Theoret. Chim. Acta (Berl.) 35, 59—68 (1974)

The Influence of Electron Correlation on Reaction Energies. The Dimerization Energies of BH_3 and LiH

Reinhart Ahlrichs

Institut für Physikalische Chemie und Elektrochemie der Universität Karlsruhe, Germany

Received February 28, 1974

Results of rigorous computations employing extended Gaussian-type basis sets are reported for BH_3, B_2H_6, LiH, and Li_2H_2 in their respective equilibrium geometries. The dimerization energy of BH_3 is calculated as -20.7 kcal/mol within the Hartree-Fock approximation and as -36.6 kcal/mol if electron correlation is included. The corresponding results for the dimerization of LiH are -47.3 kcal/mol and -48.3 kcal/mol. Partitioning of the correlation energy contributions allows to attribute the effect of electron correlation to the increase of next neighbour bond interactions on the dimerization of BH_3 and LiH. The difficulties of accurate computations of reaction energies are discussed in detail.

Key words: Reaction energies, computation of ~ – B_2H_6 – Li_2H_2

1. Introduction

B_2H_6 is the simplest electron deficient compound known from experiment, whereas Li_2H_2 may be considered as the simplest conceivable molecule of this class at all. Further small electron deficient compounds like Be_2H_4 [1] and $BeBH_5$ [2] have been investigated theoretically but are also not known experimentally, like Li_2H_2. Detailed investigations of the electron distribution [3] and the mechanism of chemical binding in B_2H_6 have been reported in the literature [4–8]. Of general interest for the understanding of the stability of electron deficient compounds is especially ΔE_f of the reaction (1)

$$2\,BH_3(g) \rightarrow B_2H_6(g)\,, \tag{1}$$

which is still rather uncertain. Experimental values between -25 and -60 kcal/mol are reported in the literature [9].

Hartree-Fock (HF) calculations with small Slater-type basis sets [10] or medium size Gaussian basis sets [8, 11] yield ΔE_f values of about -10 kcal/mol, which is not in the most favourable range of experimental values. The effect of electron correlation on ΔE_f was first investigated by Gélus, Ahlrichs, Staemmler, and Kutzelnigg (GASK) [11] by means of the IEPA-PNO method [12] (IEPA = independent electron pair approximation, PNO = pair natural orbitals). Using a Gaussian basis of double zeta quality (5*s*-, 2*p*-groups on boron and 2*s*-groups on hydrogen), GASK obtained a HF contribution of -8.5 kcal/mol and a correlation energy contribution of -16.8 kcal/mol to ΔE_f (a *p*-set on hydrogen was added for the computation of the correlation energy). The corresponding estimated true values were -11.5 and -25.2 kcal/mol respectively, yielding a total ΔE_f of -36 kcal/mol.

The most accurate HF computations for BH_3 and B_2H_6 have been reported recently by Lipscomb and coworkers [3, 13], who obtained a HF contribution of -19.0 kcal/mol to ΔE_f. It is then suggested [13], that GASK's estimate for the correlation contribution to ΔE_f might be too large, since addition of the calculated value (-15.8 kcal/mol) to the HF value of -19.0 kcal/mol would give $\Delta E_f = -35.8$ kcal/mol, which is close to a recent kinetic value [14] for ΔE_f.

Kollman, Bender, and Rothenberg (KBR) [15] have published the only theoretical investigation of Li_2H_2. They predict Li_2H_2 to be most stable in the centrosymmetric D_{2h} structure. KBR [15] reported the following ΔE_f values for the reaction (2)

$$2\,\mathrm{LiH}(g) \rightarrow \mathrm{Li_2H_2}(g) \tag{2}$$

HF approximation: $\Delta E_f = -46.2$ kcal/mol
including electron correlation: $\Delta E_f = -45.8$ kcal/mol.

These authors thus predict the correlation energy in 2 LiH to be larger than in Li_2H_2, in contrast to the result obtained by GASK [11] for B_2H_6. Unfortunately, KBR used a rather inappropriate basis set which recovered only about 50% of the total valence shell correlation energy. In consideration of this state of affairs it appeared worthwhile to repeat the computation of ΔE_f for the reactions (1) and (2) with more extended basis sets as those used previously (by GASK [11] and KBR [15]) and employing a more refined method for the computation of correlation energies.

2. Method

We use the HF approximation as starting point for the treatment of electron correlation. The difficulty in computing correlation energies by means of a conventional configuration interaction (CI) calculation is the large number of configurations that can be constructed and the slow convergence of the CI expansion. The present B_2H_6 basis of 68 groups leads e.g. to 184000 doubly substituted determinants (from the valence shell), which corresponds to 65000 pure singlet functions or 9000 spin and symmetry adapted configurations. The largest possible reduction of the number of doubly substituted configurations to be included in a CI is obtained if the latter is based on the so-called PNO's, which may be defined for arbitrary wave functions Ψ in the following way. Let u denote a spin irreducible pair [16] of occupied MO's and Φ_u the part of Ψ in which all the double substitutions of the pair u are collected (in an obvious notation)

$$\Phi_u = \Phi_{\mathrm{HF}} + \sum_{ij} c_u^{ij} \Phi_u^{ij} . \tag{3a}$$

(Throughout this paper we neglect singly substituted configurations.) The PNO's X_u^i are then defined as the natural orbitals of Φ_u. Let now Φ_u^i denote the doubly substituted configuration with the replacement $u \rightarrow X_u^i X_u^i$ if u is a singlet pair, or $u \rightarrow X_u^i X_u^{i'}$ if u is a triplet pair, for the details the reader is referred to Ref. [11]. In terms of the Φ_u^i one then has

$$\Phi_u = \Phi_{\mathrm{HF}} + \sum_i c_u^i \Phi_u^i , \tag{3b}$$

i.e. the nondiagonal replacements Φ_u^{ij} now have vanishing CI coefficients. The c_u^i and the energy contributions due to the Φ_u^i furthermore form a rapidly decreasing series and it is usually sufficient to include 10–30 terms in (3b) to exhaust the basis set. Our final B_2H_6 computation included 124 doubles only.

The disadvantage connected with the use of PNO's is their partial nonorthogonality

$$(X_u^i|X_v^j) \neq 0\,, \quad \text{if} \quad u \neq v \tag{4}$$

whereas, of course,

$$(X_u^i|X_u^j) = \delta_{ij}\,. \tag{5}$$

The relationship (4) fortunately leads to minor complications only in the evaluation of matrix elements between arbitrary doubly substituted configurations.

Various methods have been proposed to obtain accurate approximations of the correct PNO's prior to the knowledge of the total wave function [17]. In the present study we have used a new method for this purpose [18] which is more accurate and less computer time comsuming than the one used previously in our program [12, 19].

The total correlation energy ε is obtained in three different degrees of approximation, which will now be discussed. For this purpose it is convenient to use a combined lable $a=(u,i)$, i.e. we simply write Φ_a for Φ_u^i, etc. A partial summation $\sum\limits_{a\in u}$ is then understood to run over the HF term and all $a=(u,i)$ for the given u. The CI coefficients c_a (with $c_{\mathrm{HF}}=1$) and the pair correlation energies ε_u are within the IEPA obtained as solutions of the following set of equations, where $H_{ab}=(\Phi_a|H|\Phi_b)$,

$$\sum_{b\in u} H_{ab}c_b = (E_{\mathrm{HF}} + \varepsilon_u^{\mathrm{IEPA}})\,c_a\,, \qquad a\in u\,. \tag{6}$$

The total correlation energy is then within this approximation given as

$$\varepsilon^{\mathrm{IEPA}} = \sum_u \varepsilon_u^{\mathrm{IEPA}}\,. \tag{7}$$

Next we perform a CI with Φ_{HF} and all doubly substituted configurations, for which Meyer has suggested the name PNO-CI [20]:

$$\sum_b H_{ab}c_b = (E_{\mathrm{HF}} + \varepsilon^{\mathrm{PNOCI}})\,c_a\,. \tag{8}$$

The PNO-CI correlation energy $\varepsilon^{\mathrm{PNOCI}}$ can, of course, also be divided into pair distributions such that Eq. (9) holds [20]

$$\varepsilon^{\mathrm{PNOCI}} = \sum_u \varepsilon_u^{\mathrm{PNOCI}}\,. \tag{9}$$

We finally perform a computation within the coupled electron pair approximation (CEPA), first proposed by Meyer [20]

$$\sum_b H_{ab}c_b = (E_{\mathrm{HF}} + \varepsilon_u^{\mathrm{CEPA}})\,c_a\,, \qquad a\in u\,, \tag{10}$$

$$\varepsilon^{\mathrm{CEPA}} = \sum_u \varepsilon_u^{\mathrm{CEPA}}\,. \tag{11}$$

As the just listed methods to obtain approximations to the true correlation energy have already been described in the literature [21], we shall not discuss them in detail here. A few comments, however, will be helpfull for the discussion of the results presented in this paper.

1. The PNO-CI is a variational calculation, whereas the IEPA and the CEPA are not.

2. The PNO-CI wavefunction and correlation energy has an incorrect dependence on the number of electrons [22]. This may e.g. be demonstrated by a consideration of a system of n noninteracting electron pairs, like He_n at sufficiently large internuclear distances. The exact wavefunction for this system is simply the antisymmetrized product of the corresponding helium wavefunctions, and it is easily verified that the PNO-CI wavefunction has vanishing overlap with the exact wavefunction in the limit $n \rightarrow \infty$. It can further be shown that $\varepsilon^{\mathrm{PNOCI}}$ increases only like $\sqrt{n}$ for large n. These deficiences of the PNO-CI are due to the fact that higher than doubly substituted terms are neglected in this treatment.

3. The quadruple and higher substitutions are accounted for in an approximate way within the IEPA. This method thus yields, for the case under consideration, the correct n-dependence: $\varepsilon^{\mathrm{IEPA}}(\mathrm{He}_n) = n\varepsilon^{\mathrm{IEPA}}(\mathrm{He})$, provided the IEPA-treatment starts from localized MO's. This difference between the IEPA and the PNO-CI is reflected in the corresponding Eqs. (6) and (8) by the occurence of $\varepsilon_u^{\mathrm{IEPA}}$ instead of the total correlation energy $\varepsilon^{\mathrm{PNOCI}}$. The main drawback of the IEPA is the neglection of matrix elements H_{ab} for $a \in u$, $b \in v$, with $u \neq v$, which account for the interaction of the correlation functions of different electron pairs u and v.

4. Inclusion of these matrix elements in the IEPA, Eq. (6), leads to the CEPA as given in Eq. (10). This method thus avoids the main shortcomings of the IEPA-neglection of certain matrix elements – and also those of the PNO-CI, since quadruple and higher substitutions are accounted for in an approximate way. One can also say that the IEPA treats each electron pair in the field of the HF-MO's of the remaining electrons, whereas the CEPA considers each pair in the field of the correlated remaining electrons. Applications of the CEPA shows in fact that this method yields more accurate potential curves, force constants etc. than the PNO-CI or the IEPA [20, 23].

3. Basis Set Considerations

As basis sets we used linear combinations of Gaussian lobe functions. The construction of d- and f-type functions was performed as described in Ref. [25]. We started from a Huzinaga [26] $9s$, $5p$ basis for boron, contracted (5, 1, 1, 1, 1) and (3, 1, 1) and a $5s$ (3, 1, 1) basis for hydrogen. A set of polarization functions, i.e. a complete d-set on boron ($\eta = 0.5$) and a p-set on hydrogen ($\eta = 0.5$), was then added. The orbital exponents η of the polarization functions were determined in optimizing the HF plus valence shell correlation energy of BH_3. In order to save computertime it was then investigated whether it is possible to reduce this basis without sacrificing accuracy. It turns out, in fact, that leaving out the boron p-function with the smallest orbital exponent ($\eta = 0.070$) effects the total BH_3

energy by 0.4 kcal/mol only, whereas the change of ΔE_f [Eq. (1)] in the HF approximation is 0.2 kcal/mol.

In order to get an idea on how saturated the present basis set is we make the following remarks. Increasing the s-basis on boron and hydrogen gives essentially a better description of the nuclear cusp which should not effect ΔE_f of reaction (1) or (2). The HF energy of boron obtained with a $9s$, $5p$ basis is anyway only 1.5 kcal/mol higher than the HF limit. Addition of further polarization functions, an f-set and a second d-set for boron and a d-set and a second p-set for the hydrogen atoms, lowers the HF energy of BH_3 by 1 kcal/mol and the valence shell correlation energy by 9 kcal/mol. The net effect of these additional basis functions on ΔE_f is thus expected to be of the order of about 3 kcal/mol. Addition of a second p-set at the bridge hydrogen atoms lowers the HF energy of B_2H_6 by 0.05 kcal/mol only.

As far as LiH and Li_2H_2 are concerned, it is no problem to choose the basis large enough to guarantee an accuracy of about 1 kcal/mol for ΔE_f. We started with a Huzinaga $9s$ (5, 1, 1, 1, 1) basis for lithium and a $5s$ (3, 1, 1) set for hydrogen and then added a set of two p-functions ($\eta = 0.14$ and 0.56 for Li and $\eta = 0.22$ and 0.66 for H) on either atom, hereafter referred to as basis set *I*. The orbital exponents η of the p-sets were determined in minimizing the HF plus valence shell correlation energy of LiH. KBR [15] used a Huzinaga $2p$ set (contracted to one group) at the hydrogen atom, which is not suited for molecular computations since it is an approximation of the spectroscopic hydrogen $2p$-orbital. The latter has e.g. Bohr-radius of about 4 a.u. whereas the optimized p-functions, see above, have radii of about 2 a.u. and 1 a.u. Quite the same comments could be made with respect to the lithium p-set used by KBR. For these reasons KBR get only 64% of the LiH valence shell correlation energy as obtained with basis set *I*. In the final computations, reported in Table 3, we added a rather spread out s-function on hydrogen ($\eta = 0.03$) and a d-set on Li ($\eta = 0.3$) and on H ($\eta = 0.45$), basis set II, which has practically no effect on ΔE_f of reaction 2, however (less than 0.14 kcal/mol).

4. Discussion of Results

a) B_2H_6. In the present computations we included all Φ_a which contribute more than 10^{-5} a.u. to $\varepsilon^{\mathrm{IEPA}}$, the total number of which is 124 only (counting those that are equivalent on symmetry grounds only once). The energy contributions of the neglected Φ_a amounts to $2 \cdot 10^{-4}$ a.u. in BH_3 and to about $6 \cdot 10^{-4}$ a.u. in B_2H_6.

From the results collected in Table 1 we get the following values for ΔE_f of reaction (1)

$$\text{HF:}\quad \Delta E_f = -20.7\ \text{kcal/mol} \tag{12}$$

$$\text{IEPA:}\quad \Delta E_f = -44.3\ \text{kcal/mol} \tag{13}$$

$$\text{PNO-CI:}\quad \Delta E_f = E^{\mathrm{PNOCI}}(B_2H_6) - 2\,E^{\mathrm{PNOCI}}(BH_3) = -27.4\ \text{kcal/mol} \tag{14}$$

$$\text{PNO-CI*:}\quad \Delta E_f = E^{\mathrm{PNOCI}}(B_2H_6) - E^{\mathrm{PNOCI}}(2\,BH_3) = -34.2\ \text{kcal/mol} \tag{15}$$

$$\text{CEPA:}\quad \Delta E_f = -36.6\ \text{kcal/mol}\,. \tag{16}$$

Table 1. Computed HF and correlation energies of BH_3 and B_2H_6[a]

		Valence shell correlation energies			
	$-E_{HF}$[b]	pair[c]	IEPA[d]	PNO–CI	CEPA
BH_3[e]	26.39697	*tt* (3×)	0.03167 (0.02805)	0.02959	0.03085
	(26.4014)	*tt'* (3×)	0.01128 (0.00796)	0.00844	0.00889
		total	0.12887 (0.10804)	0.11410	0.11921
BH_3BH_3[f]	52.79394	*tt* (6×)	0.03167	0.02816	0.03085
		tt' (6×)	0.01128	0.00807	0.00889
		total	0.25774	0.21739	0.23843
B_2H_6[g]	52.82699	*tt* (4×)	0.03127 (0.02779	0.02749	0.03034
	(53.8331)	*bb* (2×)	0.03040 (0.02796)	0.02641	0.02915
		tt' (2×)	0.01113 (0.00778)	0.00786	0.00871
		tb (8×)	0.00859 (0.00608)	0.00597	0.00631
		bb' (1×)	0.01443 (0.01154)	0.01020	0.01124
		tt'' cis (2×)	0.00100 —	0.00062	0.00070
		tt'' trans (2×)	0.00099 —	0.00059	0.00065
		total	0.29525 (0.24284)	0.23888	0.26377

[a] In a.u. The terms IEPA, PNO–CI, CEPA are explained in Section 2. The basis set is described in Section 3.

[b] The results of Lipscomb and coworkers [3, 13] are given in parantheses.

[c] *t* and *b* denote terminal and bridge bonds respectively. *tt'* denotes a pair of adjacent bonds, *tt''* a pair of terminal BH bonds at different boron atoms.

[d] Results of GASK [11] are given in parantheses.

[e] B–H distance = 2.25 a.u., which is the equilibrium distance obtained within the CEPA.

[f] B–B distance was 50 a.u., each BH_3 in its equilibrium geometry, see [e].

[g] Experimental geometry as given in Ref. 29.

Our HF result is in good agreement with the recent work of Lipscomb and coworkers [3, 13], who obtained −19 kcal/mol. The present HF energies for BH_3 and B_2H_6 are slightly poorer than those of Lipscomb and coworkers, see Table 1. This is certainly due to the fact that these authors used a Slater-type basis which gives a better description of the nuclear cusps than a Gaussian basis. Since our basis set appears to be rather saturated for BH_3 as far as flexibility in the bond region is concerned (we have noted above that addition of further polarization functions lowers E_{HF} of BH_3 by 1 kcal/mol only) we rather consider our computed ΔE_f, see Eq. (12), as an upper bound to the HF limit. The basis of Lipscomb *et al.* contained two *s*-type AO's on hydrogen which were optimized for the BH molecular fragment [3]. This basis set may be expected to describe terminal bonds better than bridge bonds which would result in a somewhat too small ΔE_f. The present basis is more flexible in this respect since it contains three *s*-type AO's on either H. The difference between terminal and bridge bonded hydrogen atoms may be seen from the coefficients of the hydrogen *s*-AO's in the localized MO's, which are (0.191, 0.302, 0.197) for a terminal and (0.187, 0.348, 0.147) for a bridge bond.

The IEPA gives a correlation contribution of −23.5 kcal/mol to ΔE_f, see Eq. (13). Due to the approximation inherent in the IEPA, as explained in Section 2, this method is not expected to yield accurate reaction energies.

In Eqs. (14) and (15) we have given the ΔE_f values as obtained from the PNO-CI computations. The first one, Eq. (14), may be called the naive PNO-CI, since we have simply compared $E^{\mathrm{PNOCI}}(B_2H_6)$ with $2\,E^{\mathrm{PNOCI}}(BH_3)$. This procedure is unsatisfactory since the quality of the PNO-CI depends on the number of electrons involved. This is clearly shown by a comparison of the PNO-CI correlation energies obtained for BH_3 and BH_3BH_3 at large intermolecular distance (50 a.u.), see Table 1.

$$\varepsilon^{\mathrm{PNOCI}}(BH_3BH_3) = 0.2174\ \text{a.u.} < 0.2282\ \text{a.u.} = 2\varepsilon^{\mathrm{PNOCI}}(BH_3)\,. \qquad (17)$$

In order to obtain the equality sign in (17), it would be necessary to include all quadruples which arise from simultaneous double substitutions on either BH_3 in the BH_3BH_3 computation. In the modified PNO-CI, see Eq. (15), we have compared $E^{\mathrm{PNOCI}}(B_2H_6)$ with $E^{\mathrm{PNOCI}}(BH_3BH_3)$, the PNO-CI energy obtained for the system of two separated BH_3 molecules. We have thus consistently neglected the contributions of higher than doubly substituted configurations for B_2H_6 and for $2\,BH_3$, which certainly gives a more realistic ΔE_f than the naive PNO-CI, see Eq. (14).

This procedure is still not too satisfactory. On the formation of B_2H_6 from $2\,BH_3$ we find significant changes of the pair correlation energies. The intermolecular terms (which give essentially the van der Waals interaction) vanish for two separated BH_3 molecules, whereas the corresponding interpair contributions are by no means negligible for B_2H_6. These changes are, of course, accompanied by changes of the contributions of quadruples and higher terms to the wave function and the total correlation energy. As the number of non negligible interpair terms is larger in B_2H_6, which has 11 next neighbour bond interactions compared to 6 in $2\,BH_3$, one expects a larger contribution of quadruples etc. in B_2H_6. The CEPA accounts for the higher substituted configurations in a consistent although approximate way. (This is e.g. shown by the fact that $E^{\mathrm{CEPA}}(BH_3BH_3) = 2\,E^{\mathrm{CEPA}}(BH_3)$, see Table 1.) This explains why the CEPA realistically predicts a larger correlation contribution to ΔE_f (-15.9 kcal/mol) than the modified PNO-CI [-13.5 kcal/mol, see Eq. (15)]. We thus consider the CEPA result for ΔE_f, Eq. (16), to be more reliable than those given in Eqs. (12)–(15). If one prefers for some reason to compare variational computations only, the modified PNO-CI, Eq. (15), is certainly more accurate than (12) or (14).

Let us briefly compare the present results with those of GASK [11]. In the latter treatment we underestimated the HF contribution to ΔE_f and also underestimated the corrections to the IEPA contributions which are due to the interaction of correlation functions of different pairs, as was discussed in Section 2 above. The estimated IEPA limit (-25 kcal/mole as compared to -23 kcal/mol obtained now) was not too bad, however, but the IEPA is not accurate enough to predict reaction energies with an accuracy of a few kcal/mol. The present study confirms at least qualitatively the conclusion of GASK that the increase of next neighbour bond interactions on the formation of B_2H_6 results in a considerable contribution to ΔE_f, whereas the changes in intrabond correlation energies are almost negligible (2.5 kcal/mole, see Table 1). We finally note that even the non neighbour terms, denoted tt'' in Table 1, contribute about -1.7 kcal/mol to ΔE_f within the CEPA.

Table 2. Potential surface for Li_2H_2 in D_{2h} geometry[a]

Distance Li–Li	H–H	$-E_{HF}$	$-E_{IEPA}$	$-E_{PNO-CI}$	$-E_{CEPA}$
4.66	5.16	16.04282	16.11241	16.10958	16.11150
4.46	5.16	16.04474	16.11420	16.11141	16.11330
4.26	5.16	16.04607	16.11555	16.11273	16.11462
4.06	5.16	16.04424	16.11350	16.11077	16.11260
4.46	4.96	16.04450	16.11428	16.11141	16.11329
4.46	5.36	16.04398	16.11320	16.11047	16.11236

[a] All quantities in a.u. Basis set I, see Section 3, was used.

Table 3. Computed HF and correlation energies of LiH and Li_2H_2[a]

		Valence shell correlation energies			
	$-E_{HF}$	pair	IEPA	PNO–CI	CEPA
LiH[b]	7.98593[c] (7.98262)	*tt* (1×)	0.03523	0.03523 (0.02204)	0.03523
2LiH[d]	15.97185	*tt* (2×)	0.03523	0.03422	0.03523
		total	0.07047	0.06845	0.07047
Li_2H_2[e]	16.04680 (16.03894)	*bb* (2×) *bb'* (1×)	0.03449 0.00464	0.03343 0.00364	0.03432 0.00387
		total	0.07361	0.07049 (0.04247)	0.07251

[a] See footnotes of Table 1. Basis set II, see Section 3, was used. The results reported by KBR [15] are given in parantheses.

[b] Li–H distance = 3.038 a.u., which is the equilibrium distance obtained with basis set I.

[c] HF limit: $E_{HF} = -7.9867$ a.u. [30].

[d] Li–Li distance 100 a.u.

[e] Geometry D_{2h}, Li–Li = 4.28 a.u. H–H = 5.06 a.u., see text.

b) Li_2H_2. We first redetermined the geometry of Li_2H_2 in the bridge bonded D_{2h} symmetry. From the CEPA results collected in Table 2, we obtain the following equilibrium distances

$$d(\text{Li–Li}) = 4.28\ \text{a.u.} \tag{18}$$

$$d(\text{H–H}) = 5.06\ \text{a.u.} \tag{19}$$

The latter differ slightly from those found by KBR [15] who obtained 4.46 a.u. and 5.16 a.u. Additional computations for other geometries confirmed the result of KBR that Li_2H_2 has D_{2h} equilibrium geometry.

From the final computations reported in Table 3 we get the following values for ΔE_f of reaction 2, see also Eqs. (12)–(16),

$$\text{HF:}\quad \Delta E_f = -47.3\ \text{kcal/mol} \tag{20}$$

$$\text{IEPA:}\quad \Delta E_f = -49.1\ \text{kcal/mol} \tag{21}$$

$$\text{PNO-CI:}\quad \Delta E_f = -47.0\ \text{kcal/mol} \tag{22}$$

$$\text{PNO-CI*:}\quad \Delta E_f = -48.3\ \text{kcal/mol} \tag{23}$$

$$\text{CEPA:}\quad \Delta E_f = -48.3\ \text{kcal/mol}\,. \tag{24}$$

A comparison of Eq. (23) or (24) with (20) shows that electron correlation increases ΔE_f by 1 kcal/mol in contrast to the conclusions of KBR [15]. The effect of electron correlations is much smaller than in reaction 1, however. This is due to two reasons, 1. in the LiH dimer one has just one additional next neighbour bond interaction whereas one has 5 in B_2H_6, 2. due to the rather large H–H distance in Li_2H_2, see Eq. (19), the corresponding interpair correlation energy (0.00387, see Table 3) is much smaller than the corresponding term in the BH_3 dimer (0.01124, see Table 1).

5. Conclusions

The results reported in the present study demonstrate the importance of electron correlation for the computation of reaction energies even for reactions in which closed shell molecules react and the number of electron pairs remains unchanged. We thus confirm at least qualitatively the conclusion of GASK [11]. The reactions (1) and (2) may be considered as extreme cases since we find a considerable correlation contribution to ΔE_f for (1) (-16 kcal/mol), whereas it is rather small for (2) (-1 kcal/mol). This is mainly due to greater increase of next neighbour bond interactions on the formation of B_2H_6 as compared to Li_2H_2.

The author further believes that the present computations are sufficiently accurate to confirm definitely a recent experimental value [13, 14] for ΔE_f of reaction (1), -34.8 kcal/mol, in contrast to the conclusions of Edmiston and Lindner who suggested a ΔE_f of -60 kcal/mol [8].

6. Programs and Computation Times

The evaluation and further processing of two-electron integrals – which altogether makes up for more than 90% of the total computertime – has been described in a recent paper [27]. Details of the PNO-CI and CEPA parts of the program will be described elsewhere [28]. The computations were performed in double precision arithmetic with a $65\,K$ – 36 bit word program version. The UNIVAC-1108 CPU times for the B_2H_6 computation (68 groups) are as follows: integrals: 1.5 h, HF: 20′ (12 iterations, starting from a zero density matrix, E_{HF} converged to 10^{-8} a.u.), determination of PNO's: 22′, matrix elements H_{ab}: 3.7 h (most of which is required for the case that a and b corresponds to the same pair), solution of PNO-CI and CEPA equations, see (8)–(11): 2′, total 5.9 h. The corresponding times for the final Li_2H_2 calculation (62 groups) are: integrals: 55′, HF: 9′, PNO's: 4′, matrix elements H_{ab}: 30′, PNO-CI and CEPA: 7″, total 100′.

Acknowledgements. This study would not have been possible without the fruitfull cooperation with Mr. F. Driessler, Dr. H. Lischka and Dr. V. Staemmler in developping the present program. The computations were performed at the „Rechenzentrum der Universität Karlsruhe". The assistance of the staff of the computation centre is gratefully acknowledged.

References

1. Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **17**, 348 (1970)
2. Ahlrichs, R.: Chem. Phys. Letters **19**, 174 (1973)
3. Laws, E., Stevens, R. M., Lipscomb, W. N.: J. Am. Chem. Soc. **94**, 4461 (1972)
4. Burnelle, L., Kauman, J. J.: J. Chem. Phys. **43**, 3450 (1965)

5. Buenker, R. J., Peyerimhoff, S. D., Allen, L. C., Whitten, J. L.: J. Chem. Phys. **45**, 2825 (1966)
6. Duke, B. J., Linnett, J. W.: Trans. Faraday Soc. **62**, 2955 (1966)
7. Switkes, E., Stevens, R. M., Lipscomb, W. N., Newton, M. D.: J. Chem. Phys. **51**, 2085 (1969)
8. Edmiston, C., Lindner, P.: Int. J. Quantum Chem. **7**, 309 (1973)
9. See Gangulin, P. S., McGee, H. A.: J. Chem. Phys. **50**, 4658 (1969) and references therein
10. Palke, W. E., Lipscomb, W. N.: J. Am. Chem. Soc. **88**, 2384 (1966)
11. Gelus, M., Ahlrichs, R., Staemmler, V., Kutzelnigg, W.: Chem. Phys. Letters **7**, 503 (1970)
12. Jungen, M., Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **17**, 339 (1970)
Edmiston, C., Kraus, M.: J. Chem. Phys. **42**, 1119 (1965); J. Chem. Phys. **45**, 1833 (1966)
13. Hall, J. H., Marynick, D. S., Lipscomb, W. N.: Inorg. Chem. **11**, 3126 (1972)
14. Mappes, G. W., Friedman, S. A., Fehlner, T. P.: J. Phys. Chem. **74**, 3307 (1970) see also Ref. 3
15. Kollman, P., Bender, C. F., Rothenberg, S.: J. Am. Chem. Soc. **94**, 8016 (1972)
16. Sinanoğlu, O.: Advan. Chem. Phys. **6**, 315 (1964); **14**, 237 (1969)
17. For a recent review see e.g. Davidson, E. R.: Advan. Quantum Chem. **6**, 201 (1972), see also Ref. 20
18. Ahlrichs, R.: to be published
19. Kutzelnigg, W.: Theoret. Chim. Acta (Berl.) **1**, 327 (1963)
20. Meyer, W.: Int. J. Quantum Chem. S **5**, 341 (1971)
Meyer, W.: J. Chem. Phys. **58**, 1017 (1973)
21. See e.g. Ref. 20 and references therein
22. See e.g. Primas, H. in: Modern Quantum Chemistry, O. Sinanoğlu (Ed.), Vol. 2, p. 45—74. New York: Academic Press 1965
23. Meyer, W.: Private communication
Ahlrichs, R., Kutzelnigg, W., Lischka, H., Staemmler, V.: To be published
24. Foster, J. M., Boys, S. F.: Rev. Mod. Phys. **32**, 303 (1960)
25. Driessler, F., Ahlrichs, R.: Chem. Phys. Letters **23**, 571 (1973)
26. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
27. Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **33**, 157 (1974)
28. Ahlrichs, R., Kutzelnigg, W., Lischka, H., Staemmler, V.: In preparation
29. Bartell, L. S., Carrol, B. L.: J. Chem. Phys. **42**, 1135 (1965)
30. Cade, P. E., Huo, W. M.: J. Chem. Phys. **44**, 1849 (1966)

Dr. R. Ahlrichs
Institut für Physikalische Chemie und Elektrochemie der Universität Karlsruhe
D-7500 Karlsruhe, Kaiserstraße 12
Federal Republic of Germany