Theoret. Chim. Acta (Berl.) 46, 117–127 (1977)

THEORETICA CHIMICA ACTA

Theoretical Investigation of Structure and Stability of Oligomers of LiH, NaH, LiF, and NaF

Martin Rupp and Reinhart Ahlrichs

Theoretische Chemie, Institut für Physikalische Chemie und Elektrochemie der Universität Karlsruhe, D-7500 Karlsruhe, Federal Republic of Germany

The molecules Li_nH_n, Na_nH_n, Li_nF_n, $n=1,\ldots,4$, and NaF and Na_2F_2 are investigated by means of extended basis set SCF and CEPA-PNO computations. In analogy to the D_{2h} structure of dimers, it is found that trimers have a planar cyclic D_{3h} equilibrium geometry. For the tetramer of LiH and NaH, the D_{4h} structure has about the same energy as the 3-dimensional T_d structure, whereas the latter is definitely favoured for Li_4F_4. Correlation effects are investigated for the oligomerization of LiH and the dimerization of LiF. The effect of electron correlation on corresponding ΔE turns out to be small (<4 kJ/mol), except for the case that the T_d tetramer is involved which has a rather large correlation energy.

Key words: Oligomers of LiH, NaH, LiF, NaF – Correlation effect on ΔE

1. Introduction

In the present paper we report theoretical *ab initio* computations for the molecules $(LiH)_n$, $(NaH)_n$, $(LiF)_n$ for $n=1, 2, 3, 4$, and for NaF and Na_2F_2. With these investigations we want to make a contribution to the solution of the following problems.

What is the equilibrium structure of oligomers of the ionic molecules AB (A = Li, Na; B = H, F) in the gas phase?

How large is ΔE_f for the reaction

$$(AB)_n(g)+AB(g)=(AB)_{n+1}(g)+\Delta E_f^{(n+1)}(AB) \qquad (1)$$

and how does $\Delta E_f^{(n)}$ depend on n?

How much computational effort is required to determine ΔE_f with an accuracy of 5 to 10 kJ/mol? What effect has electron correlation on ΔE_f?

Relatively few experimental or theoretical investigations of oligomers of alkali-hydrides and -fluorides have been published until now. No experimental facts are known about the oligomers of LiH and NaH, although the monomers are well known, of course. Theoretical studies have been reported for the dimers Li_2H_2 [1–4] and Na_2H_2 [5], which predict a planar cyclic structure with D_{2h} molecular symmetry. The presence of dimers and trimers of LiF and NaF has been concluded from mass spectroscopic [6] and from molecular beam [7] investigations. The energies of formation obtained from the corresponding measurements are quite uncertain and range for $\Delta E_f^{(2)}$(LiF) from -246 ± 8 kJ/mol to -280 ± 17 kJ/mol [6–8]. $\Delta E_f^{(3)}$(LiF) could only be estimated to be between -200 and -265 kJ/mol [9]. On the basis of infrared spectra (obtained by matrix-isolation technique) [10] and electron diffraction measurements [11] it has been concluded that Li_2F_2 has D_{2h} [10, 11] and Li_3F_3 D_{3h} [10] equilibrium structure. The very same conclusion has been reached from simple ionic model calculations [12, 13]. The only quantum mechanical *ab initio* computation for oligomers of alkali fluorides has been performed on the SCF level for Li_2F_2, which also indicates a D_{2h} structure [5].

The computations reported in this work are mostly carried out on the SCF level. The CEPA-PNO [14, 15] method is applied to study the influence of electron correlation on $\Delta E_f^{(n)}$(LiH) and $\Delta E_f^{(2)}$(LiF) as more or less representative examples. Reactions of the kind (1) are of closed shell type – reactants and products having a closed shell electronic structure – for which correlation effects are often small [16]. Among the reactions considered in this work, correlation effects have already been studied for the dimerization of LiH, where the most elaborate computation yields a correlation contribution of -4 kJ/mol to the total $\Delta E_f^{(2)}$ (LiH) = -202 kJ/mol [3].

2. Basis Set Considerations

We always used linear combinations of Gaussian lobes as basis functions. AOs of *d* type were mimiced by lobes as described elsewhere [17].

Starting point for the basis selection are Huzinaga's atomic sets [18]. In order to reduce the computation time as much as possible we have tried to find basis sets just flexible enough to reproduce ΔE_f with an accuracy of ≈ 5 kJ/mol, mostly within the SCF approximation. Since we are dealing with typical ionic compounds

Table 1. AO Basis sets for H, F, Li, Na

Atom	Huzinaga set[a]	Additional functions type and orbital exponent
H	(5*s*/3*s*)	*p*:0.32
F	(8*s* 4*p*/4*s* 2*p*)	*p*:0.09
Li	(7*s*/3*s*)	*p*:0.28
Na	(9*s* 6*p*/5*s* 3*p*)	—

[a] Ref. [18].

little flexibility is required for the "cations" Li, Na, whereas care is necessary for the choice of the basis of "anions" H and F. The accumulation of electronic charge on H or F leads to rather spread out charge distributions which must be properly described to get reliable ΔE_f. We have performed pilot calculations for some monomers and dimers using the corresponding $\Delta E_f^{(2)}$ as measure for the quality of the basis. Due to the similarity of charge distributions in the oligomers we then expect that $\Delta E_f^{(n)}$, $n > 2$, should be obtained with roughly the same accuracy as $\Delta E_f^{(2)}$. Let us now discuss in some detail the basis sets used, which are collected in Table 1.

2.1. Li *and* H *Basis Set*

We used LiH and Li_2H_2 as test cases and the extended basis set – Li (9*s* 2*p* 1*d*/5*s* 2*p* 1*d*), H (6*s* 2*p* 1*d*/4*s* 2*p* 1*d*) – results published previously [3] as standard. After some pilot calculations we decided to use the Li (7*s* 1*p*/3*s* 1*p*) and H (5*s* 1*p*/3*s* 1*p*) set, compare Table 1. The *p* AOs on Li and H were optimized for LiH with inclusion of valence correlation. The Li basis contains little flexibility in the valence shell, only a single *s*- and *p*-group, but, as a result of the ionic character of the bond this is obviously sufficient. The SCF energies of LiH and Li_2H_2 are only 9 kJ/mol and 17 kJ/mol higher than those obtained from the large basis [3], compare also Table 5 below. We now get a dimerization energy on SCF and CEPA level of −199 kJ/mol and −202 kJ/mol which is in excellent agreement with the corresponding results computed with the large basis, −198 kJ/mol and −202 kJ/mol [3].

2.2. Na *Basis Set*

The sodium basis was chosen after pilot SCF calculations on NaH, and Na_2H_2 in D_{2h} symmetry. The results are collected in Table 2. We started with a Huzinaga [18] (10*s* 6*p*/6*s* 4*p*) basis which was the largest one for which Na_4H_4 could be

Table 2. Test of Na basis sets for NaH and Na_2H_2[a]

Huzinaga Na basis[b]		E_{SCF}[a.u.] NaH	Na_2H_2	$\Delta E_f^{(2)}$ (NaH) [kJ/mol]
1	(10*s* 6*p*/6*s* 4*p*)	−162.34975	−324.76052	−160.2
2	(10*s* 6*p*/6*s* 3*p*)	−162.34973	−324.76048	−160.3
3[c]	(9*s* 6*p*/5*s* 3*p*)	−162.34237	−324.74785	−160.3
4	(9*s* 5*p*/5*s* 3*p*)	−162.33850	−324.73846	−161.4
5	(9*s* 5*p*/5*s* 3*p*)+*p*(0.2)	−162.33942	−324.74051	−161.96

[a] H basis as specified in Table 1, structure parameters of NaH and Na_2H_2 (D_{2h}) are taken from Baskin *et al.* [5]. NaH: $R = 1.92$ Å, Na_2H_2 (D_{2h}): R(Na–Na) = 2.88 Å, R(H–H) = 3.18 Å.

[b] Ref. [18].

[c] Basis set used in further computations.

treated with reasonable effort and then tried to reduce the necessary computational labour. A stronger contraction of the p AOs ($10s\ 6p/6s\ 3p$) had virtually no effect on the SCF energies and especially on $\Delta E_f^{(2)}$ (NaH), compare lines 1 and 2 of Table 2. Replacement of the $10s$ by a $9s$ basis, line 3 Table 2, had also no effect on $\Delta E_f^{(2)}$ (NaH). The results for a ($9s\ 5p/5s\ 3p$) basis, line 4, even if augmented by an additional diffuse p AO, line 5, gave slightly different $\Delta E_f^{(2)}$ (NaH). We therefore decided to use the ($9s\ 6p/5s\ 3p$) basis, line 3, for further computations. However, the dimerization energies of NaH are remarkably insensitive with respect to the Na basis, in agreement with what one expects.

2.3. F *Basis Set*

The fluorine basis was determined from SCF computations on LiF and Li_2F_2, with the Li basis specified in Table 1. In these pilot calculations the molecular structures were chosen according to Herzberg [19] (LiF) and Baskin *et al.* [5] (Li_2F_2). The results collected in Table 3 clearly show that a careful choice of the anion basis is of great importance. The $\Delta E_f^{(2)}$ (LiF), see Table 3, differ by ≈ 50 kJ/mol corresponding to ≈ 17% of the total ΔE_f. Our results indicate that d AOs on F are not of too much importance for the computation of $\Delta E_f^{(2)}$, whereas augmentation of Huzinaga basis sets by diffuse p AOs seems to be necessary to describe the electron distribution of "F^-" and to get reliable ΔE_f. We have chosen the basis of line 3, Table 3, for the remaining investigations, since this gives a reasonable compromise between accuracy and computertime.

Table 3. Test of F basis for LiF and Li_2F_2[a]

F basis[b]		E_{SCF} [a.u.] LiF	Li_2F_2	$\Delta E_f^{(2)}$ (LiF) kJ/mol
1	I	−106.89863	−213.92402	−332.9
2	II	−106.95410	−214.02563	−308.4
3[c]	I+p(0.09)	−106.92352	−213.95735	−289.7
4	II+p(0.09)	−106.96307	−214.03580	−288.0
5	I+p(0.09)+d(1.2)	−106.92747	−213.96306	−284.1
6	II+p(0.09)+d(1.2)	−106.96698	−214.04149	−282.4

[a] Li bases as given in Table 1, structure parameters are taken from Herzberg [19] for LiF ($R = 1.51$ Å), and Baskin *et al.* [5] for Li_2F_2 (D_{2h}): R(Li–Li) = 2.22 Å, R(F–F) = 2.65 Å.

[b] I denotes a Huzinaga [18] ($8s\ 4p/4s\ 2p$) and II a ($9s\ 5p/5s\ 3p$) basis.

[c] This basis was used in the remaining computations.

3. Determination of Structure Constants

For the dimers we considered the D_{2h} structures only since all previous experimental and theoretical studies [1–5, 10–13] indicate this structure to be the most stable one. A rather extensive search for the equilibrium geometry of trimers and tetramers was carried out on the SCF level for Li_3H_3 and Li_4H_4 only. For the remaining molecules we considered only the structures that turned out to be favoured for Li_3H_3 and Li_4H_4.

3.1. *Structure of* Li_3H_3

The three structures considered for the trimer of LiH are shown in Fig. 1. The lowest energy was obtained for I, the planar cyclic case with D_{3h} molecular geometry. The corresponding equilibrium structure and energy are given in Tables 4 and 5, below. We have checked that I is stable with respect to out-of-plane distortions.

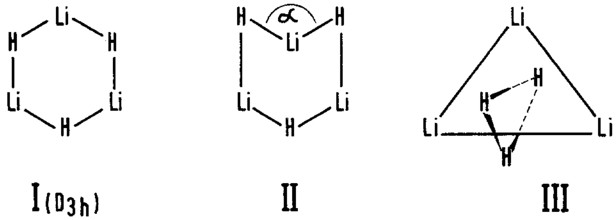

Fig. 1. Structures considered for Li_3H_3

Structure II, Fig. 1, which is also planar, consists of a chain of LiH units with antiparallel arrangement and can be obtained from the D_{2h} dimer by addition of a third LiH. We have optimized the angle α, see Fig. 1, the intramolecular and intermolecular LiH distances. The SCF energy was then still 50 kJ/mol higher than for the D_{3h} structure, and further optimizations appeared to be unnecessary since II is clearly less stable than I.

The three dimensional structure III consists of two isosceles of Li and H atoms respectively, with C_{2v} symmetry. After chain optimization of all structure parameters, keeping C_{2v} symmetry, the total energy was even 107 kJ/mol higher than for structure I.

Our computations lead to the expected result that the D_{3h} structure is the most stable one for the trimer of ionic AB molecules.

3.2. *Structure of* Li_4H_4

The three geometries considered are shown in Fig. 2. It turns out that the cyclic planar D_{4h} (I) and the three dimensional T_d structure (II), see Tables 4 and 5 for the structure parameters and SCF energies, are of comparable stability. On the SCF level the T_d structure is only 2 kJ/mol lower in energy than D_{4h}.

The geometry for the planar chain structure III was chosen in accordance with that of structure II for the trimer, see Fig. 1. The SCF energy was then 63 kJ/mol above the T_d energy. Due to this relatively large difference it appeared not worth-

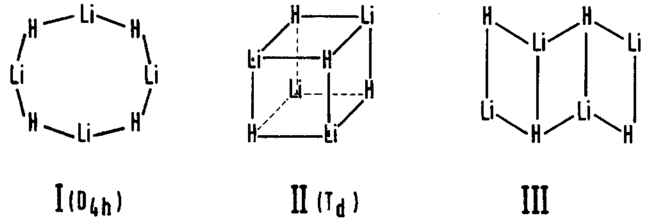

Fig. 2. Structures considered for Li_4H_4

Table 4. Structure constants [Å][a]

	Symmetry	R(M–M)	R(X–X)	R(M–X)
LiH	$C_{\infty v}$	—	—	1.62 (1.595)[b]
Li_2H_2	D_{2h}	2.29	2.72	1.78
	Ref. [3]	2.26	2.68	1.75
	Ref. [5]	2.36	2.73	1.80
Li_3H_3	D_{3h}	2.81	3.19	1.74
Li_4H_4	D_{4h}	3.04	3.32	1.73
Li_4H_4	T_d	2.49	2.75	1.86
crystal	(NaCl)	2.89	2.89	2.04
NaH	$C_{\infty v}$	—	—	1.91 (1.89)[b]
Na_2H_2	D_{2h}	2.82	3.12	2.10
	Ref. [5]	2.88	3.18	2.15
Na_3H_3	D_{3h}	3.47	3.75	2.09
Na_4H_4	D_{4h}	3.71	3.93	2.07
Na_4H_4	T_d	3.10	3.28	2.25
crystal	(NaCl)	3.45	3.45	2.44
LiF	$C_{\infty v}$	—	—	1.58 (1.564)[c]
Li_2F_2	D_{2h}	2.26	2.55	1.70
	Ref. [5]	2.22	2.65	1.73
Li_3F_3	D_{3h}	2.90	3.02	1.71
Li_4F_4	D_{4h}	3.14	3.18	1.71
Li_4F_4	T_d	2.50	2.67	1.83
crystal	(NaCl)	2.85	2.85	2.02
NaF	$C_{\infty v}$	—	—	1.95
Na_2F_2	D_{2h}	2.83	3.01	2.06

[a] Determined on the SCF level using basis sets given in Table 1.
[b] Ref. [19] (exp.).
[c] Ref. [21] (exp.).

while to perform further geometry optimizations for this case. We note that the T_d structure can be considered as a "cyclic chain" derived from III. As a result of attractive Coulomb forces between the "end" molecules, the transition from III to II is at least intuitively expected to lead to a lower energy, in agreement with our computations.

3.3. Optimized Structures for Oligomers of LiH, NaH, LiF *and* NaF

The final structure parameters collected in Table 4 were determined on the SCF level in using the basis sets specified in Table 1. As a consequence of our investigation of Li_3H_3 and Li_4H_4, we considered only the D_{3h} structure for the trimers but the D_{4h} and T_d structures for the tetramers, since the latter turned out to be of about the same stability for Li_4H_4. We cannot be sure, of course, that these do in fact correspond to the most stable structures of the corresponding molecules, but a more extensive search for equilibrium geometries is prohibitive by the huge requirements of computation time. However, if more stable structures exist, they may be expected to be only insignificantly lower in energy, which means that at least our ΔE_f values are expected to be quite reliable.

Let us discuss briefly some features of the geometrical parameters collected in Table 4. In all cases we find the anion–anion distance to be larger than that between cations.

The anion–cation distances also show a consistent pattern. The shortest distance is always found for the monomers (in the average ≈78% of the corresponding distance in the crystal), the largest for the T_d tetramer (≈91%), whereas the cyclic structures are in between (≈85%) and show little variation with n. This trend is in accordance with physical and chemical intuition: the covalent character of bonds decreases (increase of ionic character) in the order monomer, cyclic D_{nh} oligomers, T_d tetramer. The T_d tetramer is still far from being a good model for the ionic crystal since each ion is surrounded by only three counterions as compared to 6 in the NaCl crystal structure.

4. Computed Total Energies and Reaction Energies

4.1. SCF *Results*

The total SCF energies and the corresponding reaction energies $\Delta E_f^{(n)}$ (AB) are collected in Tables 5 and 6. The dominant features of the various ΔE_f may be rationalized in terms of electronegativities and ionic radii of the atoms involved. If structure parameters are virtually identical, as for corresponding hydrides and

Table 5. Computed SCF energies [a.u.][a]

	LiH	NaH	LiF	NaF
monomer	−7.98231[b]	−162.34239	−106.92634	−261.27155
dimer	−16.04032[b]	−324.74585	−213.95724	−522.64410
trimer	−24.09966	−487.15626	−320.98567	—
D_{4h} tetramer	−32.15006	−649.55778	−428.00250	—
T_d tetramer	−32.15080	−649.55678	−428.00909	—

[a] Obtained with basis sets of Table 1, for the structures specified in Table 4.

[b] Large GTO basis set results from Ref. [3] LiH: −7.98593; Li_2H_2: −16.04680.

Table 6. Computed SCF level reaction energies $\Delta E_f^{(n)}$ [kJ/mol][a]

n	LiH	NaH	LiF	NaF
2	-198.8[b]	-160.4[c]	-274.6[d]	-265.3
3	-202.3	-178.7	-268.2	—
$4(D_{4h})$	-178.8	-155.3	-237.7	—
$4(T_d)$	-180.8	-152.7	-255.0	—

[a] Obtained from SCF energies of Table 5, compare Eq. (1) for the definition of $\Delta E_f^{(n)}$.

[b] Ref. [3]: -197.9 (SCF), Ref. [5]: -193.3.

[c] Ref. [5]: -158.2.

[d] Ref. [5]: -279.1.

fluorides, see Table 4, we expect $|\Delta E_f^{(n)}|$ to be the larger the more ionic the bond (increased Coulomb interaction), i.e. the larger the difference in electronegativities. The $|\Delta E_f^{(n)}|$ for oligomers of LiF are in fact ≈ 70 kJ/mol larger than for the corresponding hydrides, see Table 6. On the other hand, as Na and Li have about the same electronegativities, but markedly different ionic radii, we may attribute the fact that $|\Delta E_f^{(n)}$ (NaH)$|$ is ≈ 25 kJ/mol smaller than the corresponding $|\Delta E_f^{(n)}$ (LiH)$|$, to the larger interatomic distances in Na_nH_n as compared to Li_nH_n.

For the tetramer of NaH we find the very same situation as for LiH; the D_{4h} and T_d structures are of comparable stability, at least on the SCF level. However, the more ionic LiF prefers the more ionic T_d structure which is 17 kJ/mol lower than the D_{4h} tetramer. Since all compounds considered have crystal structures of NaCl type, we expect that oligomers for sufficiently large n have structures with coordination number 6. This then certainly rules out chain-like structures D_{nh} for sufficiently large n.

4.2. *Influence of Electron Correlation on Oligomerization Energies*

We have performed CEPA-PNO [14, 15] computations for the oligomers of LiH and for LiF, Li_2F_2 in order to study the effect of electron correlation on the corresponding ΔE. In these computations we have accounted for valence shell correlation effects only.

The results for Li_nH_n, $n=1, \ldots, 4$, are collected in Table 7. Besides the total CEPA correlation energy E_c^{CEPA}, we also report the pair correlation energies ε_{ij} (computed on the basis of localized MOs) which add up to E_c^{CEPA}

$$E_c^{\text{CEPA}} = \sum_{i \leq j} \varepsilon_{ij} \tag{2}$$

Since the localized MOs for each individual Li_nH_n structure are equivalent for symmetry reasons, we have essentially to deal with a single interpair (ε_{ij}) and a single intrapair contribution (ε_{ii}) only for each molecular structure. In the D_{4h} tetramer we have in fact two different types of interpair terms, but the non-next neighbour terms turned out to be negligibly small.

Table 7. CEPA correlation and total energies for Li_nH_n [a.u.][a]

	LiH	Li_2H_2	Li_3H_3	$Li_4H_4(D_{4h})$	$Li_4H_4(T_d)$
Intrapair ε_{ii}	-0.03127	-0.03075	-0.03090	-0.03106	-0.03043
Interpair ε_{ij}	—	-0.00227	-0.00095	-0.00071	-0.00186
E^c_{CEPA}	-0.03127	-0.06378	-0.09557	-0.12709	-0.13287
$E_{\text{SCF}}+E^c_{\text{CEPA}}$	-8.01358	-16.10410	-24.19523	-32.27714	-32.28367
Contribution to $\Delta E_f^{(n)}$ [kJ/mol]					
Intrapair		2.72	0.17	-0.71	5.90
Interpair		-5.98	-1.55	0.04	-21.76
Total correlation		-3.26[b]	-1.38	-0.67	-15.86
SCF + CEPA		-202.09[c]	-203.68	-179.49	-196.6

[a] Basis set as given in Table 1, structures as in Table 4. The meaning of the various terms is explained in the text, see especially Eq. (2).

[b] Ref. [3]: -4.2, Ref. [3]: -202.1.

Inspection of the ε_{ij} (Table 7) shows that intrapair contributions decrease (in absolute value) and the interpair terms increase with decreasing H–H distance, which in turn is a measure for the distance between centroids of charge of corresponding localized MOs. This behaviour is expected, of course, and has already been described and discussed for a number of cases [3, 16, 20].

For the dimerization, trimerization and tetramerization to D_{4h}, we find an almost negligible influence of correlation – less than 4 kJ/mol – on the corresponding $\Delta E_f^{(n)}$ (LiH), since changes in intra- and interpair contributions almost cancel. The situation is quite different if we compare the D_{4h} and T_d tetramers. The correlation energy for T_d ($E_c^{\text{CEPA}} = -0.1329$ a.u.) stabilizes this structure as compared to D_{4h} ($E_c^{\text{CEPA}} = -0.1271$ a.u.) by 15 kJ/mol. This effect results mainly from the larger number of next neighbour interpair contributions, 6 for T_d and 4 for D_{4h}.

From the computed correlation energies we conclude that the T_d tetramer Li_4H_4 is in fact more stable than the D_{4h} ring structure. The difference in total energies ($E_{\text{SCF}} + E_c^{\text{CEPA}}$) of 17 kJ/mol is clearly not too large, but our SCF energies are probably very close to the SCF limit and the CEPA method and basis set used should at least predict the trend of correlation energies correctly.

We now turn to the discussion of correlation effects on the dimerization energy of LiF. The SCF calculation showed already the importance of a sufficiently flexible fluorine basis, and this is certainly even more crucial for the computation of correlation energies. We therefore used the following extended basis set on fluorine.

F basis: $(9s\ 5p/5s\ 3p) + p(\eta = 0.09) + 2d(\eta = 0.7, 2.0)$

With the Li basis given in Table 1, we then obtained the following energies (at geometries specified in Table 4),

LiF $E_{SCF} = -106.97135$ a.u. (3a)
$E_{CEPA} = -107.20955$ a.u. (3b)

Li_2F_2 $E_{SCF} = -214.04534$ a.u. (4a)
$E_{CEPA} = -214.52031$ a.u. (4b)

From these results we get the dimerization energies on SCF and CEPA level

SCF: $\Delta E_f^{(2)}$ (LiF) $= -270$ kJ/mol (5)

CEPA: $\Delta E_f^{(2)}$ (LiF) $= -266$ kJ/mol (6)

The SCF result differs by 5 kJ/mol only from the one obtained with the smaller basis, compare Table 5, which may be considered as a confirmation of the reliability of the smaller basis as far as reaction energies on SCF level are concerned. The net effect of electron correlation on the dimerization energy (4 kJ/mol) is virtually negligible. We do not attribute much significance to the fact that the correlation contribution to $\Delta E_f^{(2)}$ (LiF) is positive, whereas it is negative for all $\Delta E_f^{(n)}$ (LiH) and for related cases reported in the literature [3, 20]. Smaller basis sets than the one discussed above always gave an even larger positive contribution of correlation effects to $\Delta E_f^{(2)}$ (LiF), and it is quite conceivable that a more extended basis set will reduce the correlation contribution to zero or even negative values.

The results reported in this subsection for Li_nH_n, LiF and Li_2F_2 indicate in any case that correlation effects are of not too much importance for the corresponding oligomerization energies. An exception is the relative extreme case of D_{4h} and T_d tetramers of LiH, and probably also the other systems, where correlation clearly favours the T_d structure. Even in this case the correlation contribution of 16 kJ/mol corresponds to only about 8% of the corresponding tetramerization energy $\Delta E_f^{(4)}$ (LiH), see Table 7.

5. Summary

The computations reported in the present paper confirm as expected the strong tendency of NaH, LiH, NaF and LiF to oligomerize, which increases in this order, see e.g. Table 6.

The equilibrium structures of the corresponding compounds are quite similar, a planar cyclic geometry for dimers and trimers (D_{2h} and D_{3h} symmetry), and T_d for the tetramer, which points already to the crystal structure. Our SCF results predict in fact the NaH tetramer to have a D_{4h} structure, but electron correlation is expected to tip the balance in favour of T_d.

Concerning the basis set problem, we have found that relatively small basis sets are sufficient for the computation of reaction energies $\Delta E_f^{(n)}$ on the SCF level, provided the anion basis is flexible enough to describe the "diffuse" charge distribution of the anion.

Our results further show that electron correlation has rather small influence (≤ 4 kJ/mol) on $\Delta E_f^{(2)}$ (LiH), $\Delta E_f^{(3)}$ (LiH), $\Delta E_f^{(2)}$ (LiF), but contributes -16 kJ/mol to $\Delta E_f^{(4)}$ (LiH), see Table 7.

Acknowledgements. The computations reported in this paper have been performed at the "Rechenzentrum der Universität Karlsruhe". This work has been supported in part by the "Fonds der Chemischen Industrie".

References

1. Tyndall, J. R., Companion, A. L.: J. Chem. Phys. **52**, 2036 (1970)
2. Kollman, P. A., Bender, C. F., Rothenberg, S.: J. Am. Chem. Soc. **94**, 8016 (1972)
3. Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **35**, 59 (1974)
4. Dill, J. D., Schleyer, P. v. R., Binkley, J. S., Pople, J. A.: J. Am. Chem. Soc. (in press)
5. Baskin, C. P., Bender, C. F., Kollman, P. A.: J. Am. Chem. Soc. **95**, 5868 (1973)
6. Schoonmaker, R. C., Porter, R. F.: J. Chem. Phys. **30**, 283 (1959)
7. Eisenstadt, M., Rothenberg, G. M., Kusch, P.: J. Chem. Phys. **29**, 797 (1958)
8. Scheffee, R. S., Margrave, J. L.: J. Chem. Phys. **31**, 1682 (1959)
9. Porter, R. F., Schoonmaker, R. C.: J. Chem. Phys. **29**, 1070 (1958)
10. Snelson, A.: J. Chem. Phys. **46**, 3652 (1967)
11. Akishin, P. A., Rambidi, N. G.: Z. Phys. Chem. (Leipzig) **213**, 111 (1960)
12. Milne, T. A., Cubiciotti, D.: J. Chem. Phys. **29**, 846 (1958); J. Chem. Phys. **30**, 1625 (1959)
13. Welch, D. O., Lazareth, O. W., Dienes, G. J.: J. Chem. Phys. **64**, 835 (1976)
14. Meyer, W.: Intern. J. Quantum Chem. **S5**, 341 (1971); Meyer, W.: J. Chem. Phys. **58**, 1017 (1973)
15. Ahlrichs, R., Driessler, F., Kutzelnigg, W., Lischka, H., Staemmler, V.: J. Chem. Phys. **62**, 1235 (1975)
16. Keil, F., Ahlrichs, R.: J. Am. Chem. Soc. **98**, 4787 (1976)
17. Driessler, F., Ahlrichs, R.: Chem. Phys. Letters **23**, 571 (1973)
18. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965); Huzinaga, S.: Approximate atomic functions I, II, Technical Report, Division of Theoretical Chemistry, University of Alberta (1971)
19. Herzberg, G.: Spectra of diatomic molecules. Princeton, N.J.: Van Nostrand 1955
20. Ahlrichs, R., Keil, F.: Chem. Phys. **8**, 384 (1975)
21. Veazey, S. E., Gordy, W.: Phys. Rev. **A183**, 1303 (1965)

Received May 20, 1977