INVESTIGATION OF THE POSSIBILITY OF POLYMERIZATION FOR THE BeH$_2$ MOLECULE

The Ground State of the BeH$_2$, Be$_2$H$_4$ and Be$_3$H$_6$ Systems by the FSGO Method

By

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Calculations were carried out for the ground state energy and equilibrium geometry of the BeH$_2$, Be$_2$H$_4$ and Be$_3$H$_6$ molecules by the FSGO method. According to the investigations, the BeH$_2$ molecule tends to have a polymerized form. The calculated dimerization and trimerization energy values are in good agreement with other calculated values available.

Introduction

Nowadays the subject of quantum-mechanical and quantum-chemical studies shifts more and more towards the larger systems, the molecules. When a certain system is repeated several times, in principle many times, as a result of the increasing process or additional reaction, *e.g.* a chain-type compound will be formed. The polymerization process has been observed in many cases; an interesting possibility is that the polymer formation of beryllium-hidride, (BeH$_2$)$_n$, is an existing polymer structure. The BeH$_2$ molecule is a very simple one, but experimental data on its properties are actually not available. Since the experimental determination of the polymerization energy of the discrete BeH$_2$ is not easy, therefore theoretical investigations have an increased importance.

The energy, the electronic and geometrical structure and other properties of a quantum-mechanical system may be determined by the solution of the Schrödinger equation. For small molecules there are many well treatable approximation methods producing precise results, but for larger systems we must content ourselves with the use of relatively simple methods. One of these is the FSGO (Floating Spherical Gaussian Orbital) method. The main advantage of its application is that it is an *ab initio* method, without any empirical parameters, and it is very easy to determine the integrals necessary for the calculations; and on the other hand the computer demand of the method is not too large. It was BOYS [1] who first proposed Gaussian-type one-electron orbitals centered on the nuclei. Then, to achieve better results,

PREUSS [2] and others suggested to use floating-type (off-centre) spherical Gaussians having the form:

$$\psi_i = (2/\pi\varrho_i^2)^{3/4} \exp\left[-(\mathbf{r} - \mathbf{R}_i)^2/\varrho_i^2\right] \qquad (1)$$

as orbitals.

To determine the approximative wave-function of a system applying the variational method in the customary way, in (1) the orbital radii ϱ_i, but also the position vectors $\mathbf{R}_i$ have to be treated as variational parameters. In the FSGO method the wave-function of a $2n$-electron system for a singlet ground state is considered as a single Slater determinant composed from n different double occupied one-electron spherical Gaussians.

Lately FROST [3] started an extensive computation series with this model to determine the total energy, equilibrium geometrical structure and other physical properties of some systems. Previously, the method proved to be well applicable among others for the description of interaction potentials of atoms and ions [4], for the calculation of proton affinities [5], for the determination of dissociation energies [6].

In the present paper we intend to apply the FSGO method for the investigation of the polymerization of the BeH_2 molecule. Regarding the computational details, we refer *e.g.* to [5]. The calculations were carried out on the ODRA 1204 computer of the University Computer Center.

The BeH₂ system

The BeH_2 is a very symmetrical molecule. Therefore it is natural to center one of the orbitals on the Be nucleus (inner shell orbital) with orbital radius ϱ_{in} and the other two on the BeH line, equidistant from the Be (bonding orbitals) with orbital radii ϱ_B. The result of the variational calculation is, that the BeH_2 is a linear molecule. So the X-axis was chosen as molecular axis, taking the Be atom as origin, and the co-ordinates of the bonding orbitals were denoted with $\pm X_B$. The results of the calculation (total energy E; equilibrium internuclear distance R) are summarized in Table I. (Atomic units are employed throughout.) Accordingly, the BeH_2 is a stable system in the ground state, though this is not known from experiments.

Table I

	BeH₂
ϱ_{in}	0.510
ϱ_B	2.108
X_B	2.107
R	2.669
E(FSGO)	−13.214*

* See Ref. [3(b)]

The Be₂H₄ system

The Be_2H_4 molecule was considered as a planar system, in the $X - Y$ plane. The two Be atoms were placed on the X-axis, being at the same time the molecular axis, and symmetrically to the origin, with co-ordinates X_{Be}. Two H atoms were localized symmetrically to the X-axis, two others to the Y-axis with co-ordinates X_{H_i}, Y_{H_i} ($i = 1, 2, 3, 4$), (see Fig. 1). Two inner orbitals were localized on the X-axis, near the Be atoms, at the points P_1, P_2, with co-ordinates X_1, X_2 and orbital radii

ϱ_1, ϱ_2. The four further bonding orbitals were placed close to the H atoms, in the points P_i, with co-ordinates X_i, Y_i; and orbital radii ϱ_i ($i=3, 4, 5, 6$); obviously two of them were always laid symmetrically to a co-ordinate-axis, namely, the bond bridge was assumed to be of rhomboid form. According to the calculations the
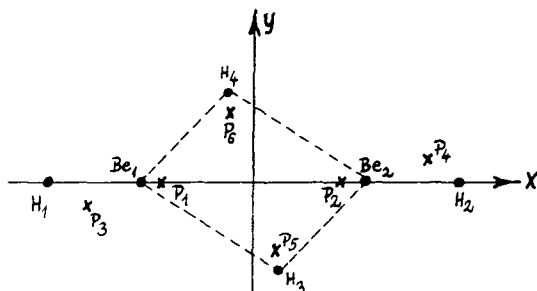

Fig. 1

two inner orbitals are centred practically on the Be atoms, two H atoms and two bonding orbitals are centred on the X-axis, and the other two on the Y-axis. The results for both cases are presented in Table II (in atomic units). Consequently, the experimentally unknown Be_2H_4 is more stable, than the configuration belonging to the separated BeH_2 molecules.

Taking into account the geometry of the Be_2H_4 molecule, first the following molecular structure was supposed for the Be_3H_6: The three Be atoms and two of

Table II

	Be₂H₄	
$\varrho_1 = \varrho_2$	0.51069	0.51068
$\varrho_3 = \varrho_4$	2.1052	2.1069
$\varrho_5 = \varrho_6$	2.0345	2.0309
$X_{Be_1} = -X_{Be_2}$	−1.9096	−1.9018
$X_{H_1} = -X_{H_2}$	−4.5831	−4.5774
$Y_{H_1} = -Y_{H_2}$	−0.0001375	0 (fixed)
$X_{H_3} = -X_{H_4}$	0.0001175	0 (fixed)
$Y_{H_3} = -Y_{H_4}$	−2.1719	−2.1708
$X_1 = -X_2$	−1.9083	$X_{Be_1} = -X_{Be_2}$ (fixed)
$X_3 = -X_4$	−4.0325	−4.0275
$Y_3 = -Y_4$	$-10^{-5} \sim 0$	0 (fixed)
$X_5 = -X_6$	$10^{-5} \sim 0$	0 (fixed)
$Y_5 = -Y_6$	−1.6481	−1.6453
E (FSGO)	−26.4742	−26.4740
$R(\overline{Be_1 Be_2})$	3.8192	3.8036
$R(\overline{H_1 Be_1})$	2.6735	2.6755
$R(\overline{H_3 H_4})$	4.3438	4.3416
$R(\overline{Be_1 H_3})$	2.8920	2.8861
$H_3 Be_1 H_4 \sphericalangle$	98.35°	97.56°

The Be_3H_6 *system*

the H atoms (H_1, H_2) were placed on the X-axis, which was chosen as the molecular axis (see Fig. 2a). Two other H atoms (H_3, H_4) and two of the Be atoms (Be_1, Be_2) were supposed to form a rhombus. The line connecting the H_3 and H_4 was considered

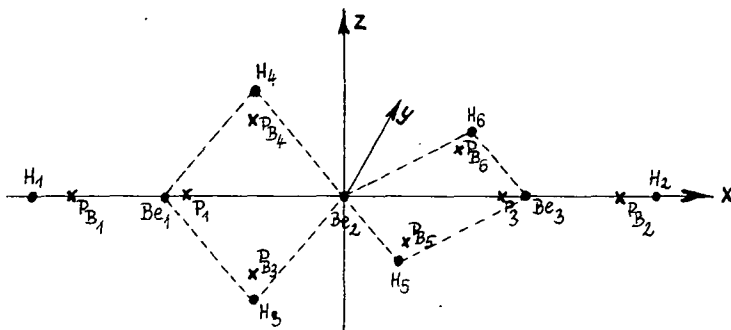*Fig. 2a*

as parallel to the Z-axis. The plane of the other rhombus determined by the Be_2, Be_3, further by the H_5, H_6 was presumed to be orthogonal to the former one, so it is lying in the $Y-Z$ co-ordinate-plane. (We shall call this form a linear form.) One inner orbital was placed on the Be_2 atom, at the origin. The other orbitals were

Table IIIa

	Be_3H_6	
$\varrho_1 = \varrho_2 = \varrho_3$	0.51095	0.51091
$\varrho_{B_1} = \varrho_{B_2}$	2.1072	2.1072
$\varrho_{B_3} = \varrho_{B_4} = \varrho_{B_5} = \varrho_{B_6}$	2.0329	2.0296
$X_{Be_1} = -X_{Be_3}$	-3.8122	-3.793
$X_{H_1} = -X_{H_2}$	-6.4905	-6.4711
$X_{H_3} = X_{H_4} = -X_{H_5} = -X_{H_6}$	-1.9106	-1.90
$Z_{H_3} = -Z_{H_4} = Y_{H_5} = -Y_{H_6}$	-2.1753	-2.1754
$X_{P_1} = -X_{P_3}$	-3.811	$X_{Be_1} = -X_{Be_3}$ (fixed)
$X_{B_1} = -X_{B_2}$	-5.9427	-5.924
$X_{B_3} = X_{B_4} = -X_{B_5} = -X_{B_6}$	-1.9071	-1.8971
$Z_{B_3} = -Z_{B_4} = Y_{B_5} = -Y_{B_6}$	-1.6609	-1.6593
E(FSGO)	-39.7398	-39.7397
$R(\overline{Be_1\,Be_2})$	3.8122	3.493
$R(\overline{H_1\,Be_1})$	2.6783	2.678
$R(\overline{H_3\,H_4})$	4.3506	4.3508
$R(\overline{Be_1\,H_3})$	2.8892	2.885
$H_3\,Be_1\,H_4 \sphericalangle$	97.68°	97.86°

centred near the Be$_1$ and Be$_3$, at the points P_1, P_3 on the X-axis with co-ordinates X_1, X_3. According to the calculations, it was nearly unimportant, whether the P_1 resp. P_3 were kept fixed on the place of the Be$_1$ resp. Be$_3$ or not. Six bonding orbitals were centred on the connecting lines of the Be$_1$—H$_1$, Be$_3$—H$_2$, H$_3$—H$_4$ and H$_5$—H$_6$, near the H atoms, symmetrically.

For both cases (inner shell orbitals centred on the Be atoms, or not) the results are collected in Table IIIa (in atomic units). The notations are used in quite similar sense as before.

Another possibility is to consider the Be$_3$H$_6$ as a system having cyclic planar molecular structure (see Fig. 2b). For reasons of symmetry the Be$_1$, Be$_2$, Be$_3$; the H$_1$, H$_2$, H$_3$ and the H$_4$, H$_5$, H$_6$ atoms were placed on the same circles. Further the centres of the orbitals P_1, P_2, P_3, the P_{B_1}, P_{B_2}, P_{B_3} and the P_{B_4}, P_{B_5}, P_{B_6}, were each also similary situated on circles. The variational procedure was carried out in such a way that the points P_1, P_2, P_3 coincided with the three Be atoms, or their co-ordinates were considered as variational parameters. The equivalent bond lengths and angles were assumed to be equal. The results obtained for both cases are collected in Table IIIb (in atomic units). As it can be seen, although the cyclic structure for the Be$_3$H$_6$ is a stable one, but the linear form is energetically more favourable, so it is the more stable conformation.

Fig. 2b

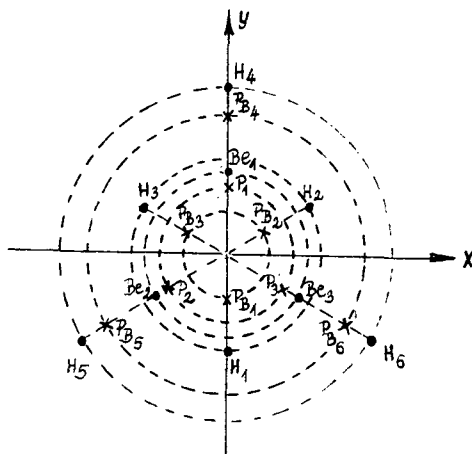Table IIIb

	Be$_3$H$_6$ (cyclic)	
$\varrho_1 = \varrho_2 = \varrho_3$	0.51089	0.5109
$\varrho_{B_1} = \varrho_{B_2} = \varrho_{B_3}$	2.0036	1.9969
$\varrho_{B_4} = \varrho_{B_5} = \varrho_{B_6}$	2.0959	2.0990
Y_{Be_1}	2.7437	2.767
Y_{H_1}	-2.8293	-2.771
Y_{H_4}	5.4261	5.455
Y_{P_1}	2.7421	Y_{Be_1} (fixed)
Y_{B_1}	-2.4221	-2.393
Y_{B_4}	4.8854	4.911
E(FSGO)	-39.6964	-39.6952

Discussion

In the last decade there are numerous theoretical calculations concerning the BeH$_2$ systems dealt with here. Now the configuration interaction study of HOSTENY and HAGSTROM [7] can be regarded as the most accurate treatment with an optimized 80-term wave-function. One can find further detailed references concerning the BeH$_2$ in [7]. According to this very precise investigation, but also those of other authors, the BeH$_2$ is a stable molecule. (This follows from the FSGO model

too, using the energetical data of the Be and H_2 [5].) All the same, the system is unobservable because of unfavourable experimental conditions of measurement. Beside this it seems that the BeH_2 has the property of polymerization. The experimental values of the polymerization energy of the BeH_2 are uncertain, but the theoretical values can be estimated. It is rather easy to get the dimerization and trimerization energies as simple energy differences. Our calculated values are given in Table IV

Table IV

	FSGO	Theor.*
E_{dim}(dimerization energy) $= 2E(BeH_2) - E(Be_2H_4)$	0.046	0.0445 resp. 0.05 $\pm$ 0.01**
E_{trim}(trimerization energy) $= E(Be_2H_4) + E(BeH_2) - \\ - E(Be_3H_6)$	0.051 (for chain structure)	0,0553 resp. 0.063 $\pm$ 0.015**

    * Values from [8]
    ** Estimated value in [8]

(in atomic units). There are no experimental data available for comparison. The only theoretical study on this subject known by the authors is the recent computation of AHLRICHS [8]. This *ab initio* investigation, starting from an SCF calculation, includes the electron correlation energy of the valence shell electrons too. Our calculated values are in good agreement with the results mentioned above (see [8]). Accordingly, the very simple FSGO model seems to be appropriate to predict the existence of the tendency for polymerization in the investigated system.

It is possible to calculate the energy of the $(BeH_2)_n$ linear polymer system for $n \leqq 4$, and the polymerization energy of polymers higher than the trimer, too. However, the computer requirements are significantly larger. It is probable that the polymerization energy generally has a value near 0.05 of order per molecule.

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ИССЛЕДОВАНИЕ СТЕПЕНИ ПОЛИМЕРИЗАЦИИ МОЛЕКУЛЫ ВеН₂

Основное состояние систем BeH₂, Be₂H₄ и Be₃H₆ по методу FSGO

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Проводились рассчёти по энергиям основных состояний и равновесных геометрий молекул BeH₂, Be₂H₄ и Be₃H₆ методом ФШГО. На основе этих исследований молекула BeH₂ показывает тенденцию полимеризоваться. Полученные значения энергий димеризации и тримеризации хорошо согласуются с известными рассчётными результатами.