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THE THEORY OF INTERMOLECULAR FORCES - A SURVEY OF RESULTS

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Abstract - The applicability of ab initio SCF and correlation energy calculations for the computation of intermolecular forces is discussed. The total interaction energy is divided into individual contributions by means of perturbation theory. The 1/R expansion is used to discuss the importance of the dispersion energy in comparison to those terms which are already included at the Hartree-Fock level. The importance of a correct description of molecular properties like multipole moments and polarizability is stressed in connection with a reliable calculation of interaction energies. Several selected examples illustrate these general considerations.

INTRODUCTION

For the quantum chemical calculation of intermolecular forces both perturbational and variational methods have been applied. We distinguish the case of larger intermolecular distances from that of intermediate distances. In the first case intermolecular overlap is negligible. Moreover, in many cases the 1/R (multipole-) expansion is very useful (For the mathematical properties of the 1/R expansion see e.g. Ref.1). At intermediate distances intermolecular overlap is non negligible. A number of methods have been proposed to overcome the difficulties arising in perturbation theory because of overlap- and exchange effects (Refs.2-6). In variational calculations these difficulties are avoided by treating the intermolecular complex as a "supermolecule" and computing the interaction energy as the difference with respect to the isolated systems. Most of the calculations on intermolecular forces follow the variational approach. Since our interests in this paper concentrate on numerical results we shall discuss mainly the variational calculations and shall use perturbation theory only for the classification of individual terms. We do not attempt to achieve any completeness of the recent literature. For that purpose we refer the reader to a number of reviews which have appeared in the last few years (Refs.7-9). We rather want to treat some selected examples and to discuss the possibilities and difficulties of different methods. In a very simple way we shall try to estimate the applicability and accuracy of ab initio calculations.

METHODS OF CALCULATION

Ab initio SCF calculations with different basis sets - ranging from minimal to near Hartree Fock quality - have been performed for a large number of systems. Electron correlation contributions may either be calculated by conventional configuration interaction (CI) or multiconfiguration SCF (MCSCF) methods. An efficient alternative is given by pair correlation methods (e.g. the CEPA-PNO scheme). For a review of current methods see Ref.10.

As mentioned in the introduction the interaction energy of the intermolecular complex A...B is computed as

$$\Delta E^{AB} = E^{AB} - E^{A} - E^{B} \qquad (1)$$

We further decompose ΔE^{AB} into contributions derived from the Hartree-Fock approximation and from electron correlation:

$$\Delta E^{AB} = \Delta E^{AB}_{HF} + \Delta E^{AB}_{CORR} \qquad (2)$$

According to the works of Morokuma (Ref.11), Dreyfus and Pullman (Ref.12) and Kollman and Allen (Ref.13) the Hartree Fock energy is decomposed into Coulomb-, polarization-, exchange- and charge transfer contributions. Starting from the Hartree-Fock wave functions ψ^0_A and ψ^0_B and the corresponding energies E^0_A and E^0_B of the isolated molecules, the Hartree-product $\psi^0_A \cdot \psi^0_B$ and the antisymmetrized product (with respect to intermolecular electron exchange) $\mathcal{A}(\psi^0_A \cdot \psi^0_B)$ are formed. In a similar way one obtains $\psi_A \cdot \psi_B$ and $\mathcal{A}(\psi_A \cdot \psi_B)$ which are the Hartree product and antisymmetrized product energy-optimized for the intermolecular complex AB. On the basis of these wavefunctions the following interaction terms are computed (H is the total molecular Hamiltonian):

$$\Delta E_{COUL} = \langle \psi_A^o \cdot \psi_B^o | H | \psi_A^o \cdot \psi_B^o \rangle - E_A^o - E_B^o$$

$$\Delta E_{POL} = \langle \psi_A \cdot \psi_B | H | \psi_A \cdot \psi_B \rangle - \langle \psi_A^o \cdot \psi_B^o | H | \psi_A^o \cdot \psi_B^o \rangle$$

$$\Delta E_{EX} = \langle \mathcal{A}(\psi_A^o \cdot \psi_B^o) | H | \mathcal{A}(\psi_A^o \cdot \psi_B^o) \rangle - \langle \psi_A^o \psi_B^o | H | \psi_A^o \psi_B^o \rangle \qquad (3)$$

$$\Delta E_{CHT} = \langle \mathcal{A}(\psi_A^o \cdot \psi_B^o) | H | \mathcal{A}(\psi_A^o \cdot \psi_B^o) \rangle - E_A^o - E_B^o - \Delta E_{COUL} - \Delta E_{POL} - \Delta E_{Ex}$$

$$\Delta E_1 = \Delta E_{COUL} + \Delta E_{EX}$$

$$\Delta E_2 = \Delta E_{POL} + \Delta E_{CHT}$$

$$\Delta E_{TOTAL} = \langle \mathcal{A}(\psi_A \cdot \psi_B) | H | \mathcal{A}(\psi_A \cdot \psi_B) \rangle - E_A^o - E_B^o = \Delta E_{COUL} + \Delta E_{POL} + \Delta E_{EX} + \Delta E_{CHT}$$

As one may see from the equations above the dispersion interaction is not accounted for by the Hartree Fock approach. It is essentially the intersystem correlation energy which represents the dispersion energy. The contributions to the interaction energy in eqs.(3) are, of course, not the exact ones since they are computed at the Hartree-Fock level. Thus, we obtain from electron correlation, in addition to the dispersion interaction, also correction terms to the contributions collected in eqs.(3).

A completely different approach has been proposed by Gordon and Kim (Refs.14&15) based on the electron gas model. An application to the system He-HF will be discussed further below.

PROPERTIES OF ISOLATED MOLECULES [+)]

In many cases, the asymptotic 1/R expansion is a good approximation to the exact interaction energy at large intermolecular distances. The molecular quantities like multipole moments and polarizabilities enter into this expansion. Therefore, it is useful to check the accuracy of the computed interaction energy without any expansion in a given basis by computing with the same basis set e.g. dipole moment and polarizability of the isolated molecules.

It is now well documented by a series of calculations of several authors (Refs.16-19) that it is not sufficient to use basis sets which give only good SCF energies for the isolated molecule. One has to add further functions (with relatively small exponents) if one wants to obtain reliable multipole moments and polarizabilities.

Basis set effects and the influence of electron correlation were studied extensively in several investigations (Refs.16-21). In tables 1 and 2 the basis set dependence of the dipole moment μ and the polarizability α is studied for H_2O and HCN. In agreement with the results of other groups one can roughly classify the basis sets into three groups:
a) basis sets without polarization functions (no.1) give unsatisfactory results. The component of the polarization tensor which points perpendicularly to the molecular plane (α_{yy}) has only 1/8 of its true value.
b) basis sets with one polarization set (no.2-5 and 7) yield intermediate results
c) basis sets containing more than one polarization set (no.6,8) including d-sets with small exponents give satisfactory results close to the Hartree-Fock limit. The importance of adding polarization functions with small exponents has been shown also by Werner and Meyer (Ref.19).

Electron correlation effects on dipole moments and polarizabilities have been studied by several groups (Refs.18-20). In case of H_2O the most extensive investigations gave a decrease of about 4% in the value of the dipole moment (Ref.20) and an increase of about 12% in the average polarizability (Ref.19).

At intermediate distances the exchange contributions to the interaction energy are determined mainly by the asymptotic form ($r \to \infty$) of the wavefunction. Since Gaussian functions decrease too fast in comparison to the correct exponential decrease (Ref.25) it is necessary to add to medium sized basis sets (e.g. double zeta quality) s and p functions with small exponents. Thereby, the superposition error is diminished also.

+)conversion factors: 1.a.e.u. = 672.57$_0$kcal/mol, 1 kcal = 4.1855 kJ
1 bohr = 0.52917 Å

TABLE 1. Basis sets applied in SCF calculations

Molecule	Basis No.	GTO's and contractions	Polariaztion functions[+)]	Ref.
H_2O	1	7s3p/3s 42/2		22
	2	9s5p/4s 53/3	$1d_O(1.0)$	22[++)]
	3	9s5p/4s 53/3	$1d_O(1.0), 1p_H(0.7)$	22[+++)]
	4	11s7p/6s 75/4	$1d_O(1.0), 1p_H(0.75)$	23
	5	11s7p/6s 43/2	$1d_O(1.0), 1p_H(0.75)$	24
	6	11s7p/6s 75/4	$3d_O(1.2,0.3,0.1), 2p_H(0.5,0.2)$	21
HCN	7	8s4p/3s 53/2	$1d_C(0.7), 1d_N(0.9), 1p_H(0.75)$	21
	8	8s4p/3s 53/2	$2d_C(0.7,0.15), 2d_N(0.9,0.15), 1p_H(0.75)$	21

[+)] Orbital exponents are given in parantheses

[++)] Huzinaga's 8s4p basis has been used as a starting point and one additional s and p function has been added and optimized subsequently.

[+++)] The contraction applied differs from that in the reference.

TABLE 2. SCF energies, electric dipole moments and polarizabilities for H_2O and HCN[+)]

Molecule	Basis No.	$-E_{SCF}$ (a.e.u.)	μ_z(D)	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$
				($\AA^3$)			
H_2O	1	75.87756	2.40	0.97	0.17	0.58	0.57
	2	76.03711	2.20	1.12	0.81	0.90	0.94
	3	76.03499	2.34	1.03	0.48	0.78	0.76
	4	76.05748	2.22	1.14	0.79	0.91	0.95
	5	76.05308	2.20	1.09	0.45	0.84	0.79
	6	76.05777	1.98	1.35	1.16	1.25	1.25
	exp.		1.85				1.46
HCN	7	92.81330	3.26	1.38	1.38	3.16	1.97
	8	92.81450	3.26	1.93	1.93	3.16	2.34
	exp.		2.99	1.92	1.92	3.92	2.59

[+)] The cartesian coordinates have been chosen in the following way: H_2O:C_2-axis=z, molecular plane = (x,z); HCN: C -axis=z

THE SYSTEMS He/HF, H_2/HF, $(HF)_2$ and $(H_2O)_2$

In this section relatively weak interactions are investigated. The He atom and the H_2 molecule serve as a model for a nonpolar species whereas HF and H_2O represent the polar part. The 1/R expansion would lead to the following prediction for the strength of the intermolecular interaction: in He/HF the dispersion interaction ($\sim 1/R^6$), and the polarization energy (dipole/induced dipole, $\sim 1/R^6$) dominate. For H_2/HF the Coulomb interaction (quadrupole/dipole $\sim 1/R^4$), the polarization energy (dipole/induced dipole; $\sim 1/R^6$) and the dispersion interaction ($\sim 1/R^6$) are of interest. For the dimers $(HF)_2$ and $(H_2O)_2$ the dipole/dipole interaction ($\sim 1/R^3$) will be most important.

From this list we conclude that for the series He/HF to $(HF)_2$ the interaction increases and the contribution of the dispersion energy, represented by the intersystem correlation energy, decreases. Thus the Hartree-Fock approximation will probably be insufficient in the case of He/HF (and similar interactions) and quite good in the case of $(HF)_2$ and $(H_2O)_2$. Since exchange and charge transfer contributions are included in Hartree Fock we may expect in the latter cases that also at intermediate distances the Hartree-Fock approximation will be reliable.

These qualitative considerations, strictly valid only at large intermolecular distances, are illustrated by a series of ab initio SCF and correlation energy calculations (Ref.18,26,27). The structures investigated are shown in Fig.1. Corresponding energy curves are given in Figs.2 and 3. (ΔE_{tot} in figs.2 and 3 is given by $\Delta E_{tot} = E_{SCF} + E_{corr}(IEPA)$. $\Delta E_{corr}(IEPA)$ is the intersystem correlation energy calculated with IEPA. For more information see Refs.26& 27). These two figures clearly confirm our conclusion from above. In the case of He/HF the question whether IA or IB is more stable is determined by electron correlation.

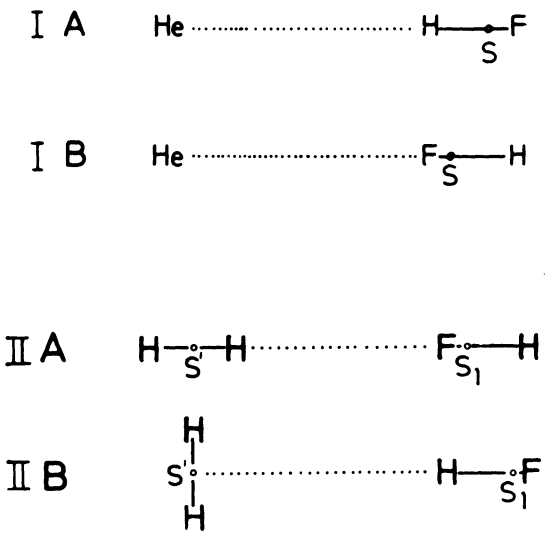

Fig.1. Geometries for the He/HF and H_2/HF interaction. The distances are measured from the center of gravity of the electric charge in HF (0.133 a.u. off from F).

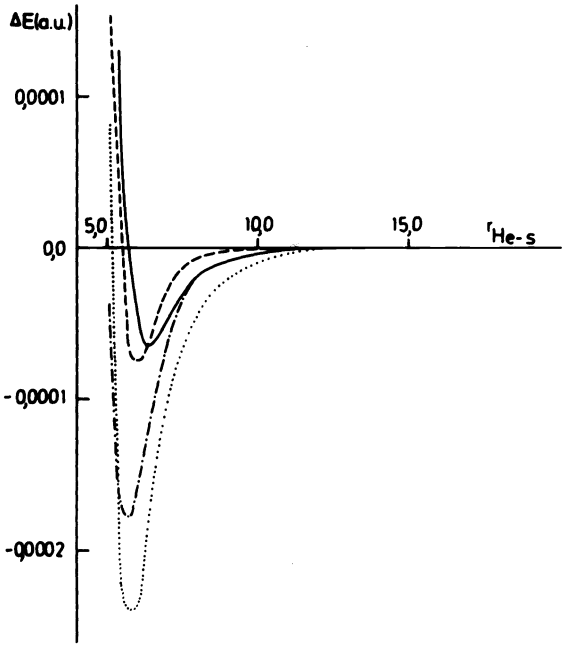

Fig.2. Interaction energies for the system He...HF: —— ΔE_{SCF} (Structure IA); - - - - - - ΔE_{SCF}(structure IB); ····· ΔE_{tot}(structure A); -·-·- ΔE_{tot}(structure B).

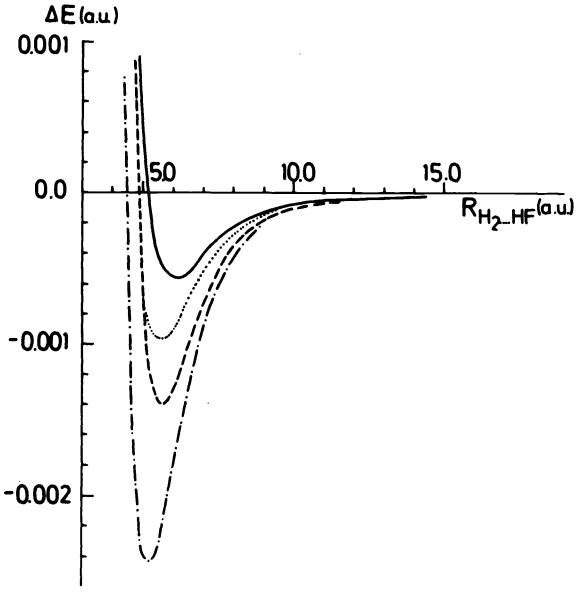

Fig.3. Interaction energies for H_2...HF.—— ΔE_{SCF}(IA), - - - - - ΔE_{SCF}(IB), ····· ΔE_{tot}(IIA) -·-·-·- ΔE_{tot}(IIB).

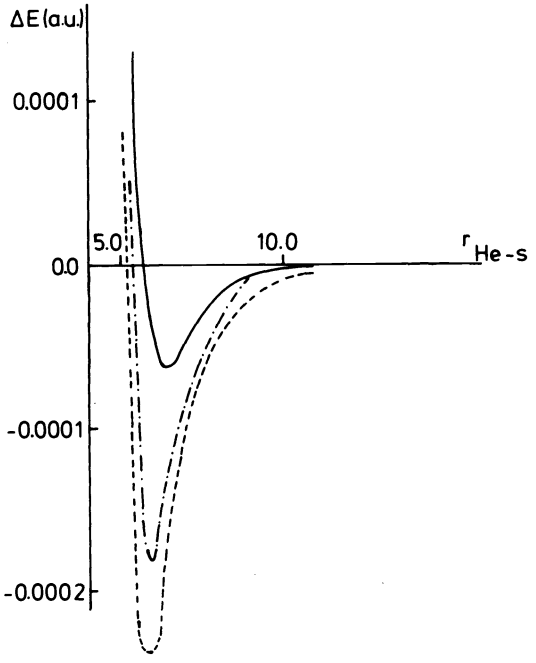

Fig. 4. Comparison of ab initio results (see also fig.2) and the Gordon Kim potential for He...HF.—— ΔE_{SCF}, - - - ΔE_{tot}, -·-·- GK potential (Ref.28).

In fig.4 our SCF and IEPA results for structure IA are compared with calculations by Detrich and Conn (Ref.28) using the Gordon-Kim (GK-)method. Their results lie inbetween the SCF and IEPA curves. As the authors conclude from their investigations some care has to be taken when interpreting GK results for the long range region since neither dispersion nor polarization contributions are included in their calculations.

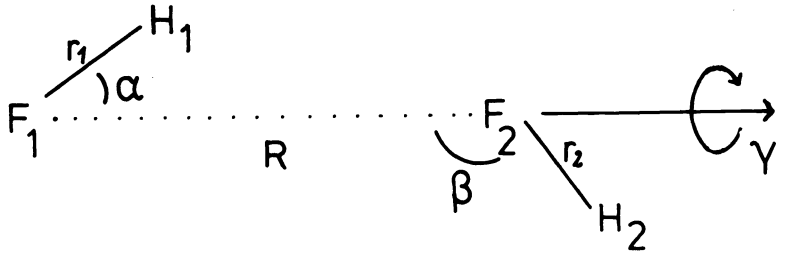

Fig.5. Geometry parameters for $(HF)_2$

Results for the HF dimer are collected in tables 3 and 4. For the definition of geometry see fig.5. Comparison with previous calculations demonstrate the importance of large s and p sets and the use of d functions with small exponents. Even with respect to the large scale computations performed by Diercksen and Kraemer (Ref.30) we still find a significant reduction in $|\Delta E|$. A similar decrease in $|\Delta E|$ was also found by Popkie et al. (Ref.31) and by Jeziorski and van Hemert (Ref.32) for $(H_2O)_2$ (see also table 6). The harmonic force constants change drastically in going from a 4-31 G basis set to our larger sets (see table 4).

TABLE 3. SCF results for $(HF)_2$ [1]

	This work[2]	Ref.29[3]	Ref.30
R	2.830	2.72	2.85
r_1	0.904	0.906[4]	0.917[4]
r_2	0.902	0.906[4]	0.917[4]
α	6.0	15	0[4]
β	123	100	140
ΔE_{SCF}	-3.80	-6.0	-4.50

[1] Distances are given in Å, angles in degrees and energies in kcal/mol.

[2] The same basis as in Ref.18 was used. R_{HF} of the isolated molecule is obtained with this basis as 0.900 Å.

[3] 6-31 results

[4] not optimized.

TABLE 4. Harmonic force constants (mdyn/Å) for $(HF)_2$ [1]

intermolecular vibration	k_{RR}	$k_{\alpha\alpha}/R^2$	$k_{\beta\beta}/R^2$	$k_{R\alpha}/r_1$	$k_{R\beta}/r_2$	$k_{\alpha\beta}/(r_1r_2)$	$k_{\gamma\gamma}/R^2$
this work[4]	0.126	0.119	0.0389	-0.0076	0.0074	-0.0444	0.00012
ref.29	0.20[2]	0.15[2]	0.068[2]	0.017[3]	0.005[3]	0.054[3]	0.0009[2]

intramolecular vibration	$k_{r_1r_1}$	$k_{r_2r_2}$	$k_{r_1r_2}$
this work	10.76	10.98	-0.0682
ref.29	9.17[3]	9.37[3]	-0.040

[1] $k_{r_1r_1}$ for the isolated HF molecule is 11.17 mdyn/Å in this work and 9.55 mdyn/Å for the 4-31G basis

[2] 6-31G** basis [3] 4-31G basis [4] the same basis set as in Ref.18 was used.

For the linear configuration of $(HF)_2$ a negligible effect of electron correlation energy on bond distances and force constants is observed (Ref.18). Table 5 shows intermolecular electron correlation contributions corresponding to dispersion energy and the intramolecular terms (corrections to Hartree-Fock, see also sec.2).

TABLE 5. Analysis of correlation energy contributions in $(HF)_2$(linear arrangement, (Ref.18))[1].

R_{FF}(Å)	ΔE_{SCF}	ΔE_{CORR}^{ias}[2]	ΔE_{CORR}^{irs}[2]	ΔE_{CORR}^{tot}	ΔE_{tot}
2.91	-3.46	1.01	-0.805	0.209	-3.25
6.35	-0.424	0.078	-0.0044	0.0734	-0.351

[1] Energies are given in kcal/mol

[2] ΔE_{CORR}^{ias} and ΔE_{CORR}^{irs} are the intrasystem and intersystem correlation energy respectively, calculated by IEPA.

At large distances the intrasystem correlation energy is an order of magnitude larger than the intersystem correlation energy. This behaviour represents well the fact that the former contribution is (to a first approximation) a correction to the Coulomb energy ($\sim 1/R^3$) and that the latter term describes the dispersion energy ($\sim 1/R^6$). Since the dipole moment of the HF molecule is too large at the Hartree Fock level (Refs.18&19), the respective Coulomb energy is too attractive within the Hartree-Fock approximation. Thus the intrasystem correlation compensates this error and is positive (repulsive). At smaller distances near the energy minimum these considerations are of course not strictly applicable any more. However, the qualitative trends do not change as the distance decreases. At the energy minimum intra- and intersystem correlation energy compensate in our calculation almost completely. This example shows that it is very difficult to include electron correlation correction to hydrogen bonded systems in a consistent way. It is certainly not adequate to include the dispersion part only, since the other contributions are of equal importance and have, at least in our example, the opposite effect.

CI calculations have been performed for $(H_2O)_2$ by Diercksen et al. (Ref.33) and Matsuoka et al. (Ref.34). In both investigations a stabilizing effect of electron correlation is observed. Numerical results are collected in Table 6. by comparison of the results obtained with one and two d sets on oxygen, respectively, one finds a significant influence on ΔE_{SCF} by the second d set. (compare first line in table 6 with second and third one). This parallels our findings for $(HF)_2$. We expect further effects by the second d set on the correlation energy contributions to ΔE also.

TABLE 6. The water dimer. Energies are given in kcal/mol

	basis for oxygen	ΔE_{SCF}	ΔE_{CORR}	ΔE_{TOT}
Ref.33	11s7p1d	-5.14	-0.91	-6.05
Ref.32	11s7p2d	-4.02	-	-
Ref.31	11s7p2d1f	-3.90	-	-
Ref.34	11s7p1d	-4.55	-1.08	-5.63

ION-WATER INTERACTIONS

From our qualitative considerations of the previous section we may expect that for the ion-water complexes the Hartree-Fock approximation will be a good one. This fact is well established by the calculations of Diercksen et al. (Ref.33).

Table 7 shows the basis set dependence of the interaction energy for Li^+/H_2O and Li^+/HCN at various geometries (Ref.21). The two basis sets compared differ with respect to the number of polariaztion functions only. Around the minima of the energy surfaces the basis set effects are rather small. But as one can see from the individual contributions ΔE_1 and ΔE_2 to ΔE (see also the second section) a favourable error cancellation occurs.

TABLE 7. Partitioning of SCF energies of interaction in the complexes Li^+OH_2 and Li^+.NCH (Ref.21).

Complex	Geometry[+)]	Basis No.	Energies of interaction (kcal/mole) ΔE_1	ΔE_2	ΔE_{SCF}
$Li^+.OH_2$	a:R_{OLi}=3.4	4	-25.6	-8.6	-34.1
	γ=0	6	-22.0	-11.7	-33.7
	a:R_{OLi}=3.5	4	-22.8	-7.9	-30.8
	γ=45°	6	-20.5	-10.8	-31.3
	a:R_{OLi}=4.0	4	-10.4	-6.3	-16.7
	γ=90°	6	-10.6	-8.0	-18.5
Li^+.NCH	b:A,d=4.0	7	9.9	-9.6	0.3
		8	9.6	-11.8	-2.2
	b:B,d=4.0	7	1.7	-9.1	-7.3
		8	1.3	-11.5	-10.2
	b:C,d=4.0	7	-6.4	-9.0	-15.4
		8	-6.8	-11.3	-18.0
	b:D,R_{NLi}=3.69	7	-24.1	-12.5	-36.6
		8	-23.1	-13.5	-36.7

[+)] For the geometries of the complexes see fig.6. All distances are given in atomic units. For the definition of the basis sets see Table 1.

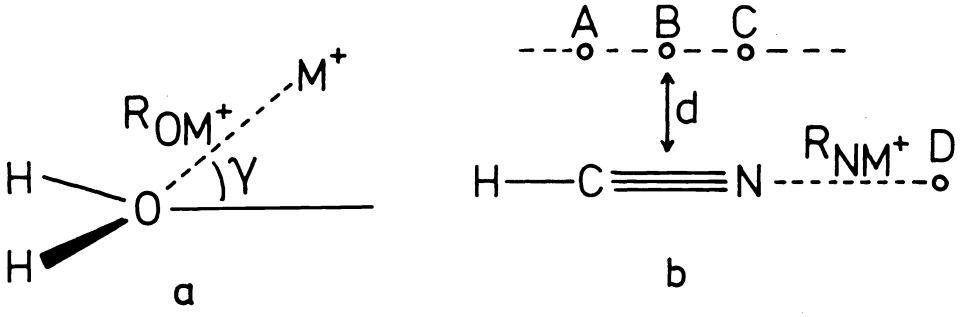

Fig. 6. Intermolecular geometries applied in the calculations reported here (a: $Li^+.OH_2$; b:Li^+.NCH, A,B,C and D refers to different positions of the cation).

Changes in the electrostatic contribution enter into ΔE_1 and changes in the polarization energy enter into ΔE_2. As we saw from table 2 addition of a flat d set results in a reduction of μ and an increase of α. Thus $|\Delta E_1|$ is reduced and $|\Delta E_2|$ is increased by going from basis no.4 to 6 leading to the above mentioned error cancellation. For other structures (e.g. Li^+.HCN, structure A,B,C) such a compensation does not occur and larger net effects of the basis set are found. Especially the region where the interaction changes from attraction to repulsion is strongly dependent on the basis set used.

The interaction energies for a series of cation-water complexes are given in Table 8 and agree quite well with results obtained by Kistenmacher et al.(Ref.36) and Kollman and Kuntz (Ref.37). Table 9 shows the changes of the water geometry in the complex with respect to the isolated water molecule. The bond distance ion is increased in the series Li^+, Mg^{2+}, Al^{3+}.

TABLE 8. Water-cation interactions[+)]

	ΔE (kcal/mole)	R(Å)[++)]
Li^+	-33.9	1.86
Na^+	-24.1	2.24
Mg^{2+}	-78.0	1.93
Al^{3+}	-178.6	1.76

[+)] Ref.35

[++)] Oxygen-cation distance

TABLE 9. Deformation of the bond distance r_{OH} and bond angle α in cation-water complexes with respect to the isolated water molecule.

	Δr_{OH}(Å)	Δα(deg.)	Lit.
Li^+	+0.005	-0.5	38
Mg^{2+}	+0.017	-0.01	35
Al^{3+}	+0.053	+1.13	35

The bond angle α of water is decreased for Li^+ and Mg^{2+} but is increased in the case of Al^{3+}/H_2O.

CONCLUSIONS

For a correct computation of molecular properties which are relevant for intermolecular interactions relatively large basis sets containing several polarization functions are necessary. Since errors in individual contributions to the total energy difference add up in one part of the energy surface and cancel in another part, a balanced description of the whole energy surface is possible only with extended basis sets.

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