Theoret. Chim. Acta (Berl.) 49, 123–130 (1978)

THEORETICA CHIMICA ACTA

Potential Energy Surfaces for BeH_2 and BH_2

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The diatomics-in-molecules method has been used to obtain potential energy surfaces (PES) for the molecules BeH_2 and BH_2. The method is used in a way proposed by Tully [1]. The present paper contains an analysis of some features of PES in the vicinity of their crossing near linear configurations of the molecules.

Key words: BeH_2 and BH_2, potential energy surfaces of ~

1. Introduction

PES are necessary for the theoretical description of molecular collision processes. If the collision process is slow it is necessary to know a single isolated PES in the relatively wide region of the conformation space. On the other hand, a fast collision process leads to non-adiabatic transitions which are localized in the relatively narrow regions in the vicinity of crossing or pseudocrossing of the different PES. At present the complete isolated PES are known for a large number of molecular systems, whereas the characteristics of the PES near crossings have not been systematically studied. The most significant results have been obtained for diatomic collision complexes and diatomic molecules [2]. Carrington [3] has studied crossings of two potential surfaces only. His analysis does not contain any calculations of the potential curves for the molecular systems. Davidson [4] has introduced a new coordinate system for the description of triatomic molecules. Within this coordinate system particular emphasis is made on the resulting branch-cut on potential surfaces. The purpose of the present work is to study PES of the simple dihydrides and to classify possible types of their crossings. The diatomics-in-molecules (DIM) method is the most adequate one for this purpose. This method was proposed by Ellison [5] and modified by Tully [1]. The DIM method allows to deduce the PES of polyatomic systems using a small amount of experimental dates for atomic and diatomic fragments. We have applied this method to study the PES for the molecules BeH_2 and BH_2.

0040-5744/78/0049/0123/$01.60

Additionally, some inaccuracies of Ref. [1] have been eliminated and some constants have been changed to get a better accordance with experimental data.

2. Hamiltonian Matrices

The molecule (abc) is assumed to be in the xz plane, atom a being in the origin of the coordinate system. We take into account only the ${}^2S$ ground state of the hydrogen atoms, two lowest ${}^1S$ and ${}^3P$ states of atom Be and two lowest ${}^2P$ and ${}^4P$ states of atom B. These states of beryllium and boron form localized chemical bonds in the ground states of BeH_2 and BH_2. We construct now the polyatomic basis functions (PBF), which correspond to the specific values of s and s_z, (0, 0) for BeH_2 and $(\tfrac{1}{2}, \tfrac{1}{2})$ for BH_2 ·

$$\psi_1 = \hat{\mathscr{A}}\,{}^1S_a\,{}^2S_b\,{}^2S_c\left[(0\,\tfrac{1}{2}-\tfrac{1}{2})-(0-\tfrac{1}{2}\,\tfrac{1}{2})\right]\frac{1}{\sqrt{2}} \tag{1}$$

$$\psi_{2,3,4} = \hat{\mathscr{A}}\,{}^3P_{a(x,y,z)}\,{}^2S_b\,{}^2S_c\left[(1-\tfrac{1}{2}-\tfrac{1}{2})-\frac{1}{\sqrt{2}}(0\tfrac{1}{2}-\tfrac{1}{2})\right.$$
$$\left.-\frac{1}{\sqrt{2}}(0-\tfrac{1}{2}\,\tfrac{1}{2})+(-1\,\tfrac{1}{2}\,\tfrac{1}{2})\right]\frac{1}{\sqrt{3}} \tag{2}$$

$$\bar{\psi}_{1,2,3} = \hat{\mathscr{A}}\,{}^2P_{a(x,y,z)}\,{}^2S_b\,{}^2S_c\left[(\tfrac{1}{2}\,\tfrac{1}{2}-\tfrac{1}{2})-(\tfrac{1}{2}-\tfrac{1}{2}\,\tfrac{1}{2})\right]\frac{1}{\sqrt{2}} \tag{3}$$

$$\bar{\psi}_{4,5,6} = \hat{\mathscr{A}}\,{}^2P_{a(x,y,z)}\,{}^2S_b\,{}^2S_c\left[2(-\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})-(\tfrac{1}{2}\,\tfrac{1}{2}-\tfrac{1}{2})-(\tfrac{1}{2}-\tfrac{1}{2}\,\tfrac{1}{2})\right]\frac{1}{\sqrt{6}} \tag{4}$$

$$\bar{\psi}_{7,8,9} = \hat{\mathscr{A}}\,{}^4P_{a(x,y,z)}\,{}^2S_b\,{}^2S_c\left[(\tfrac{3}{2}-\tfrac{1}{2}-\tfrac{1}{2})-\frac{1}{\sqrt{3}}(\tfrac{1}{2}-\tfrac{1}{2}\,\tfrac{1}{2})\right.$$
$$\left.-\frac{1}{\sqrt{3}}(\tfrac{1}{2}\,\tfrac{1}{2}-\tfrac{1}{2})+\frac{1}{\sqrt{3}}(-\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})\right]\frac{1}{\sqrt{2}} \tag{5}$$

where $\hat{\mathscr{A}}$ is the antisymmetrization operator.

The functions $\psi_{2,3,4}$, $\bar{\psi}_{1,2,3}$ and $\bar{\psi}_{4,5,6}$ are transformed in the same manner as the polar vector $\boldsymbol{r}=(x, y, z)$, and the functions $\bar{\psi}_{7,8,9}$ are transformed just as the axial vector $[\boldsymbol{r}_1 \times \boldsymbol{r}_2]$. The irreducible representations of groups for BPF can easily be obtained.

Now, it is necessary to determine the energy matrices of the systems under consideration on the basis of PBF (1)–(2) and (3)–(5). In the DIM method the total Hamiltonian $\hat{H}$ is written as a sum of atomic and diatomic parts:

$$\hat{H} = \hat{H}_{ab} + \hat{H}_{ac} + \hat{H}_{bc} - \hat{H}_a - \hat{H}_b - \hat{H}_c \tag{6}$$

To determine the diatomic fragment matrices, a special PBF basis for every diatomic fragment should be used. The functions of this basis are eigenfunctions of the total spin operators $\hat{s}^2$, $\hat{s}_z$, of the diatomic spin operators $\hat{s}^2(ik)$, $\hat{s}_z(ik)$ and of the projection $\Lambda(ik)$ of the orbital angular momentum upon the (ik) molecular axis. In addition the functions of this basis have the same spatial symmetry as the corresponding polyatomic basis functions. The choice of the proper linear combinations, i.e. the special basis functions, is governed by the rules given in Ref. [1]. The eigenfunctions of the diatomic spin angular momentum operators $\hat{s}^2(ik)$ and $\hat{s}_z(ik)$ have been expressed in terms of Racah coefficients [6]. The eigenfunctions of the projection $\hat{\Lambda}(ik)$ of the orbital angular momentum operator have been expressed in terms of the rotation matrix [1]. The final transformation from the special basis to the starting basis is then carried out by the similarity transformation. The atomic fragment matrices are diagonal due to orthogonality of PBF's.

The necessary quantitative data for diatomic terms are given in the Appendix and in Ref. [1]. If the molecule belongs to some group of space symmetry higher than $\mathfrak{C}_s$, then the number of zero elements increases and the other elements in the energy matrices become simpler.

The availability of more reliable diatomic potential curves and the use of large enough basis sets might improve the accuracy of the method. DIM, modified by Tully [1], has the following limitations: diatomic fragment terms in the molecule are considered as corresponding terms in isolated diatomic molecules; it is necessary to use some approximations for the energy matrix elements; it is difficult to take into account the overlap of PBF's in some reasonable way; the hybridization of atomic orbitals is not taken into account.

The disadvantages of the DIM method mentioned may evidently result in some uncertainties in PES values which would displace degeneration points. But it seems to be rather improbable that several crossing points would coincide in their positions or disappear if more accurate calculations would be performed. However, there is no doubt that the PES shape in the vicinity of crossing points is governed by the symmetry of crossing terms and by general analytical features of PES but not by the accuracy of expressions for elements in energy matrices.

Nevertheless, the DIM method gives reliable results for PES within the wide range of internuclear distances [1, 5].

It should be noticed that the basis set used makes low-lying terms of any symmetry more reliable than other terms of the same symmetry.

3. Potential Energy Surfaces in the Vicinity of Their Crossing

PES for the molecules under consideration are the solutions to the following secular equations:

$$\det\|H_{MN}^{(\mathrm{BeH_2})} - U\delta_{MN}\| = 0; \qquad \det\|H_{M'N'}^{(\mathrm{BH_2})} - U\delta_{M'N'}\| = 0$$
$$(M, N = 1, \ldots, 4) \qquad (M'N' = 1, \ldots, 9)$$

In accordance with the previous results [7, 8], the BeH_2 ground state is found to be linear, with the ${}^1\Sigma_g^+$ symmetry and the atomization energy of 6.8 eV. The BH_2

ground state corresponds to the bond angle of 131°, to the ${}^2A_1$ symmetry and has the atomization energy of 8.6 eV.

The excited state PES have a complex geometrical structure. However, in the crossing regions these surfaces are amenable to the detailed analysis. The simplest information about crossing of PES can be obtained for the linear configurations, which are characterized by the $\mathbb{D}_{\infty h}$ group symmetry (Figs. 1, 2). PES depend then on the single parameter $r=r_{ab}=r_{ac}$.

In accordance with a general rule, the terms of the same symmetry do not cross but the terms of different symmetry do so (point $\mathscr{A}$ in Fig. 1 and points $\bar{\mathscr{A}}$, $\bar{\mathscr{B}}$, $\bar{\mathscr{C}}$ and other in Fig. 2). At these points electronic states of molecules are degenerated. The BeH_2 electronic state is triply degenerated at the point $\mathscr{A}$, where the doubly degenerated ${}^1\Pi_g$-term crosses the ${}^1\Sigma_g^+$-term. Such a triple degeneration occurs at the points $\bar{\mathscr{A}}$, $\bar{\mathscr{B}}$, $\bar{\mathscr{C}}$, $\bar{\mathscr{D}}$, $\bar{\mathscr{E}}$ for BH_2 and double degeneration takes place at $\bar{\mathscr{M}}$, $\bar{\mathscr{L}}$. The degeneration disappears due to the deformation of molecules. If they are in

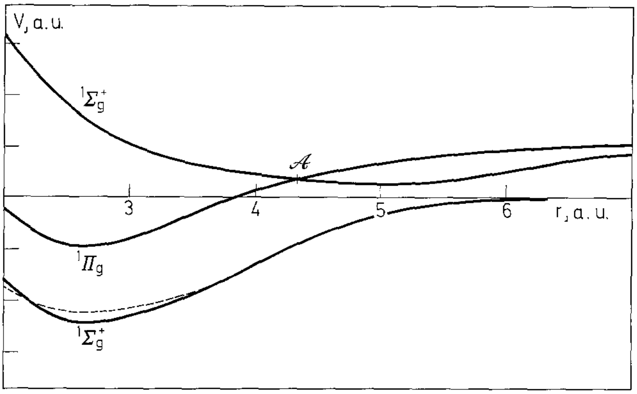


Fig. 1. Linear HBeH potential energy curves as a function of BeH bond length (r); dashed lines, *ab initio* results of Ref. [8] for the ground ${}^1\Sigma_g^+$ term of HBeH

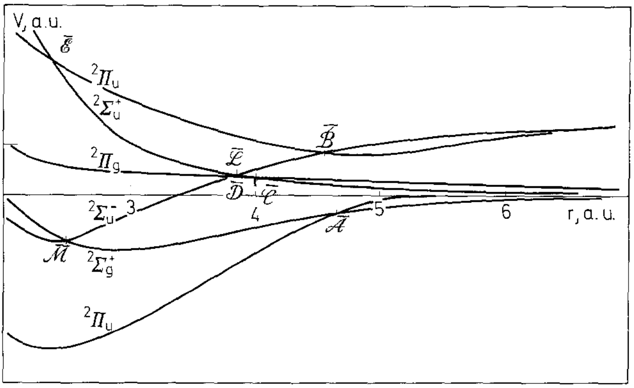


Fig. 2. Linear HBH potential energy curves as a function of BH bond length (r)

the isoscale triangle's configuration (symmetry group $\mathbb{C}_{2v}$), the splitting of Π-terms can be characterized by angular diagrams (Figs. 3, 4). In the coordinates of the doubly degenerated bending vibration E_{1u} of a linear molecule the two resulting terms (A_2+B_1 or A_1+B_2) have the shape of rotation paraboloids with touching tops. This is Renner effect. Such a form of PES is governed by vanishing nondiagonal elements of the energy matrices among the states of different symmetry, A_2 and B_1 or A_1 and B_2. In accordance with the noncrossing rules touching of the terms of $\mathbb{C}_{2v}$ molecular symmetry, arising from the Π-term corresponds to the "crossing" of the terms of different symmetry (depending upon two coordinates) along the line in the configurational space (in the present case $U=U(r,\theta)$ and the crossing line is determined by the equation: $\theta=180°$).

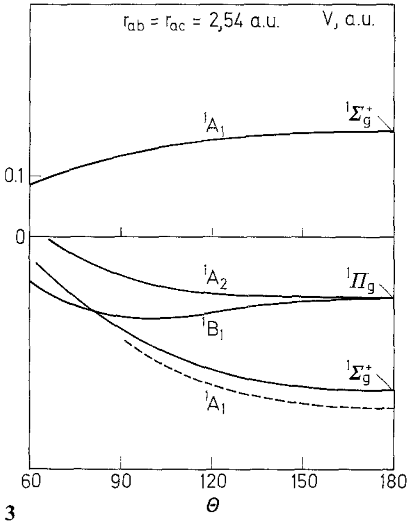
The qualitative behavior of the terms for BeH_2 in the vicinity of the point $\mathscr{A}$ is clear from Fig. 5. In the vicinity of point $\mathscr{A}$ the energy matrix for BeH_2 has the form:

$$\left\| \begin{array}{cccc} a_{11}+b_{11}^{(1)}\rho^2+\cdots & a_{12}+b_{12}^{(1)}\rho^2+\cdots & 0 & 0 \\ a_{12}+b_{12}^{(1)}\rho^2+\cdots & a_{22}+b_{22}^{(1)}\rho^2+\cdots & 0 & 0 \\ 0 & 0 & a_{33}+b_{33}^{(1)}\rho^2+\cdots & 0 \\ 0 & 0 & 0 & a_{33}+b_{33}^{(2)}\rho^2+\cdots \end{array} \right\|$$

where a_{ij}, $b_{ij}^{(1,2)}$ are constants,

$$a_{33}=(a_{11}+a_{22})/2+[(a_{11}-a_{22})^2/4+a_{12}^2]^{1/2}$$

$$\rho\simeq r^*(\pi-\theta)$$



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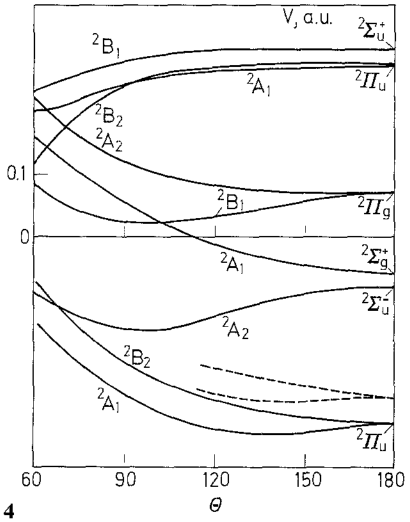

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Fig. 3. BeH_2 potential energy curves as a function of angle θ ($r=2.54$); dashed lines, *ab initio* results of Ref. [7] for the ground $^1A_1$ term of BeH_2

Fig. 4. BH_2 potential energy curves as a function of HBH angle θ ($r=2.28$); dashed lines, *ab initio* results of Ref. [9] for the ground $^2A_1$ and first exited $^2B_2$ states of BH_2

and r^* is the internuclear distance corresponding to the point $\mathscr{A}$ ($r^* \approx 4.3$). If $\rho = 0$ triple degeneration takes place. In the vicinity of crossing, potential surfaces have the form shown in Fig. 5.

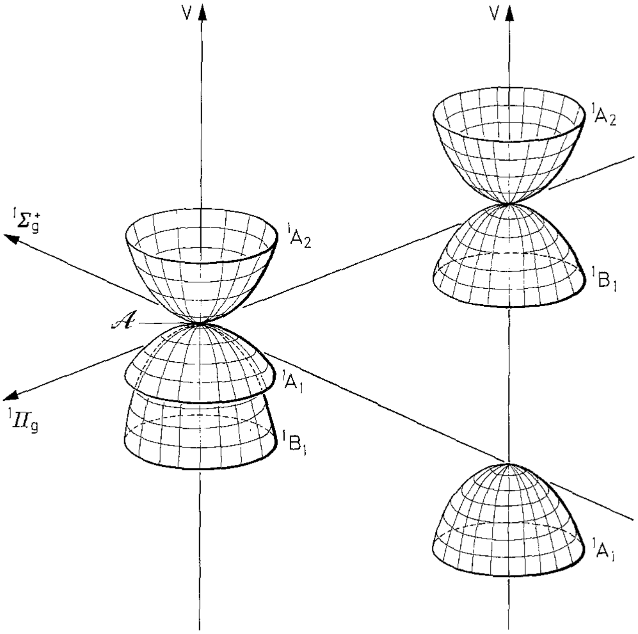

Fig. 5. Geometry of electronic terms of HBeH at the point $\mathscr{A}$

A similar picture is also valid for BH_2 in the vicinity of the points $\overline{\mathscr{B}}, \overline{\mathscr{E}}, \overline{\mathscr{G}}$. It would be easy to find the PES near $\overline{\mathscr{L}}$ and $\overline{\mathscr{M}}$. In this case the crossing of two-dimensional terms of different symmetry occurs at some point of the two-dimensional conformation space (a counterpart of possible noncrossing of the terms of different symmetry in the one-dimensional case).

The crossings which occur at the points $\overline{\mathscr{A}}, \overline{\mathscr{D}}$ and $\overline{\mathscr{C}}$ are of a new type. An important feature of these points is that in their vicinity one of two terms arising from the Π-term have the same symmetry in the quasilinear configuration $\mathbb{C}_{2v}$, just as the approaching Σ-term. In the vicinity of point $\overline{\mathscr{A}}$ the energy matrix for BH_2, including $^2A_1$ and $^2B_2$ states, has the form:

$$\left\| \begin{array}{ccccc}
\bar a_{22}+\bar b^{(1)}_{22}\bar\rho^2 & \bar a_{23}\bar\rho & \bar a_{25}+\bar b^{(1)}_{25}\bar\rho^2 & 0 & 0 \\
\bar a_{23}\bar\rho & \bar a_{33}+\bar b^{(1)}_{33}\bar\rho^2 & \bar a_{35}\bar\rho & 0 & 0 \\
\bar a_{25}+\bar b^{(1)}_{25}\bar\rho^2 & \bar a_{35}\bar\rho & \bar a_{55}+\bar b^{(1)}_{55}\bar\rho^2 & 0 & 0 \\
0 & 0 & 0 & \bar a_{22}+\bar b^{(2)}_{22}\bar\rho^2 & \bar a_{25}+\bar b^{(2)}_{25}\bar\rho^2 \\
0 & 0 & 0 & \bar a_{25}+\bar b^{(2)}_{25}\bar\rho^2 & \bar a_{55}+\bar b^{(2)}_{55}\bar\rho^2
\end{array} \right\|$$

where $\bar{a}_{ij}$, $\bar{b}_{ij}^{(1,2)}$ are constants, $\bar{\rho} \simeq r^{**}(\pi-\theta)$,

$$\bar{a}_{33}=(\bar{a}_{22}+\bar{a}_{55})/2-[(\bar{a}_{22}-\bar{a}_{55})^2/4+\bar{a}_{25}^2]^{1/2}$$

and r^{**} is the internuclear distance corresponding to the point $\overline{\mathscr{A}}$ ($r^{**} \simeq 4.6$). If $\bar{\rho}=0$, triple degeneration takes place. In the vicinity of crossing potential surfaces have the form shown in Fig. 6.

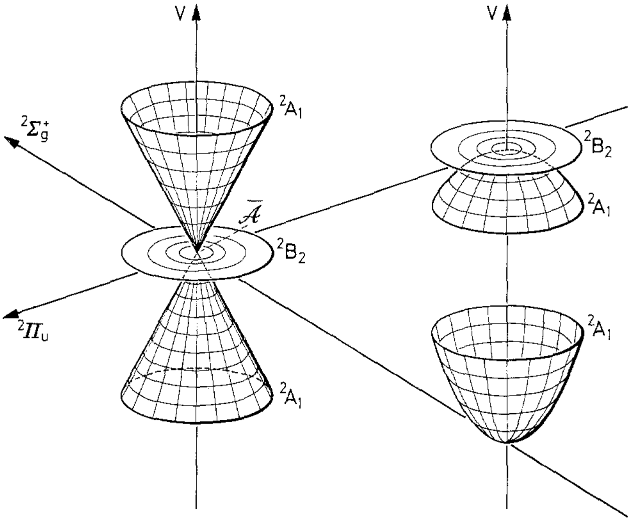

Fig. 6. Geometry of electronic terms of HBH at the point $\overline{\mathscr{A}}$

Nondiagonal elements of the energy matrix, which connect the $^2A_1$ states, are first order in $\bar{\rho}$. In this case conic crossing is expected. In accordance with the general rule this is the crossing of two-dimensional terms of the same symmetry at the point on the plane.

4. Conclusion

A short study of electronic adiabatic terms of the three-atomic molecules BeH_2 and BH_2 in the vicinity of crossing of the terms near quasilinear configurations of the atoms has been carried out. Specific cases considered enable us to draw a general conclusion which is important for the theory of the non-adiabatic transitions: the large number of term crossings in the molecules AH_2 is caused by the degeneration of three PES. Up to now such situations have not been investigated though they are rather often encountered. The results reported have been obtained by the diatomics-in-molecules method, which is quite useful not only for deriving complete isolated PES, which are needed in the adiabatic collision studies, but also for the analysis of the terms in the crossing regions where non-adiabatic transitions are known to be localized.

Appendix

The next approximation is used for the elements $\tilde{H}_{MN}^{(ik)}$ of diatomic energy matrix in the basis of special PBF's:

$$\tilde{H}_{MN}^{(ik)} = \begin{cases} V_M^{(ik)} + T_M^{(ik)} & M = N \\ D[V_M^{(ik)} - V_N^{(ik)}] & M \neq N \end{cases}$$

where $T_M^{(ik)} = \text{const}$,

$$V_M^{(ik)} = A\{\exp[-2B(r_{ik} - C)] \mp 2\exp[-B(r_{ik} - C)]\}$$

The values of the constants A, B, C, D and $T_M^{(ik)}$ for the considered states of diatomic fragments are given in the Table V of Ref. [1]. New values of the next constants are used:

$A = 0.221$ $({}^3\Pi_2, \text{BH})$
$D = 0.23$ $({}^2\Sigma_{12}^+, \text{BeH})$
$D = 0.1$ $({}^3\Pi_{12}, \text{BH})$

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Received August 11, 1977/December 19, 1977