

Commentationes

Ab initio Calculations on Small Hydrides Including Electron Correlation

I. The BeH₂ Molecule in Its Ground State

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Received January 12, 1968

A method of calculating directly approximate natural orbitals in the electron pair approximation is applied to the ground state of the BeH₂ molecule, which is not known from experiment. The question of optimum localization of the electron pairs for asymmetric nuclear configuration receives particular attention. The interpair correlation energy is estimated. The physical properties of the molecule are predicted and experimental conditions are indicated under which it should be observed.

Die Methode zur direkten Berechnung genäherter natürlicher Orbitale in der Elektronenpaar-näherung wird auf den Grundzustand des vom Experiment her unbekanntes BeH₂-Moleküls angewandt. Die Frage der optimalen Lokalisierung der Elektronenpaare für asymmetrische Anordnung der Kerne findet besonderes Interesse. Die Interpaar-Korrelationsenergie wird abgeschätzt. Die vorausgesagten physikalischen Eigenschaften dieses Moleküls sind in einer Tabelle zusammengestellt. Bedingungen, unter denen das Molekül experimentell beobachtet werden sollte, werden angegeben.

La méthode basée sur le calcul direct des orbitales naturelles approchées est appliquée à l'étude de l'état fondamental de la molécule BeH₂, qui est inconnu du point de vue expérimental. La question de la localisation optimale des paires d'électrons pour des configurations asymétriques des noyaux est discutée en détail. La corrélation interpaires est estimée. On prédit les propriétés physiques de la molécule et on indique les conditions qui devraient permettre de l'observer.

I. Introduction

Good numerical approximations to the solutions of the molecular Hartree-Fock equations for sufficiently small molecules can nowadays be obtained in reasonable computer times e. g. with the use of Gaussian lobe basis functions [24]. Although Hartree-Fock wave functions furnish reliable theoretical estimates for several interesting properties, Hartree-Fock *energies* are deceptively inaccurate and completely useless for accurate calculations of binding energies [30], spectral transition energies and even potential hypersurfaces for chemical reactions [6, 27].

In the Hartree-Fock model, which has the advantage of being computationally simple and close to physical intuition, one neglects what is commonly called the "electron correlation". In a previous paper [1] a method has been developed and described in detail that allows to calculate the *intrapair correlation energy* of atomic and molecular systems in a rather simple way. The method is based on a direct calculation of approximate natural orbitals. It starts with a usual atomic or molecular Hartree-Fock calculation and subsequent optimum localization of the canonical Hartree-Fock orbitals. It has first been applied to the Be and LiH ground

states [1] and its application to more complicated systems is straightforward. For details of the method the reader is referred to Ref. [1].

The BeH₂ molecule is – surprisingly enough – not known from experiment, whereas the BeH molecule is [14, 32]. Solid BeH₂ can be synthesized [5, 33], it decomposes at about 125° C into Be metal and H₂.

One is therefore challenged to find out whether or not the BeH₂ molecule is stable, under which experimental conditions it should exist and why it has not been observed so far. We were particularly concerned with the equilibrium geometry, the binding energy, the harmonic force constants, the normal vibrations and with the influence of electron correlation on these properties.

II. Choice of the Basis Functions

For polyatomic calculations a basis of Gaussian lobe functions

$$\varphi_i(\mathbf{r}) = N e^{-\eta_i(r-r_i)^2} \quad (1)$$

is rather convenient.

It has the advantage that all integrals can be programmed easily and be computed quickly. The drawback of the incorrect asymptotic behaviour near each nucleus and very far from it is probably more serious than has been presumed so far (see e.g. [28]), and one has to be very careful if one wants to calculate other properties than the energy (or those that are determined by the energy, like e.g. force constants). One can, fortunately come very close to the – within the chosen scheme – best possible energy (in the sense of the variation principle), if one chooses carefully the η_i and r_i values and if one uses a sufficiently extended basis set. Experience has shown [9, 18, 26], that it is inappropriate to vary all linear parameters independently from each other, but that one gains computer time without losing accuracy, in “contracting” the basis functions i.e. in keeping the ratios between certain basis functions fixed, e.g. in choosing these ratios as they are obtained for the free atoms with the same basis set.

After some pilot calculations we have decided to use the following basis for the treatment of small hydrides like LiH, BeH₂, BH₃ etc.

Central Atom (Li, Be etc.)

s-functions. Optimum 9s basis of S. Huzinaga [16], of which the 4 Gaussians with largest η are contracted to one group with their coefficients in the 1s-SCF-orbital of the corresponding atom. So we are left with 6 *s*-groups, i.e. 6 variable coefficients.

p-functions are constructed from a pair of Gaussian lobes with coefficients +1 and –1 respectively [24] and with the distance $2d$ between the centers of the lobes; two types of *p*-functions occur, we used for the *p π* functions two groups with the η 's given by Csizmadia et al. [9], i.e. $d=0.5$, $\eta=0.6$ and $d=1.0$, $\eta=0.1$, whereas only one *p σ* group is taken, with $\eta=0.8$, $d=0.7$. The d -values are such, that no overlap integral between a pair of lobes is bigger than 0.98 [18].

H-Atom

s-functions. Three groups contracted from Huzinaga's 5s-basis, where the three steepest Gaussians are contracted to one group with their coefficients in the Hydrogen 1s-orbital. The centers of the Gaussians were shifted somewhat to the central atom as is suggested by the H₂ calculation of Hoyland [15], which improves slightly the energy.

Table 1. BeH₂-calculation with σ -NO's only

	a)	b)
E_{SCF}	– 15.76123	– 15.76116
$E_{\text{corr}}(\sigma)$	– 0.01700	– 0.01679
t	10.8	3.01

$E_{\text{corr}}(\sigma)$ = σ -correlation energy per bond pair. All energies in atomic units.

t = total computer time in minutes on an IBM 7094 (model I).

a) 22 Gaussians uncontracted.

b) 22 Gaussians contracted to 15 groups as described in section II.

p-functions. Two groups with $\eta = 1.0$, $d = 0.3$ and $\eta = 0.3$, $d = 1.0$.

In the *middle of the bond axis* an additional Gaussian lobe with $\eta = 0.2$ has been used.

The effect of contracting the basis is demonstrated by the example of a calculation of BeH₂ in Table 1. In contracting the Gaussians in the way indicated above one reduces the necessary computer-time by a factor of more than three, but the energy is only changed in the sixth decimal place.

One sees clearly that not to contract the basis would be a waste of computertime (see also Ref. [18] and [26]).

III. Equilibrium Geometry and Force Constants

The results of our calculations of the potential hypersurface of the BeH₂ ground state in the vicinity of its equilibrium configuration are summarized in Tables 2 to 4. In Table 2 the adiabatic energy of the molecule in the symmetric linear configuration is given as function of the Be–H distance.

The minimum energy E_0 , the equilibrium distance r_0 and the force constant k_s have been obtained both by fitting a 2nd order polynomial to 3, 4 or 5 points close to the minimum and by fitting a 4th order polynomial to all the points indicated in the table. The results agree up to the last figures indicated in the tables. In

Table 2. *Symmetric-stretching potential curve of BeH₂ in different approximations*

r (in a.u.) ^a	2.2	2.4	2.45	2.5	2.55	2.6	2.65	2.8
E_{SCF}	15.74068	15.75964	15.76146	15.76239	15.76261	15.76204	15.76073	15.75455
$E_{\text{corr}(\sigma)}$	0.03042	0.03146	0.03184	0.03224	0.03262	0.03322	0.03376	0.03568
$E_{\text{corr}(\pi)}$	0.02588	0.02500	0.02475	0.02448	0.02430	0.02392	0.02362	0.02266
E_{corr}	0.05630	0.05646	0.05659	0.05672	0.05692	0.05714	0.05738	0.05834
$E = E_{\text{SCF}} + E_{\text{corr}}$	15.79698	15.81610	15.81805	15.81911	15.81953	15.81918	15.81811	15.81289
<i>Equilibrium distances and force constants</i>								
			r_0	k_s	E_0	g_s		
SCF-approximation			2.54 a.u.	0.075 a.u.	15.76261	-0.035 a.u.		
SCF-approximation + σ -corr.			2.57 a.u.	0.068 a.u.	15.79531	-0.036 a.u.		
SCF-approximation + $(\sigma + \pi)$ corr.			2.55 a.u.	0.075 a.u.	15.81953	-0.037 a.u.		

^a r = BeH-bond distance.

Table 3. BeH₂ *anti-symmetric deformation*

q_a (in a.u.)	0.0	± 0.1	± 0.2
$E_{\text{SCF}} - E_{\text{SCF}}^0$	0.0	0.00037	0.00154
$E_{\text{corr}(\sigma)}$	0.03262	0.03233	0.03278
$E_{\text{corr}(\pi)}$	0.02430	0.02434	0.02438
E_{corr}	0.05692	0.05667	0.05716
$E_{\text{SCF}} + E_{\text{corr}} - E_{\text{SCF}}^0 - E_{\text{corr}}^0$	0.0	0.00062	0.00130
β_{opt}	0.7071	0.78	0.84

Force constants (k_a)

SCF-approximation	0.078 a.u.
SCF-approximation + σ_{corr}	0.070 a.u.
SCF-approximation + $(\sigma + \pi)_{\text{corr}}$	0.067 a.u.

agreement with what we have found for the LiH molecule [1] (but in contrast to Das' [10] results for Li_2) r_0 and k_s are rather well predicted on the Hartree-Fock level. Inclusion of σ -correlation (mainly "left-right" correlation; as to a more precise definition see Ref. [1]) increases r_0 and decreases k_s slightly, whereas inclusion of both σ - and π -correlation leaves r_0 and k_s almost unchanged. A calculation that includes σ -correlation only accounts for the correct asymptotic behaviour at large internuclear separation, but yields too large equilibrium

Table 4. BeH_2 bending deformation

q_b (in a.u.)	0.0	0.1	0.2	0.6
$E_{\text{SCF}} - E_{\text{SCF}}^0$	0.0	0.00004	0.00017	0.00153
$E_{\text{corr}}(a')$	0.04450	0.04448	0.04450	0.04459
$E_{\text{corr}}(a'')$	0.01224	0.01224	0.01224	0.01219
E_{corr}	0.05674	0.05672	0.05674	0.05678
$E_{\text{SCF}} + E_{\text{corr}}$				
$-E_{\text{SCF}}^0 - E_{\text{corr}}^0$	0.0	0.00006	0.00017	0.00149

Force constants (k_b)

SCF approximation	0.0085 a.u.
SCF approximation + σ_{corr}	0.0085 a.u.
SCF approximation + $(\sigma + \pi)_{\text{corr}}$	0.0085 a.u.

distances and too small force constants. For small distances the π -correlation increases because one approaches "near degeneracy" in the vicinity of the united atom limit.

That the equilibrium configuration is really the linear one, in accordance with Walsh's rules [31] and in agreement with other authors' predictions [4, 22, 23] can be seen from Tables 3 and 4 which show the variation of the energy as function of the two other normal coordinates.

In terms of the "inner coordinates" Δr_1 , Δr_2 and $\Delta \alpha$ the normal coordinates q_s (symmetric stretching), q_a (antisymmetric stretching) and q_b (bending) can be expressed as

$$q_s = \Delta r_1 + \Delta r_2, \quad q_a = \Delta r_1 - \Delta r_2, \quad q_b = r_0 \cdot \Delta \alpha. \quad (2)$$

There are two equivalent expansions for the electronic energies V .

$$2V = 2E_0 + k_s q_s^2 + k_a q_a^2 + k_b (q_b^2 + q_b'^2) + g_s q_s^3 + g_{sa} q_a^2 q_s + g_{sb} (q_b^2 + q_b'^2) q_s + \mathcal{O}(q^4) \quad (3)$$

$$2V = 2E_0 + f_r (\Delta r_1^2 + \Delta r_2^2) + 2f_{rr'} (\Delta r_1 \Delta r_2) + 2f_\alpha r_0^2 (\Delta \alpha)^2 + \mathcal{O}(\Delta^3). \quad (4)$$

We have calculated directly k_s , k_a , k_b and g_s . We do not think that the accuracy is sufficient for the calculation of fourth-order force constants, which are necessary if one wants to obtain the anharmonic corrections to the normal vibrations. We limit ourselves therefore to indicating the "harmonic" vibration frequencies (Table 6).

The force constants corresponding to the expansion (4) are also given in Table 6.

It is worth noting that the equilibrium distances and force constants of BeH_2 and BeH agree almost perfectly. For BeH the values $r_0 = 1.343 \text{ \AA} = 2.538 \text{ a.u.}$,

$f_r = 2.26 \text{ mdyn}/\text{\AA}$ have been observed [14, 32]. The numerical value of f_{rr} , actually even its sign, depends very much on correlation. On the Hartree-Fock level it is obtained as $f_{rr} = -0.04 \text{ mdyn}/\text{\AA}$, a calculation including σ -correlation does not effect this value, whereas the inclusion of the π -correlation changes it to $+0.12 \text{ mdyn}/\text{\AA}$. It may be that inclusion of the "interpair-correlation energy" leads to another substantial change, although we do not think so (see also section IV as to the role of the optimum localization for non-symmetric nuclear configuration).

IV. The Problem of Optimum Localization of the Pairs

As we have outlined previously [1] our separated-electron-pair approach is a valid and a good approximation if two conditions are fulfilled.

a) The occupation number of the weakly occupied natural orbitals (or rather pseudo-natural orbitals [11]) have to be small compared to those of the strongly occupied ones, which can to first order be identified with the Hartree-Fock orbitals.

b) It has to be possible to transform the "occupied" canonical Hartree-Fock orbitals by a unitary transformation to a set of orbitals that are essentially localized in different regions of space.

If condition a) is fulfilled the sum of the individual pair correlation energies differs by much less than 1% from the exact intrapair correlation energy, a fact which simplifies the calculation very much, but still allows us to regard the energies obtained, as upper bounds to the true ones. For the ground state of the Be *atom* due to the $2s/2p$ near degeneracy condition a) is actually not fulfilled and this is why the sum of the K and L pair energies cannot without criticism be interpreted as the true intra-pair correlation energy [1]. In the BeH₂ molecule however (like in LiH) we are so far from this "near degeneracy" that condition a) is excellently fulfilled.

Condition b) guarantees that the *inter-pair* correlation energy is much smaller than the *intra-pair* one, so that the latter is a good approximation to the total correlation energy, provided that the *number* of interpair terms is of the same order of magnitude as that of *intra-pair* terms.

There is strong evidence that the unitary transformation which performs the optimum localization does not mix K and L shell orbitals to an appreciable extent [1] and that – for the symmetric molecule – the two equivalent orbitals [20] χ_1, χ_2 to be constructed from the canonical valence shell MO's φ_g and φ_u

$$\begin{aligned}\chi_1 &= \frac{1}{\sqrt{2}} \varphi_g + \frac{1}{\sqrt{2}} \varphi_u \\ \chi_2 &= \frac{1}{\sqrt{2}} \varphi_g - \frac{1}{\sqrt{2}} \varphi_u\end{aligned}\tag{5}$$

are better localized (independent of the criterion of "best" localization [7, 12]) than any other unitary linear combinations of φ_g and φ_u .

We therefore renounced on mixing K and L shell orbitals and on finding the respective optimum mixing coefficient by the criterion of maximum intra-pair correlation energy. Our experience from the LiH case let us conclude that by such a mixing one would not get an improvement of more than 1% of the total intra-

pair correlation energy. On the other hand we did vary the mixing coefficient between φ_g and φ_u and we found in fact the maximum of intra-pair correlation energy for the equivalent orbitals.

The situation becomes more complicated if the two BeH-bond distances are not equal. Then the labels g, u loose their meaning and equivalent orbitals are no longer defined. Rather than to try any of the localization criteria [7, 12] known from the literature, we applied ours of maximum intra-pair correlation energy, i.e. we performed the calculation for different unitary transformations

$$\begin{aligned} \chi_1 &= a\varphi_{v1} + b\varphi_{v2} & a^2 + b^2 &= 1 \\ \chi_2 &= b\varphi_{v2} - a\varphi_{v1} \end{aligned} \quad (6)$$

and interpolated the optimum values of a and b . One point of Table 2 took 10 min on a IBM 7094 model 1, one point of Table 3 about 50 min. (About 5 different choices of a were necessary to find the optimum localizations for each $q_a (\neq 0)$, the pseudo-NO's of two different pairs had to be calculated, the time-consuming Hartree-Fock-part of the calculation had, however, only to be performed once.) The dependence of the intra-pair correlation energy on the coefficient a can be seen for a typical point in Table 5.

Table 5. Dependence of the total valence correlation energy on the localization parameter b for an asymmetric nuclear configuration ($q_a = 0.2$ a.u.)

b	0.6	0.707107	0.8	0.866025	0.9	1.0	b_{opt}
$E_{\text{corr}}(\sigma)$	0.0266	0.3090	0.0333	0.0336	0.0329	0.0195	0.8429
$E_{\text{corr}}(\pi)$	0.0195	0.0232	0.0253	0.0254	0.0248	0.0132	
E_{corr}	0.0461	0.0541	0.0586	0.0590	0.0577	0.0328	0.8413

It is an open question whether or not the goodness of the independent electron pair approach based on optimum localization remains the same along the anti-symmetric – stretching potential curve, in other words whether the “interpair” – correlation energy remains constant, if one defines the “intrapair” contribution with respect to optimum localized pairs.

For the potential curve of the bending vibration equivalent orbitals are always defined and there is no problem how to choose the best localization. The following point merits attention. The terms σ and π orbital, and so σ and π correlation, have a conceptually different meaning for linear and for planar molecules. In order to avoid confusion we have designated by a' and a'' what is often called σ and π in the planar (bent) configuration. In the limit of the linear molecule the a' correlation energy converges towards the σ - plus half of the π -correlation energy.

For the bent configuration p_y -orbitals had to be taken into account even in the Hartree-Fock part of the correlation. This is why the necessary amount of computer time was 16 rather than 10 min.

V. The Correlation Energy and the Binding Energy of BeH_2

For the equilibrium geometry a more refined calculation, using a larger basis set was carried out. The basis was augmented by one p -group in the bond direction with $\eta = 2.0$ and $d = 0.15$, the two Gaussians with $\eta = 0.8$ were not contracted to a p_x -group and three $p\pi$ -groups at the H atoms (with $\eta = 2.0; 0.5; 0.15$) were used rather than two.

The result of this calculation was:

$$E_{\text{SCF}} = -15.76821 \text{ a.u.}; \quad E_{\text{corr}} = -0.02963 \text{ a.u. per valence pair.}$$

From our previous calculation on diatomics, where very good HF energies are known, we can estimate that our HF energy is about 0.005 a.u. \sim 3 kcal/mol above the exact Hartree-Fock energy. This is in perfect agreement with the quite reliable Hartree-Fock energy of -15.7730 a.u. obtained recently by Goldberg and Ritter [13], who used the McLean-Yoshimine SCF-program for linear molecules. That SCF-program, although being superior to Gaussian SCF-programs for linear molecules, does not allow the calculation of bent configurations.

We have not tried to calculate the *K* shell correlation energy of the BeH₂ molecule. We are however allowed to conclude from our LiH calculation [1] that the *K* shell correlation energy is independent of the molecular geometry and practically the same as in the Be atom i.e. equal to -0.0417 a.u. [1]. If we add the correlation energy for the three pairs to the Hartree-Fock energy we obtain $E = -15.8692$, which has to be regarded as an upper bound to the true energy. Our result for LiH obtained in the same way, $E = -8.0586$ a.u., differs by ~ -0.012 a.u. from the experimental value (-8.0707 a.u.) [1].

There is evidence ([1, 21]¹) that the interpair correlation energy between a *K*-shell and a *L*-shell pair is generally about -0.006 a.u., so that we can conclude that of the -0.012 a.u. by which our value for the LiH ground state differs from its experimental counterpart about one half is due to the neglect of the interpair correlation and the other half due to the limitation of the basis (and the limitation to σ - and π -orbitals). In order to estimate the correct ground state energy of BeH₂ we can assume that the *relative* error due to the limitation of the basis is about the same as in our LiH calculation, i.e. that the best value obtainable by a calculation that accounts for intrapair correlation only is close to $-15.869 - 0.012 = -15.881$, which corresponds to a total *intra-pair-correlation energy* of $-15.881 + 15.773 = -0.108$ a.u. ~ -70 kcal/mol. This result has then to be corrected for the *inter-pair* correlation energy, which can in this context be simply added [29]. Two contributions between the *K* pair and either valence (*V*) pair amount to about 0.006 a.u. each, whereas the *interpair* correlation energy between the two valence pairs is hard to guess. It is probably higher than a typical *K-L* interpair correlation energy (~ 0.006 a.u.), but lower than the interpair correlation energy between two valence pairs in the methane molecule [2] (~ 0.018 a.u.). A crude guess is therefore $\sim 0.013 \pm 0.005$ a.u. which leads to the estimate:

$$E = -15.906 \pm 0.01 \text{ a.u.}$$

for the total non-relativistic energy of the BeH₂ molecule (where the uncertainty is probably rather less than 0.01 a.u.) and $E_{\text{corr}} = -0.133 \pm 0.01$ a.u. for the overall correlation energy¹.

¹ The importance of interpair correlation contributions has probably first been stressed by Sinanoğlu and coworkers [V. McKoy and O. Sinanoğlu: J. chem. Physics **41**, 2689 (1964); O. Sinanoğlu: J. chem. Physics **33**, 1212 (1960), **36**, 706, 3198 (1962), Proc. Roy. Soc. (London) A **260**, 379 (1962); O. Sinanoğlu and E. M. Mortenson: J. chem. Physics **34**, 1078 (1961)], and has also been observed by other authors [F. Bender and E. R. Davidson: J. physic. Chem. **70**, 2675 (1966), J. chem. Physics **46**, 402, 3313 (1967); F. Grimaldi: J. chem. Physics **43**, 559 (1965) and communication at the NATO summer school on electron correlation, Frascati 1967]. We thank the referee for drawing our attention to these papers.

From the extrapolated total energy the binding energy given in Table 6 is obtained. The sum of the dissociation energies differs (except for sign) from the binding energy by accounting for the zero-point-vibrations. The experimental dissociation energy of BeH (the second dissociation energy of BeH₂) is rather uncertain. Experimental values between 2.2 e.V. and 2.5 e.V. can be found in the literature [14, 17, 25, 34]. Although the lowest of these [14] seems to be the most reliable, since it gives (together with the Hartree-Fock energy of Cade and Huo [8]) the

Table 6. Predicted physical properties of the BeH₂ molecule in its ground state $X = 1^1\Sigma_g^+$

Equilibrium distance r^0 (Be-H)	2.55 ± 0.02 a.u. = 1.35 ± 0.01 Å		
Minimum adiabatic energy E	-15.906 ± 0.010 a.u.		
Binding energy $E_b = -(D_e^{(1)} + D_e^{(2)})$	-150 ± 5 kcal/mol		
Dissoziation energies			
first bond $D_0^{(1)}$	$89 \pm$ kcal/mol		
second bond $D_0^{(2)}$	53 ± 7 kcal/mol		
sum $D_0^{(1)} + D_0^{(2)}$	142 ± 5 kcal/mol		
Lowest ionisation potential (from Koopmanns' theorem)			
I_1	12.1 eV		
Harmonic force constants			
f_r	2.230 mdyn/Å	$f_{rr'}$	0.120 mdyn/Å
f_α	0.134 mdyn/Å		
Harmonic vibration frequencies			
ω_s	1997 cm ⁻¹		
ω_a	2078 cm ⁻¹		
ω_b	738 cm ⁻¹		
Zero-point vibration energy ~ 8 kcal/mol			

most plausible value for the correlation energy of BeH (namely -0.089 a.u.) we have used Gaydon's estimate [17] of 2.3 ± 0.3 e.V.

It is intuitively quite understandable that the second hydrogen is stronger bond than the first one, because the Be atom has to be promoted to the same "valence state" irrespective of whether it is going to use one or two valences. The bond length and the stretching force constants are about the same irrespective of whether one or two hydrogens are bound is understandable in terms of the same argument.

VI. On the Thermodynamic Stability of BeH₂

Quantum chemistry has now reached a stage where it is possible to predict the existence and the physical properties of (small) unknown molecules by *ab initio* calculations.

BeH₂ is a very stable molecule with respect to a dissociation into BeH + H, Be + 2H, BeH + $\frac{1}{2}$ H₂, or Be + H₂ (see Fig. 1). Its stability relative to metallic Be and solid BeH₂ can be discussed in terms of its thermodynamic functions which are easily calculable from our quantum chemical results. Unfortunately almost nothing is known about solid BeH₂, but from the fact that it is stable (in absence of moisture) at room temperature and that it decomposes into the elements at

about 125° C [33] one can conclude that the free energy of solid BeH₂ at 400° K is about that of solid Be plus that of H₂ of 1 atm. pressure at the same temperature. Neglecting differences in the specific heat of solid Be and solid BeH₂ one obtains an estimate of -10 kcal/mol. for ΔF at 0° K for the reaction Be(solid) + H₂(gas) → BeH₂(solid) which was used in Fig. 1 and which is supposed not to be in error by more than a few kcal/moles.

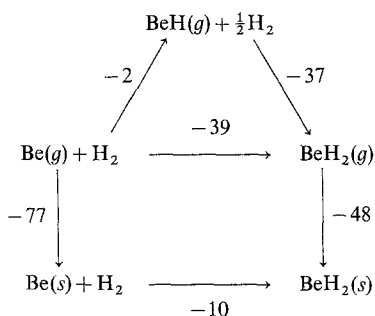


Fig. 1. ΔH values at 0° K (in kcal/mol) for the system Be + H₂. Most of the numbers are uncertain by about ± 5 kcal/mol. g: gas, s: solid

Simple thermodynamic arguments show that at room temperature the vapor pressure of BeH₂ in equilibrium with solid Be is no more than $10^{-27 \pm 5}$ times the H₂ pressure. Even at the decomposition temperature of solid BeH₂ the BeH₂ vapor pressure is so small ($10^{-18 \pm 3}$ atm) that one cannot hope to obtain BeH₂ molecules by heating solid BeH₂. One can, however, estimate that at 1000° K in equilibrium with solid Be and H₂ of 1 atm the partial pressures of BeH₂ and BeH should be $10^{-7 \pm 2}$ atm and $10^{-12 \pm 2}$ atm respectively. At much higher temperatures and small H₂ pressures BeH is favoured thermodynamically relative to BeH₂. This makes partially plausible why BeH (and not BeH₂) has been observed in gas discharge of H₂ with a Be cathode [32].

If one wants to observe BeH₂ one should let react Be metal with H₂ of at least 1 atm at a temperature of 1000 to 1500° K. BeH₂ could be identified through its IR spectrum although this may be experimentally rather difficult. In what concerns the UV spectrum of BeH₂ one has to be aware that the first allowed electronic transition to a ¹ Π state is to be expected in the far UV (at about 150 m μ or less) and that the excited state is bent [31] and has longer Be-H distances so that the transition is almost Franck-Condon forbidden. That BeH₂ has not been observed so far, may come from the fact it is not easily detectable – in contrast to BeH.

VII. Conclusions

It seems that *ab initio* calculations that account for electron correlation are able to give informations about the physical properties of molecules which, for one reason or another, cannot be observed experimentally.

The purely methodological aspect were not so much stressed in this paper. It should be emphasized, however, that the uncertainties in our predictions are essentially based on the fact that the *interpair*-correlation corrections have only been estimated rather than calculated. We are now planning to program the

calculation of interpair-correlation energies as well and to study in how far they can be simply added to the intrapair energy.

Our calculated upper bound for the energy of BeH_2 differs by about 0.037 ± 0.01 a.u. $\sim 17 \pm 6$ kcal/mol from the extrapolated total energy. Although this discrepancy is still unsatisfactory one should not forget that the Hartree-Fock energy [13] is 0.133 ± 0.01 a.u. $\sim 84 \pm 6$ kcal above the extrapolated value and that the minimum basis set MO-LCAO-SCF value [19] is even 0.183 a.u. $\sim 114 \pm 6$ off the probably correct value.

The task of calculating the physical properties of a molecule like BeH_2 is not completely solved if one indicates typical ground state properties and the thermodynamic functions. One should also predict the UV spectrum (which amounts to calculate the lowest excited state) and predict, whether the BeH_2^+ is stable (and can therefore be observed in a mass spectrometer). Insofar our investigation is still incomplete.

An interesting problem is finally to understand the high cohesion energy of solid BeH_2 and to study whether BeH_2 has a tendency to polymerize or oligomerize via H bonds, as has been supposed [33]. Work on this question is in progress.

Acknowledgement. The numerical calculations have been carried out at the DRZ Darmstadt. Financial support by "Deutsche Forschungsgemeinschaft" and by a NATO-grant for research and collaboration on electron correlation is gratefully acknowledged.

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