Ab initio Calculations on Small Hydrides Including Electron Correlation

IV. A Study of the Molecules BeH_2, Be_2H_4 and Be_3H_6

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The molecules BeH_2, Be_2H_4 and Be_3H_6 are investigated by means of *ab initio* calculations including the electron correlation of the valence shell electrons. It is found that BeH_2 shows a strong tendency to polymerize in linear chains. The polymerization energy is estimated to be 40 Kcal/Mol.

Die Moleküle BeH_2, Be_2H_4 und Be_3H_6 werden mit Hilfe von *ab initio* Rechnungen unter Einschluß der Elektronenkorrelation der Valenzelektronen untersucht. Es zeigt sich, daß BeH_2 eine starke Tendenz hat, in linearen Ketten zu polymerisieren. Die Polymerisationsenergie wird zu 40 Kcal/Mol abgeschätzt.

Les molécules BeH_2, Be_2H_4 et Be_3H_6 sont étudiées au moyen de calculs *ab-initio* avec corrélation électronique des électrons de la couche de valence. On trouve que BeH_2 présente une forte tendance à polymériser en chaînes linéaires. L'énergie de polymérisation est estimée à 40 Kcal/mole.

1. Introduction

In some recent publications [1, 7–10, 18] rather detailed studies of the ground state of BeH_2 have been reported. Though all the investigations show that the BeH_2 molecule is very stable with respect to dissociation into $BeH + H$ or $Be(gas) + H_2$, it has not been observed experimentally so far. The difficulty to detect BeH_2 is mainly due to the low BeH_2 partial vapor pressure under normal experimental conditions [1].

Solid BeH_2 can be synthesized [4, 17]. Unfortunately almost nothing is known about its physical properties because one has not yet obtained sufficient pure samples. From the investigation of a product containing about 76% BeH_2 it has been suggested [14], that this sample contained $(BeH_2)_x$ chains with $x \approx 70$, but no X-ray diffraction pattern has been obtained. The IR-spectrum showed a broad absorption at 1758 cm^{-1} which can possibly be interpreted as a BeH_2Be vibration [3, 14].

The aim of the investigations reported in the present paper was to study whether BeH_2 has a tendency to polymerize via H bonds, as has been supposed [17]. We further wanted to get a better understanding of the high cohesion energy of solid BeH_2 which has been estimated at 48 Kcal/Mol [1].

The computations have been performed with a method that starts from an SCF calculation and then includes the correlation energy within the independent

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electron pair approach (IEPA) [15, 16]. A short description of the present computer program is given in [12], a detailed treatment of the theoretical background will be published elsewhere [13]. Our computer program differs mainly in three aspects from the conventional IEPA computation schemes.

1. As starting point for the treatment of pair correlation energies ε_{ij} we always use localized SCF orbitals rather than the canonical SCF orbitals. The localization procedure follows the method proposed by Foster and Boys [6].

2. The computation of pair correlation functions and energies is based on a direct calculation of approximate natural orbitals of the corresponding two electron functions, which have been denoted as quasi-NO's [2, 12].

3. The pair functions under consideration are always chosen to have a definite spin (singlet or triplet), which is different from Nesbets approach [15] who uses simple product-type pair substitutions.

The present method is an extension of the one described previously [2] which accounted for the intrapair correlation only.

As the K shell intrapair and the K shell-valence shell interpair correlation is not expected to have a considerable effect on binding energies and equilibrium geometries for the molecules considered in this paper we have decided to treat the valence shell correlation only. This makes the computations considerably shorter.

2. Basis Functions

As basis functions $\varphi_i(r)$ we used linear combinations of gaussian functions $f_v(r)$:

$$\varphi_i(r) = \sum_v C_{iv} f_v(r), \qquad f_v(r) = N e^{-\eta_v(r-r_v)^2}$$

as indicated in Table 1. The s-type gaussians centered at Be and H are taken from Huzinaga's optimized atomic s-basis [11]. The contraction coefficients C_{iv} for the functions $1s(Be)$, $4s(Be)$ and $1s(H)$ were obtained from pilot calculations with uncontracted basis sets. The parameters which specify the groups $1p\sigma(Be)$, $2p\sigma(Be)$ and b (see Table 1) were determined by optimizing the SCF energy of BeH_2 for basis set A and B respectively (see Table 2). During this procedure the ratio of η values for the $p\sigma(Be)$ functions was kept fixed. The basis sets A' and B' (see Table 2) differ from A and B by the further contraction of $1s(H)$ and $2s(H)$ to $1s'(H)$. For the computation of correlation energies the functions $p\pi(Be)$ and $p\sigma(H)$ and $p\pi(H)$ were added to the SCF basis. The parameters specifying these additional basis functions were varied to optimize the valence shell intrapair correlation energy of BeH_2.

3. Results

A. BeH$_2$

Although we have already reported a detailed study of the ground state of BeH_2 [1] it seems worthwhile to discuss briefly the new results summarized in Table 3. As a consequence of the careful basis optimization the SCF and correlation energies obtained with basis set B or B' are slightly better than in our best

Table 1. *Basis functions*

η	d^{a}	c^{a}	Label
1741.4	—	0.00261	$1s$(Be)
262.14	—	0.01988	
60.3255	—	0.9594	
17.6240	—	0.31652	
5.9326	—	0.70247	
2.1847	—	1.0	$2s$(Be)
0.8590	—	1.0	$3s$(Be)
0.20		0.45520	$4s$(Be)
0.06		0.76145	
0.28	0.5	1.6244	$1p\sigma$(Be)
1.4	0.2	0.5000	
0.9	0.5	1.1870	$2p\sigma$(Be)
4.5	0.2	0.2425	$2p\sigma$(Be)
0.233	0.5	1.0	$1p\pi$(Be)
30.2	—	0.0579	$1s$(H)
4.76	—	0.3830	
1.24	—	1.3092	
0.377	—	1.0	$2s$(H)
0.118	—	1.0	$3s$(H)
30.2	—	0.0145	$1s'$(H)
4.76	—	0.0960	
1.24	—	0.3273	
0.377	—	0.6300	
0.4	0.4	1.0	$p\sigma$(H), $p\pi$(H)
0.27	middle of BeH-bond		b

^a *c* are the coefficients with which the lobes are contracted to groups. $2d$ is the distance between two lobes forming a *p*-orbital.

Table 2. *Specification of the different basis sets*

Basis	HF-part		Correlation-part
A	Be: $1s, 2s, 3s, 4s, 1p\sigma$	H: $1s, 2s, 3s$	
A'		H: $1s', 3s$	Be: $p\pi$ H: $p\sigma, p\pi$
B	Be: $1s, 2s, 3s, 4s, 2p\sigma$	H: $1s, 2s, 3s;$ b	
B'		H: $1s', 3s;$ b	

For the notation of basis functions see Table 1.

Table 3. HF *and correlation energies for* BeH_2, *Be-H-distance* 2.5 a.u.

Basis	$-E_{HF}$	$-\varepsilon_{vv}$	$-^1\varepsilon_{vv'}$	$-^3\varepsilon_{vv'}$	$-\varepsilon_{vv'}$	$-\varepsilon$	NHF, NT, NG		
A	15.7617	0.0308	0.0022	0.0026	0.0048	0.0664	11	19	39
A'	15.7570	0.0305	0.0021	0.0025	0.0046	0.0656	9	17	39
B	15.7698	0.0312	0.0024	0.0030	0.0054	0.0678	13	21	41
B'	15.7691	0.0309	0.0024	0.0029	0.0053	0.0671	11	19	41

ε_{vv}: Intrapair correlation per valence pair.

$^1\varepsilon_{vv'}, {}^3\varepsilon_{vv'}, \varepsilon_{vv'}$: Singulett-, triplett and total interpair correlation energies for valence electrons. $\varepsilon_{vv'} = {}^1\varepsilon_{vv'} + {}^3\varepsilon_{vv'}$.

ε: Total valence shell correlation energy.

NHF: Number of basis functions (groups) for HF-calculation.

NT: Total number of basis functions.

NG: Total number of gaussian lobes.

previous calculation, though the latter was performed with a larger number of basis functions, namely 53 gaussians contracted to 29 groups.

In our previous paper on BeH_2 [1] we have in a crude way guessed the interpair correlation energy between the valence electrons to be $\varepsilon_{vv'} = -0.013 \pm 0.005$ a.u. The actual calculation performed now leads to $\varepsilon_{vv'} = -0.0068 \pm 0.0008$ a.u. The unexpected smallness of $\varepsilon_{vv'}$ is a consequence of the good localizability of the SCF-MO's of the valence electrons (see Fig. 1) (This result does not affect the estimate for the total energy of BeH_2 given in [1]). For a comparison of the different basis sets let us recall that the SCF-limit for BeH_2 is approximately 15.7730 a.u. [8], whereas the valence shell correlation energy ε can be estimated from the present calculations to be $\varepsilon = 0.080 \pm 0.004$ a.u.[1].

The SCF-energies given in Table 3 differ from the SCF-limit by 0.016 a.u. (basis A') to 0.003 a.u. (basis B), whereas the error of the correlation energy ε varies from 0.014 a.u. (basis A') to 0.012 a.u. (basis B). The basis set A' is hence rather poor with respect to the calculation of the SCF energy but it accounts for almost the same amount of correlation energy as the more refined basis sets B and B'. This discussion indicates that it is sufficient to use the basis set A' for the calculation of correlation energies whereas one should use the basis set B' or B (without the correlation part of course, see Table 2) to obtain reliable SCF energies.

The plots of contour lines of the quasi NO's given in Fig. 1 show very clearly that the NO's describing the intrapair correlation are concentrated in the same region of space as the localized SCF-MO's are. The NO's of the interpair correlation functions are of course extended over the region where the two localized SCF-MO's are essentially different from zero, which is the whole molecule in this case.

B. Be_2H_4

Our first task was to determine the ground state equilibrium geometry for this unknown molecule. Previous experience has suggested that for a molecule of this kind certain simplifications can be made which do not significantly change the results but lead to a considerable reduction of computation time.

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[1] The error bounds given in this paper have been estimated from the experience of calculations on systems like H_2 and LiH where rather exact data are available [2].

BeH$_2$ LOK MO R

BeH$_2$ NO R 2

BeH$_2$ NO R 3

BeH$_2$ NO 2 1—S

BeH$_2$ NO 3 1—S

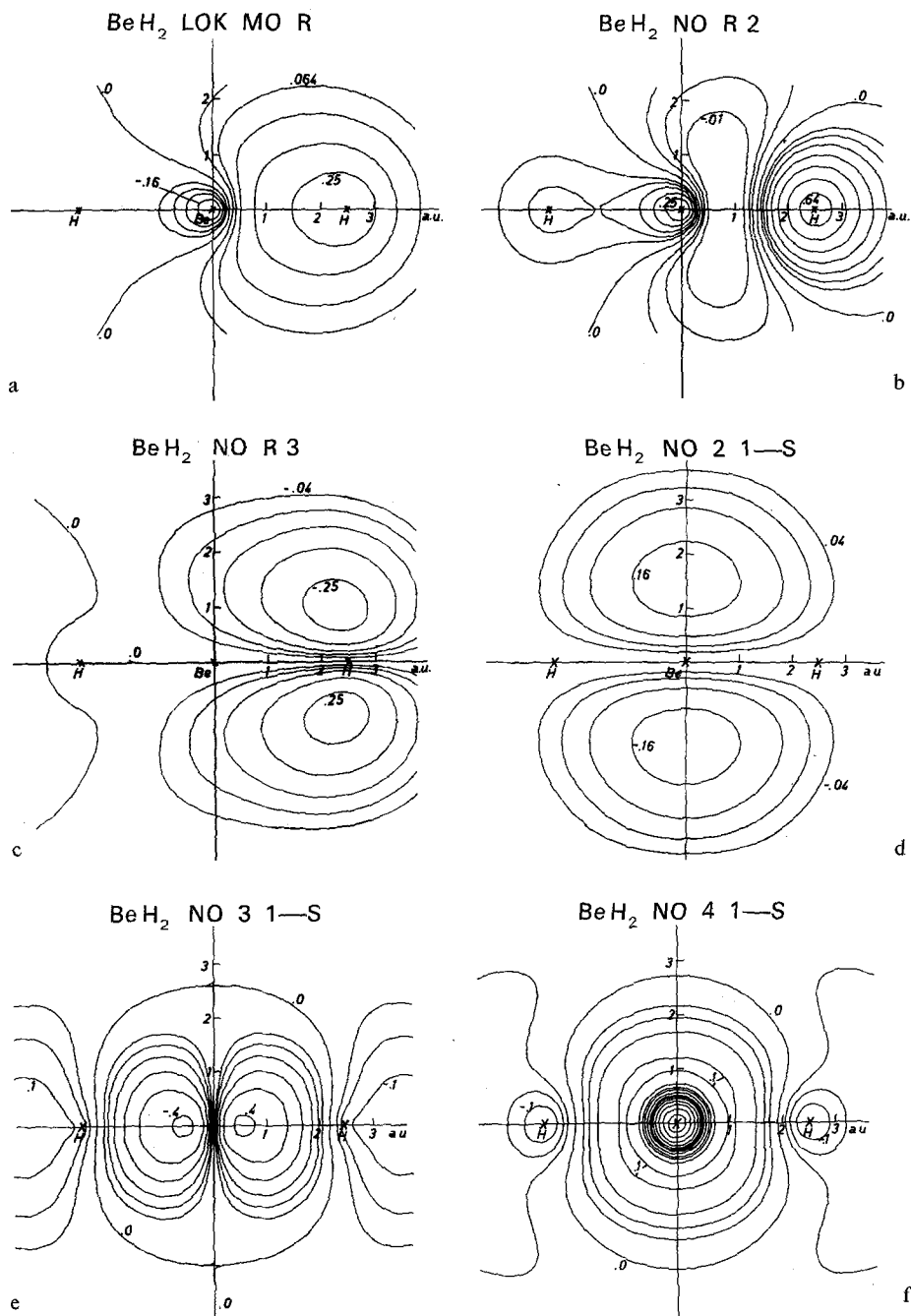BeH$_2$ NO 4 1—S

a

b

c

d

e

f

Fig. 1a–h. Contour lines of localized SCF-MO's and some important NO's of pair functions for BeH$_2$. a) Localized valence shell SCF-MO, b–c) NO's of the corresponding intrapair correlation function, d–f) NO's of the singlett interpair correlation-function, g–h) NO's of the triplett interpair correlation function. – The corresponding numerical values of the contour lines are: 0.0, ±0.04, ±0.064, ±0.1, ±0.16, ±0.25, ±0.4, ±0.64
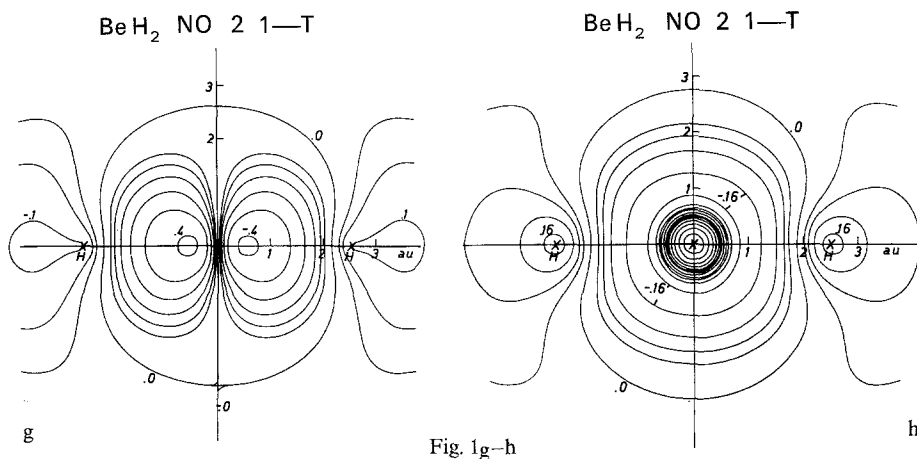
BeH$_2$ NO 2 1—T

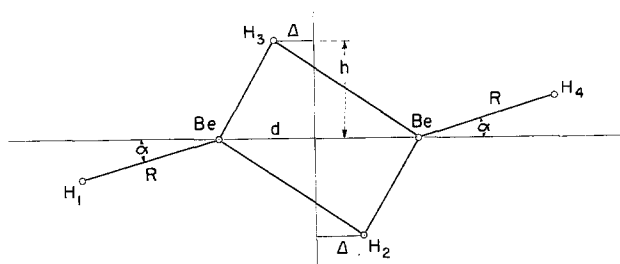BeH$_2$ NO 2 1—T

g

Fig. 1g–h

h

Fig. 2. Nuclear Coordinates of Be$_2$H$_4$
Equilibrium geometry: $R = 2.5$, $d_0 = 3.9$, $h_0 = 2.0$, $\Delta_0 = \alpha_0 = 0$ (in a. u.)

Table 4. HF-*energies for* Be$_2$H$_4$, *basis A.* $R = 2.5$, $\Delta = 0$, $\alpha = 0$

h \ d	2.5	3.2	3.9	4.6
1.5	− 31.2154	− 31.4409	− 31.5060	− 31.5012
2.0	− 31.3494	− 31.5111	− 31.5448	− 31.5262
2.5	− 31.3462	− 31.4923	− 31.5200	− 31.5021

For the meaning of R, h, d, Δ, α see Fig. 2.

Only the planar configuration of Be$_2$H$_4$ was considered. The bond distance for the terminal BeH bond was kept fixed at $R = 2.5$ a.u. as in BeH or BeH$_2$ [1]. Only SCF-energies were calculated. The basis set A was used (see Table 2) which should contain enough flexibility to give reliable results at least for the bond distances.

As the lowest electronic energy was expected for D_{2h} symmetry a series of calculations for several values of d and h (see Fig. 2) was performed first. From the results, which are given in Table 4, the following equilibirium distances have

Table 5. HF-*energies for* Be_2H_4, *basis A*. $R = 2.5, d = 3.9, h = 2.0$

$R \cdot \alpha$ \ $\varDelta$	0.0	0.2
0.0	− 31.5448	− 31.5418
0.1	− 31.5446	− 31.5410

For the meaning of $R, d, h, \varDelta, \alpha$ see Fig. 2.

been obtained:

$$d_0 = 3.9 \pm 0.2 \text{ a.u.}, \qquad h_0 = 2.0 \pm 0.1 \text{ a.u.} \, .$$

Some results for the subsequent calculations for the lower symmetry $C_{2h}(\varDelta \neq 0, \alpha \neq 0,$ see Fig. 2) are collected in Table 5. These did not lead to a lowering of the energy and suggest that the molecule has in fact D_{2h} symmetry.

From the values for d_0 and h_0 the H_2BeH_3 equilibrium bond angle (see Fig. 2) is calculated to be 89°. The BeH bond distance in a BeH_2Be bridge is 2.8 a.u., which is about 10 % larger than the corresponding value for a terminal bond. For the B_2H_6 molecule, which should be comparable to Be_2H_4 in this context, the corresponding experimental [5] data are 97° and 12%. The slight increase of this bridge bond angle (in going from Be_2H_4 to B_2H_6) can be explained easily: with increasing nuclear charge of the first row atom the p-character of the hydrogene bond increases (in LiH a rather pure s-bond is formed whereas FH is mainly $p\sigma$ bonded) and the bond becomes more directed. Consequently the bond angles in B_2H_6 are closer to the tetrahedral angle than in Be_2H_4. For the latter molecule even a 120° bond angle could have been expected in the case of a strongly directed bond as only sp^2 hybridization is necessary.

After having determined the equilibrium geometry of Be_2H_4 further calculations were performed to obtain correlation energies and more reliable results for the SCF energy. From the experience with the BeH_2 calculations it seemed to be sufficient to use the basis A' for the treatment of correlation energies, whereas the basis set B' was taken for a more precise SCF calculation (see Table 6). The most striking fact is the relatively large deviation of SCF energies obtained with different basis sets. This effect becomes still more apparent from Table 7, where the contributions to the energy difference $\varDelta E$ of the reaction $2 BeH_2 \rightarrow Be_2H_4 + \varDelta E$ obtained with different basis sets are listed. The large variation of $\varDelta E_{HF}$ (see Table 7) was not expected to that extent before the computations were done. This demonstrates drastically the disadvantage of small basis sets with respect to the calculation of binding energies. Nevertheless one would assume $\varDelta E_{HF}$ obtained with basis set B' to be in error by not more than 0.005 a.u.

The slight decrease of the intrapair correlation energy (in going from $2 BeH_2$ to Be_2H_4) has been expected of course, since in Be_2H_4 only one $2p$-AO at each Be atom is completely available for substitutions describing electron correlation, whereas in BeH_2 there are two.

The rather large contribution of the interpair correlation to the dimerisation energy (see Table 7) is mainly due to the fact that the number of interpair con-

Table 6. HF- and valence shell correlation energies of Be_2H_4 for the equilibrium configuration $d = 3.9, h = 2.0$

Basis	$-E_{HF}$	$-\varepsilon_{11}$	$-\varepsilon_{22}$	$-^1\varepsilon_{12}$	$-^3\varepsilon_{12}$	$-\varepsilon_{12}$	$-^1\varepsilon_{23}$	$-^3\varepsilon_{23}$	$-\varepsilon_{23}$	$-\sum_i \varepsilon_{ii}$	$-\sum_{i<j} \varepsilon_{ij}$	$-\sum_{i\leq j} \varepsilon_{ij}$
A	31.5448	—	—	—	—	—	—	—	—	—	—	—
A'	31.5296	0.0303	0.0300	0.0011	0.0022	0.0033	0.0026	0.0048	0.0075	0.1206	0.0207	—
B'	31.5726	—	—	—	—	—	—	—	—	—	—	0.1413

ε_{ii} = intrapair correlation energy of localized pair i,
$^1\varepsilon_{ij}, ^3\varepsilon_{ij}$: singulett and triplett interpair correlation energy.
$\varepsilon_{ij} = {}^1\varepsilon_{ij} + {}^3\varepsilon_{ij}$.
(Labeling of the localized MO's corresponds to that of H-atoms in Fig. 2).

Table 7. Contributions to the dimerisation energy of BeH_2

Basis	ΔE_{HF}	$\Delta \sum_i \varepsilon_{ii}$	$\Delta \sum_{i\leq j} \varepsilon_{ij}$
A	−0.0214	—	—
A'	−0.0156	0.0014	−0.0101
B'	−0.0344	—	—

$$\Delta E_{HF} = E_{HF}(Be_2H_4) - 2E_{HF}(BeH_2)$$
$$\Delta \sum_i \varepsilon_{ii} = \sum_i \varepsilon_{ii}(Be_2H_4) - 2\sum_i \varepsilon_{ii}(BeH_2)$$
$$\Delta \sum_{i\leq j} \varepsilon_{ij} = \sum_{i\leq j} \varepsilon_{ij}(Be_2H_4) - 2\sum_{i\leq j} \varepsilon_{ij}(BeH_2)$$

tributions is 5 for Be_2H_4 but only one for each BeH_2. (We have not considered $\varepsilon_{14}{}^2$, because the corresponding localized MO's are not next neighbours and are separated by a distance of about 4.0 a.u. which causes ε_{14} to be very small.) The different contributions to the dimerisation energy listed in Table 7 should rather be considered as upper bounds to the exact numbers, since the basis sets were all optimized for BeH_2 and are hence more appropriate for this molecule than for Be_2H_4. Having this in mind one can estimate the dimerisation energy (see Table 8):

$$2\,BeH_2 \rightarrow Be_2H_4 + 0.05 \text{ a.u.} \pm 0.01 \text{ a.u.} (31 \pm 6 \text{ Kcal/Mol}).$$
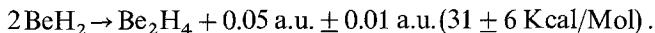
The contour lines of the localized MO's and some NO's describing the intrapair correlation of the BeHBe bridge electron pair are given in Fig. 3. The dominant feature of these plots is the good localizability of the SCF-MO's for Be_2H_4 which expains the smallness of the interpair correlation energies. Obviously only the MO's describing the bridge bonds have a considerable differential overlap which makes it understandable that ε_{23} is twice as large as ε_{12} (see Table 6). We further note, that the localized SCF-MO's describing a terminal BeH bond are almost the same in BeH_2 and Be_2H_4 (see Fig. 1, Fig. 3).

C. Be_3H_6

SCF calculations on Be_3H_6 were performed for two different molecular geometries: a linear chain (Fig. 4) and a cyclic structure (Fig. 5). No attempt was made to find out exactly the equilibrium geometry because of the relatively large amount of computer time necessary for these calculations. For the chain structure the bond distances were simply taken to be the same as found for Be_2H_4 ($d = 3.9$ a.u., $h = 2.0$ a.u., see Fig. 2 and Fig. 4). The result of the SCF calculation using basis set B' was

$$E_{SCF} = -47.3847 \text{ a.u. (chain structure)}.$$

For the cyclic structure all angles and the bond distances of the terminal BeH bonds were kept fixed but the BeHBe bridge bond distance $S = 2.74$ a.u. was obtained from a series of SCF calculations with basis set A'. The final SCF calculation with basis set B' yielded the energy

$$E_{SCF} = -47.3494 \text{ a.u. (cyclic structure)}.$$

The large difference of SCF energies in the two geometries (0.0353 a.u.) shows that the chain structure is more stable. Even by inclusion of correlation energies it is hardly conceivable the SCF energy difference is overcompensated. Consequently no further calculations on the cyclic structure were performed.

Concerning the pair correlation energies ε_{ij} of Be_3H_6 in its linear conformation it was first of all realized that the localized SCF-MO's describing a terminal BeH or a BeHBe bridge bond hardly change in going from Be_2H_4 to Be_3H_6. One would thus expect the corresponding pair correlation energies in Be_2H_4

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[2] ε_{ij} denotes the interpaircorrelation energy between the electron pairs occupying the localized SCF-MO's i and j. The localized SCF-MO's are labeled in the same way as the H atoms (see Fig. 2) at which they are centered.
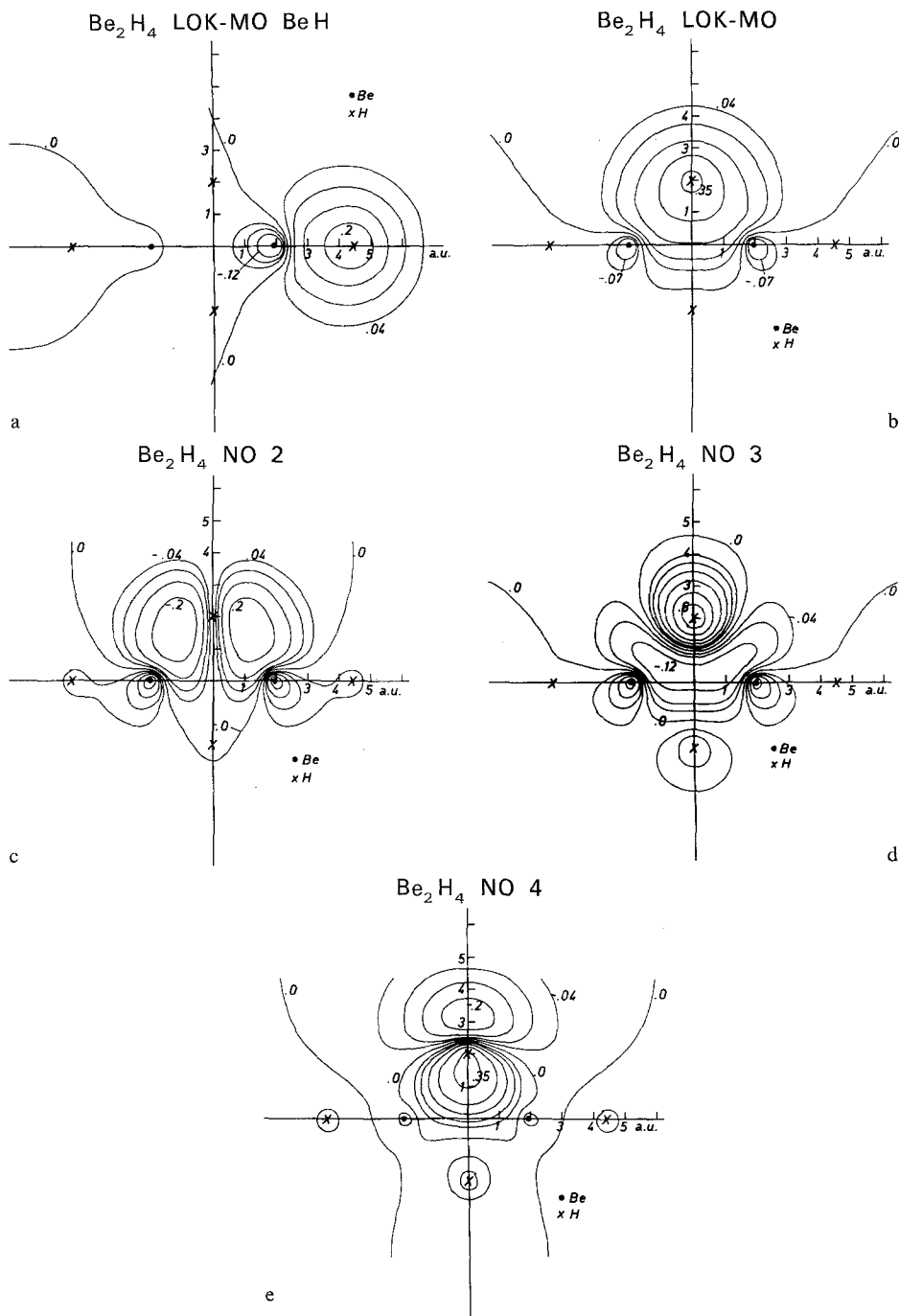
Fig. 3a–e. Contour lines of localized SCF-MO's and NO's of pair functions for Be_2H_4. a) localized SCF-MO of terminal Be-H bond. b) localized SCF-MO of Be-H-Be bridge bond. c–e) NO's of the intrapair correlation function of the Be-H-Be bridge bond pair. – The corresponding numerical values of the contour lines are: 0.0, ± 0.04, ± 0.07, ± 0.12, ± 0.2, ± 0.35
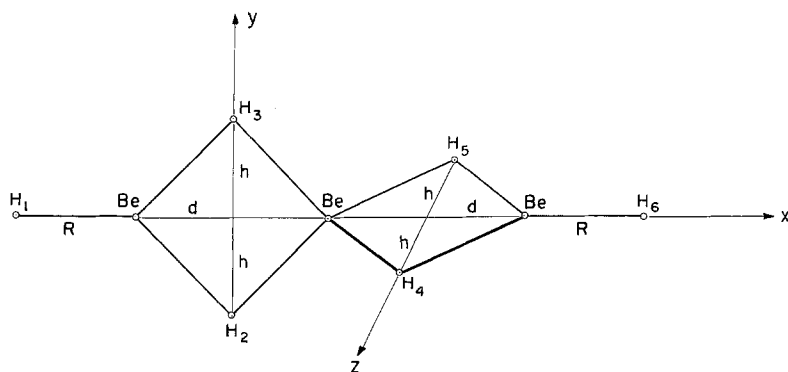
Fig. 4. Chain structure geometry of Be_3H_6
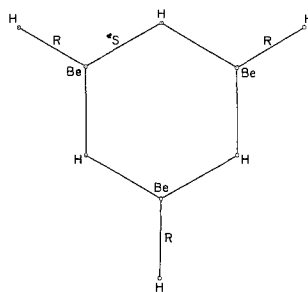$R = 2.5, d = 3.9, h = 2.0$ (in a. u.)

Fig. 5. Cyclic structure geometry of Be_3H_6
$S_0 = 2.74, R = 2.5$ (in a. u.)

and Be_3H_6 to be quite the same. This assumption was indeed confirmed by the computation of ε_{22} and ε_{23} for Be_3H_6 (using basis set A') which differ by less than 0.3 % (maximal 0.0001 a.u.) from the corresponding values for Be_2H_4 listed in Table 6. Deviations of this order of magnitude are of course negligible for the purpose of the present investigation. The surprisingly good transferability of ε_{ij}'s from Be_2H_4 to Be_3H_6 furthermore is a confirmation of the original ideas of Foster and Boys [6] that properties of corresponding localized electron pairs should not change significantly in going from one molecule to another. Consequently it is not necessary to compute all ε_{ij}'s for Be_3H_6, it is sufficient to treat ε_{24} only which has no counterpart in Be_2H_4. A calculation using basis set A' gave the following results:

$$^1\varepsilon_{24} = -0.0008 \text{ a.u.}, \quad ^3\varepsilon_{24} = -0.0018 \text{ a.u.}, \quad ^1\varepsilon_{24} + {}^3\varepsilon_{24} = -0.0026 \text{ a.u.} .$$

Taking for the other pair correlation energies the corresponding ε_{ij} values from the Be_2H_4 calculation (Table 6) one obtains the following valence shell correlation energies for Be_3H_6 (in the chain structure, see Fig. 4).

$$\sum_i \varepsilon_{ii} = -0.1806 \text{ a.u.}, \quad \sum_{i<j} \varepsilon_{ij} = -0.0386 \text{ a.u.}, \quad \sum_{i \le j} \varepsilon_{ij} = -0.2192 \text{ a.u.}$$

Table 8. ΔEn values (in atomic units) of the reactions $2\,\mathrm{BeH_2} \to \mathrm{Be_2H_4} + \Delta E_1$ and
$\mathrm{Be_2H_4} + \mathrm{BeH_2} \to \mathrm{Be_3H_6} + \Delta E_2$ obtained in different approximations

	SCF[a]	% error[b]	SCF + intrapair[c]	% error[b]	total[d]	estimated
ΔE_1	0.0344	23	0.0330	26	0.0445	0.050 ± 0.010
						$(31 \pm 6\ \mathrm{Kcal/Mol})$
ΔE_2	0.0430	22	0.0420	24	0.0553	0.063 ± 0.015
						$(40 \pm 10\ \mathrm{Kcal/Mol})$

[a] From the SCF energies calculated with basis set B'.
[b] Percentage errors with respect to the total ΔE values given in Column 5.
[c] Including the valence shell intrapair correlation energies ε_{ii}.
[d] Including the total valence shell correlation energies calculated with basis A'.

(Here we have again neglected the interpair correlation energies between non-neighbouring localized SCF-MO's which are expected to be very small, see discussion above.)

In Table 8 we finally summarize the energy differences for the reactions $2\,\mathrm{BeH_2} \to \mathrm{Be_2H_4}$ and $\mathrm{Be_2H_4} + \mathrm{BeH_2} \to \mathrm{Be_3H_6}$ obtained within different approximations. The most striking effect is that inclusion of intrapair correlation gives even slightly poorer results than the SCF approximation and that about 25 % of the dimerisation and trimerisation energies are due to interpair correlation effects. The importance of the interpair correlation for the reactions considered in Table 8 is easily explained, if we observe that the number of pairs of neighbouring localized SCF-MO's which give rise to non-negligible interpair correlation energy contributions increases from 1 in $\mathrm{BeH_2}$ to 5 in $\mathrm{Be_2H_4}$ and to 10 in $\mathrm{Be_3H_6}$. Though each individual $\varepsilon_{ij}(i \neq j)$ is rather small (compared to the ε_{ii}) the increasing number of such terms makes the interpair correlation rather important for $\mathrm{Be_2H_4}$ and $\mathrm{Be_3H_6}$.

4. The Polymerization Energy of the Hypothetical $(\mathrm{BeH_2})_\infty$ Chain

From the results reported above one can give at least a rough estimate for the energy difference ΔE_n of the reaction

$$(\mathrm{BeH_2})_n + \mathrm{BeH_2} \to (\mathrm{BeH_2})_{n+1} + \Delta E_n .$$
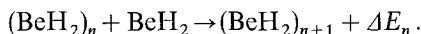
The geometry of $(\mathrm{BeH_2})_n$ is assumed to be that of a linear chain as in indicated for $\mathrm{Be_3H_6}$ in Fig. 4. For the case $n \geq 2$ we rewrite the above reaction in the form

$$R_n \mathrm{BeH_2BeH} + \mathrm{BeH_2} \to R_n \mathrm{BeH_2BeH_2BeH} + \Delta E_n$$
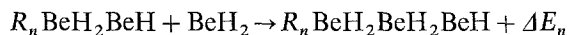
where R_n stands for $\mathrm{H(BeH_2)_{n-1}}$. The investigations reported in the present paper have shown the shape of the localized SCF-MO's describing the $\mathrm{BeH_2Be}$ bridge bonds is quite the same for $\mathrm{Be_2H_4}$ and $\mathrm{Be_3H_6}$ and will probably not change if we go over to $(\mathrm{BeH_2})_n$ for general n. Consequently one would expect ΔE_n to be almost independent of n if $n \geq 2$, as the different R_n should have a rather small influence only. We arrive hence at the conclusion that the polymeriza-

tion energy of the hypothetical $(BeH_2)_\infty$ chain is approximately

$$\Delta E_n \approx -0.063 \text{ a.u. } (40 \text{ Kcal/Mol}) \quad n \geqq 2,$$

which is the estimated value for E_2 given in Table 8.

The case $n = 1$ is different from $n \geqq 2$ for two reasons. In the reaction $2\,BeH_2 \rightarrow Be_2H_4 (n = 1)$ the sp hybrid valence orbitals on each Be atom have to be promoted to sp^2 hybrids. In the case $n \geq 2$ however one promotion from sp to sp^2 and one from sp^2 to sp^3 is involved. As the promotion from sp^2 to sp^3 requires less promotion energy than the one from sp to sp^2, it is evident that in the SCF approximation ΔE_1 is smaller than ΔE_n for $n \geq 2$ (see Table 8).

Concerning the correlation energy contributions to ΔE_n we have already seen that the intrapair correlation has only a rather small effect on ΔE_n. The interpair correlation however is by no means negligible, which is due to the growing number of pairs of neighbouring localized SCF-MO's with increasing n. It is easily verified that for the reaction under consideration the number of pairs of neighbouring SCF-MO's increases by 3 if $n = 1$ and by 4 for the case $n \geq 2$.

5. Conclusions

The present investigations show that BeH_2 has a strong tendency to oligo-merize via H bonds. The calculations performed for Be_3H_6 in a cyclic and a linear chain structure furthermore indicate that $(BeH_2)_n$ has probably a chain structure, at least if n is not too large.

From these results one can of course draw no conclusions concerning the possible crystal structures of solid BeH_2. The present results however do not contradict the assumption [17] that solid BeH_2 consists of $(BeH_2)_n$ chains (with large n) and has hence a SiS_2 like crystal structure. The estimated polymerization energy for the linear BeH_2 chain of 40 Kcal/Mol is in sufficient agreement with the cohesion energy of solid BeH_2 which has been estimated at 48 Kcal/Mol [1].

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