiWW'}}$, for two different configurations of the $\mathrm{Li^+(H_2O)_2}$ complex (all energies in kJ/mol)

	Configuration A[a]			Configuration B[a]		
	MINI-1 uncorr.	MINI-1 corr.[c]	Extended[b]	MINI-1 uncorr.	MINI-1 corr.[c]	Extended[b]
$\Delta E_{\mathrm{LiWW'}}$	−231.5	−207.4	−194.1	−125.7	−100.9	−100.7
$V_{\mathrm{WW'}}$	−21.6	−17.0		−21.6	−14.2	
V_{LiW}	−175.7	−158.7		+23.3	+24.0	
$V_{\mathrm{LiW'}}$	−23.5	−24.4		−133.7	−114.3	
$V_{\mathrm{LiWW'}}$	−10.7	−7.4	−10.7	+6.2	3.6	6.4

[a] Taken from Ref. [29], the structures are shown in Fig. 1, for details see Ref. [29].
[b] Ref. [29].
[c] The values corrected for the basis set superposition error were obtained by using the functions of all three subsystems when calculating the energies of any subsystem or any two-body interaction.

results properly corrected for the BSSE. Obviously the BSSE compensates for the lack in polarizability.

Table 6 lists the results for the two isomers $\mathrm{CO\cdots Li^+}$ and $\mathrm{Li^+\cdots CO}$ and for the $\mathrm{N_2\cdots Li^+}$ complex. MINI-1 describes all the structures correctly. In addition to the interaction energy for $\mathrm{CO\cdots Li^+}$, which is 30% too large, the values obtained are comparable to the 6-31G* values. The preference for the $\mathrm{CO\cdots Li^+}$ structure is a feature of the SCF potential surface. When correlation effects are included,

Table 6. Results for complexes of $\mathrm{Li^+}$ with CO and $\mathrm{N_2}$. Distances R in pm, interaction energies before and after correcting for the BSSE (ΔE and ΔE_c) in kJ/mol

Complex		MINI-1[a]	6-31G*[d]	Extended[e]
$\mathrm{C{\equiv}O\cdots Li^+}$	$R(\mathrm{OLi^+})$	184.7	195.5	190
	$R(\mathrm{CO})$	123.6 (+1.1)[b]	112.8 (+1.4)[b]	112.8[f]
	$-\Delta E$	96.7	65.3	61
	$-\Delta E_c$	82.4	—	—
$\mathrm{Li^+\cdots C{\equiv}O}$	$R(\mathrm{Li^+C})$	226.1	226.8	220
	$R(\mathrm{CO})$	121.5 (−1.0)[b]	110.2 (−1.2)[b]	112.8[f]
	$-\Delta E$	50.6	60.7	51
	$-\Delta E_c$	48.0	—	—
$\mathrm{N{\equiv}N\cdots Li^+}$	$R(\mathrm{NLi^+})$	203.0[c]	200.5[g]	210
	$-\Delta E$	64.4	50.2	54
	$-\Delta E_c$	60.3	—	—

[a] This work.
[b] Change compared to the free molecule.
[c] The $\mathrm{N{\equiv}N}$ bond length was fixed at 109.8 pm (experimental value).
[d] Ref. [25].
[e] Ref. [30], the $\mathrm{C{\equiv}O}$ and $\mathrm{N{\equiv}N}$ distances were fixed at 112.8 and 109.4 pm, respectively.
[f] Not optimized.
[g] The $\mathrm{N{\equiv}N}$ bond length was fixed at 108.3 pm (3-21G value [25]).

the stability order of the two isomers is reversed [30]. Complete gradient optimizations were performed for the $Na^{+}\cdots CH_4$ and $Na^{+}\cdots C_2H_4$ complexes. The energy minimum structures are shown in Fig. 1. The following results were obtained: $Na^{+}\cdots CH_4$, $R(Na^{+}C) = 279$ pm, $\Delta E = -18.6$ and $\Delta E_c = -15.2$ kJ/mol; $Na^{+}\cdots C_2H_4$, $R = 268$ pm (cf. Fig. 1), $\Delta E = -51.6$ and $\Delta E_c = -42.6$ kJ/mol. These values are virtually identical with the results of calculations employing the combined 4-31G (ligand)/STO-3G (cation, inner shell exponents reoptimized) basis set ($Na^{+}\cdots CH_4$: $R(Na^{+}C) = 276$ pm, $\Delta E = -16.7$ kJ/mol [17]; $Na^{+}\cdots C_2H_4$: $R = 267$ pm (cf. Fig. 1), $\Delta E = -48.5$ and $\Delta E_c = -44.0$ kJ/mol [10]). We are not aware of any extended basis set calculation for these complexes.

3. Ion pair

The binding of cations to anionic ligands, which is frequently encountered in molecular biology or zeolite chemistry (e.g. [17]), is a particularly difficult problem to tackle for minimal basis sets. We selected $(HO)_2PO_2^{-}\cdots Mg^{2+}$ as a test system as for this system extended basis set results have recently become available [31].

Table 7. Equilibrium distances, R (pm), and stabilization energies, ΔE (kJ/mol), for the complex formation $Mg^{2+} + H_2PO_4^{-} \rightleftharpoons (H_2PO_4Mg)^{+}$

Basis set	R	R_c	$-\Delta E$	$-\Delta E_c$ [d]	$\Delta\varepsilon(H_2PO_4^{-})$ [d]
MINI-1	244	249	1387	1298	83.3
STO-3G [b]	243	—	2079	—	—
Extended [c]	234	—	1445	1444	1.0

[a] This work, fixed geometry (cf. Ref. [31]) for $H_2PO_4^{-}$.
[b] Ref. [32], complete optimization.
[c] Ref. [31], fixed geometry for $H_2PO_4^{-}$.
[d] Basis set superposition error of the $H_2PO_4^{-}$ anion calculated at R_c.

Table 8. Atomic charges in the $(H_2PO_4Mg)^{+}$ system

		Net atomic charges					Charge transfer
Species	Basis set	P	$O_{1/2}$	$O_{3/4}$	H	Mg	to Mg^{2+}
$H_2PO_4^{-}$	MINI-1	1.86	−0.93	−0.80	+0.30	—	—
	MINI-1 [a]	1.87	−0.89	−0.79	+0.31	−0.12	0.12
	Extd. [b]	1.71	−0.97	−0.75	+0.35	—	—
$(H_2PO_4Mg)^{+}$ [c]	MINI-1	1.86	−0.92	−0.72	+0.37	+1.69	0.31 (0.18) [d]
	Extd. [b]	1.71	−0.77	−0.59	+0.38	+1.25	0.75

[a] Within the basis set of the whole complex, i.e. the ghost orbitals of Mg were present.
[b] Ref. [31].
[c] At a distance of $R = 234$ pm (cf. Fig. 1). This is the optimum distance found in the extended basis set calculation.
[d] After correcting for the BSSE.

The bond lengths and angles of $(HO)_2PO_2^-$ were taken from Ref. [31] and remained unchanged in the complex. The only parameter optimized was the $P \cdots Mg^{2+}$ distance (Fig. 1). The MINI-1 results together with the extended basis set values [31] and STO-3G values [32] are given in Table 7. While STO-3G heavily exaggerates the interaction energy which is certainly due to the BSSE, the BSSE with MINI-1 is only 6.5%. The corrected MINI-1 interaction energy is 90% of the reference value. Again, too small polarizabilities calculated at the MINI-1 level may account for this result. Although we feel that, for very extended basis sets involving rather diffuse functions, a Mulliken population analysis is of limited value, a comparison of the net charges obtained is provided in Table 8. A substantial charge transfer to the cation emerges in this representation which is only partially reproduced by the MINI-1 calculations.

4. Anion-molecule complexes

The results for the $Y^- \cdots H_2O$ complexes ($Y^- = F^-$, Cl^-, Br^-) are presented in Table 9. The experimental geometry for water was kept rigid and the potential curves for the linear structures of $F^- \cdots H_2O$ and $Cl^- \cdots H_2O$ and for the bifurcated structure of $Br^- \cdots H_2O$ were investigated (cf. Fig. 1). The MINI-1 BSSE for the

Table 9. Equilibrium distance, R (pm) and interaction energy ΔE (kJ/mol), for the linear hydrogen bonded structures of $F^- \cdots HOH$ and $Cl^- \cdots HOH$ complexes and the bifurcated (C_{2v}) structure for the $Br^- \cdots H_2O$ complex. The results obtained after correcting for the BSSE are indicated by a subscript c

Y^-	Method	R	R_c	$-\Delta E$	$-\Delta E_c$	$\Delta\varepsilon(Y^-)$[d]	Time[g]
F^-	MINI-1	231	238	239	143	89.5	1.0
	MINI-1, 2*p* reopt[a]	246	248	137	111	22.9	1.0
	MINI-1 +*p*(0.102)[b]	258	271	84	68	3.4	2.4
	4-31G	246	248	165	121	42.0	4.3
	Extended[c]	255	—	95	—	—	—
Cl^-	MINI-1	305	314	73	58	12.7	1.0
	MINI-1, 3*p* reopt[a]	320	325	58	51	5.3	1.0
	MINI-1 +*p*(0.181)[b]	317	321	60	53	4.4	1.4
	4-31G +*p*(0.07)[3]	328[e]	—	57	—	—	—
	Extended[c]	331	—	48	—	—	—
Br^-	MINI-1	338	350	51	45	4.6	
	MINI-1, 4*p* reopt[a]	346	356	47	44	2.4	
	Extended[f]	344	—	54	—	—	

[a] The scale factors for the outer *p*-shells of F^-, Cl^- and Br^- are 0.920, 0.945 and 0.952, respectively.

[b] A single flat gaussian function has been added to the basis set of F^- and Cl^-. The optimum orbital exponent is shown in parenthesis.

[c] Ref. [34].

[d] Basis set superposition error of the anion Y^- calculated at R_c.

[e] Ref. [15], complete geometry optimization was performed.

[f] Ref. [33].

[g] Relative values with respect to the times consumed by MINI-1 for $F^- \cdots H_2O$ and $Cl^- \cdots H_2O$, respectively.

$F^-\cdots H_2O$ complex (−89.5 kJ/mol) is almost as large as the interaction energy expected (−95 kJ/mol) (for an explanation see the introduction). Passing to the split valence 4-31G basis set, which makes one additional orbital available to the electrons in F^-, the BSSE (−42 kJ/mol) is still not acceptable and the computer time is increased by a factor of 4.3. The situation becomes more favorable with the heavier anions. In the $Cl^-\cdots H_2O$ complex the BSSE obtained by MINI-1 calculations (−12.7 kJ/mol) is about one fourth of the interaction energy expected (−48 kJ/mol). In the $Br^-\cdots H_2O$ complex it seems that the relative magnitude of the BSSE is further decreased although the comparison is hampered by the fact that the basis set employed in the reference calculations [33] is not extended enough to ensure that the BSSE is negligible.

In an initial attempt to improve the results, a single additional *p*-function was added to the basis set for the F^- and Cl^- anions. The exponents were optimized for the free anions, resulting in total energies of −98.85210 and −457.37348 a.u. for $\zeta = 0.102$ and 0.181, respectively. The energies obtained with the standard basis sets are −98.62407 and −457.27501 a.u. It can be seen from Table 9 that the problem of the large BSSE at the anion has disappeared. After adding flat *p*-functions to the MINI-1 and 4-31G basis sets for the $Cl^-\cdots H_2O$ complex both yield virtually the same result. For the $F^-\cdots H_2O$ complex a corrected interaction energy is obtained which is smaller (in absolute terms) than the extended basis set value. The additional function increases the computer time by factors of 2.4 and 1.4 for the $F^-\cdots H_2O$ and $Cl^-\cdots H_2O$ complexes, respectively. In considering basis sets which are least modified compared to the original atomic basis sets, we alternatively tried to improve the basis sets for the anions by applying a common scale factor to the exponents of all 3 primitive functions in the outer *p*-shell. Thus, the minimal contraction scheme of the basis set is retained and the computing time is not increased. For this scale factor, values of 0.920, 0.945 and 0.952 were obtained by minimizing the total energies for F^-, Cl^- and Br^-, respectively. The following energy values were obtained: −98.72404, −457.30863, and −2562.20043 a.u. (the standard basis set yields −2562.17662 for Br^-). By virtue of this procedure, the BSSE is strongly reduced for $F^-\cdots H_2O$ and $Cl^-\cdots H_2O$. The resulting equilibrium distances are too small by only 4 and 3%, respectively, and the interaction energies are overestimated by only 17 and 6%, respectively. For $Br^-\cdots H_2O$, reoptimizing the 4*p*-exponents has little effect.

In conclusion, the MINI-1 basis set can be successfully applied to anionic complexes provided that a scale factor is introduced for the outermost *p*-shell.

5. Comparison with other minimal basis sets

The above discussion has clearly shown that MINI-1 is far superior to STO-3G. The greater time consumed for the integral computation will not be important, as in calculations including the Boys–Bernardi procedure for evaluating the BSSE the time of the iterations predominates. Two other attempts, those by Clementi [11, 12, 13] and by Kołos [16] (see Part I for further references), to employ minimal basis sets, which are better suited for intermolecular interactions, were already mentioned. Kołos has studied several points of various potential curves for the $F^- \cdots H_2O$ and $H_2O \cdots Be^{2+}$ complexes using van Duijneveldt's basis set (called "OLD" in a later paper by Kołos). The result for the linear structure of $F^- \cdots H_2O$ at $R(FO) = 265$ pm $\Delta E = -118$ and $\Delta E_c = -104$ agrees surprisingly well with the extended basis set result $\Delta E = -93$ kJ/mol. This is because special basis functions were used for F^-. This result supports our approach of reoptimizing some exponents in the basis set for the fluorine atom to make it applicable to the F^- anion. Kołos stated for cations that his results for the $H_2O \cdots Be^{2+}$ complex were so poor that no numerical values were given in the paper.

Clementi's results for the $H_2O \cdots Zn^{2+}$ complex [13] $R = 198$ and $R_c = 204$ pm, $\Delta E = -316$ and $\Delta E_c = -305$ kJ/mol can be directly compared with the entries for $H_2O \cdots Zn^{2+}$ in Table 1. For the $(CH_3)_2O \cdots Li^+$ complex [11], the calculated interaction energy is -131 kJ/mol and the experimental value is -159 kJ/mol. Thus, this basis set tends to yield too large cation–molecule distances and too small (in absolute terms) interaction energies. No investigation of anionic systems has come to our attention.

It can be concluded that MINI-1 is at least as efficient as the other minimal basis sets considered.

6. Conclusions

The MINI-1 basis set can be successfully applied without any modifications to cation-molecule complexes. The magnitude of the BSSE shows that there is a balance between the description of the cation and the ligand. For anion–molecule complexes this level is reached if a scaling factor (derived once for the atomic anions) is introduced for the outermost *p*-shell. It was not surprising that MINI-1 proved far superior to the STO-3G basis set. Moreover, it yields results which are comparable with or even better than those obtained using other minimal or near minimal (e.g. 4-31G) basis sets. The primary virtue of the MINI-1 basis set is that it gives uniformly good results for a broad variety of systems and many elements (up to Rb^+ or Br^-). In fact, with all the complexes investigated not one failure of the basis set was observed. Some minor deficiencies indicate a lack of polarizability – an inherent feature of minimal basis sets. Thus, the recommendation made in Part I is confirmed. This basis set should be employed if (i) considering an interaction problem for the first time, (ii) it is necessary to calculate and compare many systems, (iii) the subsystems involved are growing larger, and (iv) interaction energies are required for many geometry points of a complex.

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