

On the interaction of two conical intersections: the H_6 system

A.J.C. Varandas *, A.I. Voronin, I. Borges Jr.

Departamento de Química, Universidade de Coimbra, P-3049 Coimbra Codex, Portugal

Received 7 August 2000; in final form 21 September 2000

Abstract

We report a study on the interaction of two H_3 systems, which are known to possess a conical intersection when infinitely separated from each other. The topology of the crossing seam is analysed for different geometrical arrangements of the two interacting partners. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The study of systems possessing conical intersections is becoming a major issue in molecular physics. Such an interest is mainly due to the topological effects, which arise from such crossing seams. Recently, Baer, Englman and one of the authors [1,2] have suggested to study the interaction between two conical intersections, and considered to describe each interacting partner as a model system formed by one electron housed by a vibrating molecule. Such an one-electron model has previously been suggested [3] as a prototype of a conical intersection. In spite of the great simplifications introduced, it is expected that such a model may illuminate in situations such as dimerization reactions where each monomer is known to have a conical intersection, e.g., the $Li_3 \cdots Li_3$ dimer. From the studies in Ref. [1], it was concluded that the coupling of the two interacting systems removed the original degeneracy almost entirely, although leading to other types of degeneracies. The implications of such topological

changes on the behavior of the electronic and nuclear wave functions have also been investigated [1]. Clearly, the importance of such results calls for a study on a realistic system using accurate ab initio methods. The major aim of this work is to report such a study by considering the $H_3 \cdots H_3$ prototype interaction. Although it is well known that H_3 is an extremely floppy van der Waals molecule [4,5], it has obvious advantages due to the small number of electrons involved.

The Letter is organized as follows. Section 2 describes the ab initio calculations, while the results are reported in Section 3. The final remarks are in Section 4.

2. Ab initio calculations

All calculations have been carried out using the MOLPRO [6] suite of programmes, and the one electron cc-pVTZ basis set of Dunning [7]. In the survey calculations, the lowest three roots of singlet symmetry have been obtained at both the CAS and MR CISD levels. They covered the geometries shown in panels (a) to (c) of Fig. 1, which can be characterized in terms of two parameters: r , the H–H side of the equilateral triangle, and R , the

* Corresponding author. Fax: +351-39-27703.

E-mail address: varandas@qtvsl.uc.pt (A.J.C. Varandas).

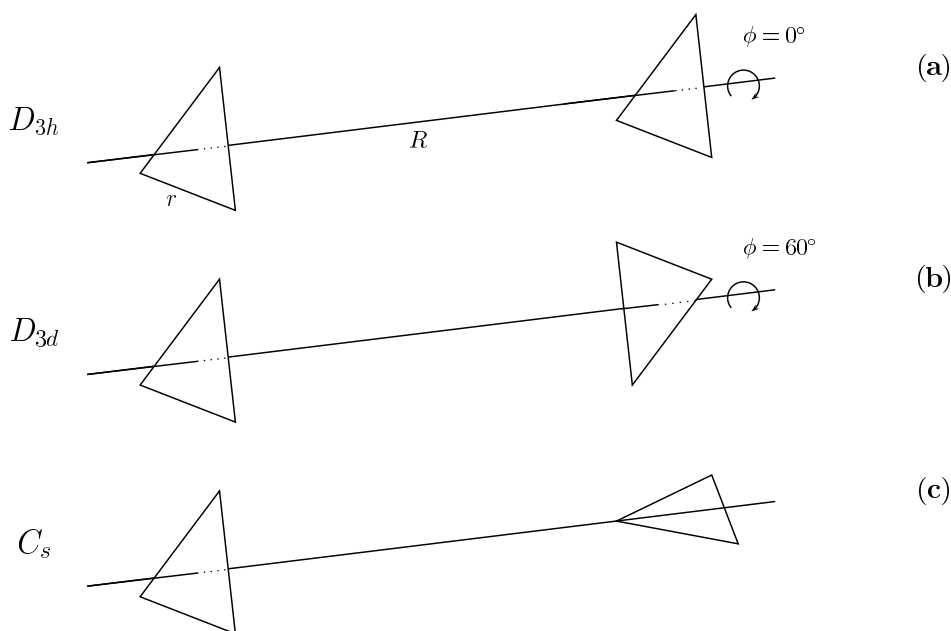


Fig. 1. Structures considered in the ab initio calculations from the present work.

distance between the centers of symmetry of the two equilateral triangles. Note that the arrangement in panel (a) of Fig. 1 has D_{3h} symmetry and corresponds to a value of the ϕ angle equal to 0° ; ϕ is the rotation angle of the right-hand-side equilateral triangle with respect to the left-hand-side one, which is assumed to be fixed. In turn, the staggered arrangement in panel (b) corresponds to the angle $\phi = 60^\circ$, and belongs to the D_{3d} symmetry point group. Since the character tables and irreducible representations of the above two symmetry point groups can be found in textbooks [8], they will not be given here. The final arrangement considered in this work is shown in panel (c) of Fig. 1, and has only C_s symmetry. For all three arrangements described above, calculations have been carried for a series of r values over the range $0.5 \leq r/a_0 \leq 5.5$ at intervals of $0.25a_0$. Similarly, the R coordinate has been covered from $R = 0.5a_0$ ($R = 0$ in the case of arrangement (c)) up to $R = 10a_0$.

3. Results and discussion

The ab initio results calculated in the present work are illustrated in Figs. 2–4. Specifically, Fig. 2

shows the resulting two-dimensional (r, R) potential energy surfaces corresponding to the interaction in panel (a) of Fig. 1. An illustrative cut along these 2D surfaces is displayed in Fig. 3a. It corresponds to fix the side of the H_3 equilateral triangle at $r = 1.5a_0$, which is approximately the most stable D_{3h} geometry in the isolated hydrogen trimer. The notable feature from this plot is the

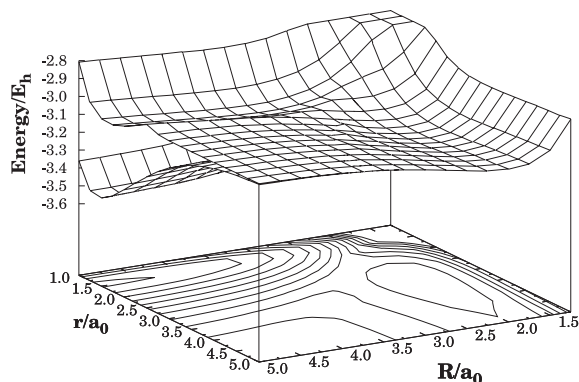


Fig. 2. Two-dimensional (r, R) perspective/contour plot of the $H_3 \cdots H_3$ interaction potential energy surface corresponding to geometries (a) of Fig. 1.

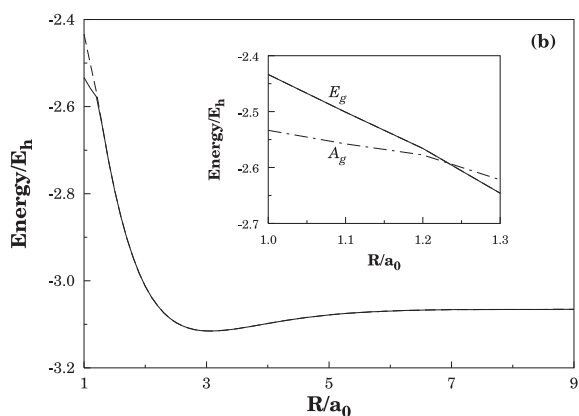
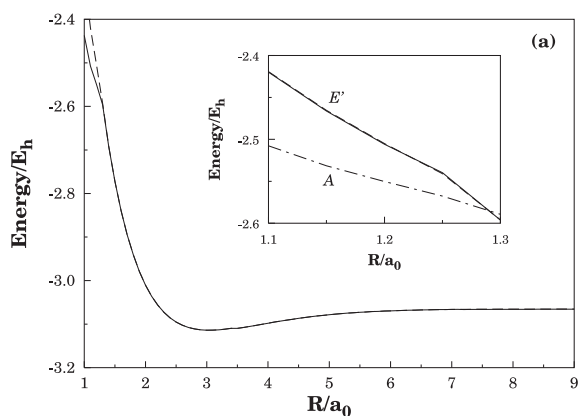


Fig. 3. Panel (a) shows a cut along the 2D surface of Fig. 2a for $r = 1.5a_0$. The main figure shows the two lowest energy states, while the insert indicates that the lowest energy state for $R \leq 1.28a_0$ is the third lowest non-degenerate state (see the text). Panel (b) shows a similar plot but for the staggered arrangement (b) in Fig. 1 with $r = 1.5a_0$.

coincidence of the curves for the two lowest states almost over the complete range of the R coordinate. This may be explained in terms of the appropriate symmetry point group. In fact, the arrangement (a) has a regular prism shape which obeys the D_{3h} symmetry point group, i.e., it has a third-order rotation axis C_3 (along R), three second-order axes (which are perpendicular to the three equivalent faces of the prism) and associated σ'_v planes, and a mirror plane (σ_h) between the two equilateral triangular H_3 species. Note that each isolated H_3 system obeys the same D_{3h} symmetry point group. Note especially that such a symmetry

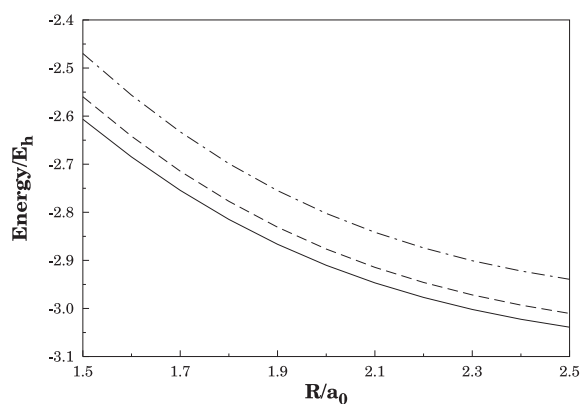


Fig. 4. Similar to Fig. 2 but for the arrangement (c) of Fig. 1 with $r = 1.5a_0$.

point group has an E' and an E'' double degenerate representations. Recall that, for the D_{3h} point group, the direct product of two E' degenerate representations gives $E' \otimes E' = A_1 \oplus A_2 \oplus E'$. Similarly, for the D_{3d} point group, one has $E_g \otimes E_g = A_{1g} \oplus A_{2g} \oplus E_g$. This implies that the two lowest singlet roots of the $H_3 \cdots H_3$ interaction in arrangement (a) of Fig. 1 will correspond to the two E' components of such a doubly degenerate group. It also implies that the locus of conical intersection is now a 2D symmetry preserving manifold, since the crossing seam (which occurs for each isolated interacting partner along the D_{3h} line) is maintained for each pair of values (r, R) . Thus, the apparent split seen in Fig. 3b for distances about $R \leq 1.23a_0$ is in fact due to the lowest state having a different symmetry (A symmetry) in this region. This can be best seen from the insert in the plot of Fig. 3b, which shows a detailed view of all three states over the region of intersystem coordinates defined by $R \leq 1.3a_0$.

Similar considerations to those invoked for arrangement (a) of Fig. 1 can be applied to the staggered arrangement in panel (b) of the same figure. In this case, the symmetry point group is D_{3d} , with the appropriate doubly degenerate representation being now E_g . Not surprisingly therefore are the results presented in Fig. 3b, which shows that the two members of E_g representation becomes degenerate for almost all values of R (note that this is a symmetry preserving axis). Note that these considerations apply for any value

of the rotating angle ϕ provided that such an angle is kept fixed for all values of R .

Regarding the arrangement in panel (c) of Fig. 1, it is clear that it now belongs to the symmetry point group C_s , which has only one-dimensional representations. Thus, as shown in Fig. 4, the three lowest states become non-degenerate for all values of the coordinate R .

Another interesting feature of the title system is related to the fact that it may be considered a prototype of two colliding triatomics yielding three diatomics. In fact, the two reactant $H_3(^2E')$ systems lead for small values of R to three interacting diatomics. This is best seen from the 2D plot in Fig. 2, which clearly shows this process to be a very exothermic one at least for values of r close or larger than the equilibrium geometry of the triatomic ($r_e \sim 2a_0$). However, the apparent minima in the cuts of Fig. 3 are really not true minima since there is always a vibrational normal mode that leads to the more stable three isolated H_2 molecules.

Finally, we may wish to consider the simplest analytical form of the H_6 potential energy surface in the vicinity of the degeneracy locus. Let us define the coordinate set as

$$\begin{pmatrix} Q_1^i \\ Q_2^i \\ Q_3^i \end{pmatrix} = \begin{bmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \end{bmatrix} \begin{pmatrix} \Delta r_1^i \\ \Delta r_2^i \\ \Delta r_3^i \end{pmatrix}, \quad (1)$$

where $\Delta r_j^i = r_j - r_j^{0,i}$ are the displacement coordinates from a reference geometry $r_j^{0,i}$, index i labels the interacting subsystem, index j the specific coordinate in a given subsystem, and index 0 denotes a reference geometry ($i = 1, 2, j = 1 - 3$). By analogy with the well-known potential matrix for X_3 systems, we then have in first-order with respect to the displacements from the seam, the following 2×2 potential matrix:

$$V = \begin{bmatrix} k_1 \Delta R + k_2 \sum_{i=1,2} Q_1^i & k_3 \sum_{i=1,2} Q_2^i \\ +k_3 \sum_{i=1,2} Q_2^i & k_1 \Delta R + k_2 \sum_{i=1,2} Q_1^i \\ k_3 \sum_{i=1,2} Q_3^i & \\ & k_2 \sum_{i=1,2} Q_3^i \\ & +k_3 \sum_{i=1,2} Q_2^i \end{bmatrix}, \quad (2)$$

where $\Delta R = R - R^0$ is the intersystem displacement coordinate from a reference geometry R^0 , and k_i are parameters which may be determined from a fit to the calculated ab initio data. No attempt will be done here to numerically determine the parameters in Eq. (2).

4. Final remarks

We have shown that two systems, each possessing a conical intersection when isolated, may preserve such a topological feature when interacting with each other. This is the case for the $H_3 \cdots H_3$ system when the geometrical arrangement of two interacting subsystems belongs to a symmetry point group having a doubly degenerate representation. In this case, the crossing seam becomes a 2D manifold defined by the two coordinates (r, R) . Such a manifold has a complicated structure showing a minimum energy for a special geometry (r_m, R_m) . However, for geometrical arrangements whose symmetry point group possesses no such doubly degenerate representations, the interaction between the two conical intersections destroys the crossing seam in the many-dimensional space of the H_6 system. This result is therefore in partial agreement with the conclusions extracted from the model studies reported in Ref. [1], where no such symmetry restrictions could, of course, be imposed. Since H_3 is known to be a very floppy van der Waals molecule, it would be interesting to carry out similar studies on systems with more practical interest such as dimers of Li_3 or NO_2 , which are known to be stable when isolated and possess conical intersections for D_{3h} and C_{2v} geometries, respectively.

Acknowledgements

This work has been supported by the Fundação para a Ciência e Tecnologia, Portugal, under programme PRAXIS XXI.

References

- [1] M. Baer, A.J.C. Varandas, R. Englman, J. Chem. Phys. 111 (1999) 9493.

- [2] M. Baer, R. Englman, A.J.C. Varandas, *Mol. Phys.* 97 (1999) 1185.
- [3] M. Baer, R. Englman, *Mol. Phys.* 75 (1992) 293.
- [4] A.J.C. Varandas, J. Tennyson, *Chem. Phys. Lett.* 77 (1981) 151.
- [5] A.J.C. Varandas, F.B. Brown, C.A. Mead, D.G. Truhlar, N.C. Blais, *J. Chem. Phys.* 86 (1987) 6258.
- [6] H.-J. Werner, P.J. Knowles (Eds.), *MOLPRO is a package of ab initio programs written by H.-J. Werner, P.J. Knowles, 1998 (contributions from J. Almlöf et al.)*.
- [7] T.H. Dunning, *J. Chem. Phys.* 99 (1993) 9790.
- [8] F.A. Cotton, *Chemical Applications of Group Theory*, Wiley-Interscience, New York, 1971.