Modeling of multiple conical intersections in adiabatic single-sheeted potential energy surfaces: the case of ground-state C_3

C. M. R. Rocha and A. J. C. Varandas

Departamento de Química, and Centro de Química, Universidade de Coimbra
3004-535 Coimbra, Portugal.

Homonuclear triatomic (X_3-type) molecules have enjoyed a great theoretical interest for many decades, and still provide a challenging target for electronic structure calculations. At high-symmetry configurations, such elemental clusters assume equilateral triangular geometries with some of the electronic states transforming according to the E'(E") irreps of the D_{3h} point group. Not surprisingly, therefore, symmetry-required conical intersections (CIs) between the associated potential energy surfaces (PESs) are often realized for such molecules [1].

Apart from the well-studied linear $E \otimes e$ Jahn-Teller (JT) systems, the locus of CI can be of remarkable intricacy. Referred to as small linear parameter (SLP) JT molecule [1,2], besides the usual D_{3h} seam, the title species shows three additional symmetry-allowed CIs along the line of C_{2v} symmetry which lie close to the D_{3h} one [3,4].

In previous work [3], we have reported a single-sheeted DMBE PES for ground-state $C_3(1^1A')$. We first outlined there the presence of the 4 CIs and because a third electronic state of $^1A'_1$ symmetry comes close in energy to the $^1E'$ pair, such unusual topological attributes have been ascribed to a combined JT plus pseudo-JT (PJT) case. Most recently, the $(E' + A'_1) \otimes e'$ problem in C_3 has been further exploited [4] and the results so obtained clarified. Accordingly, the three additional C_{2v} seams are not static objects with respect to the D_{3h} CI but instead fluctuates as a function of the perimeter of the molecule.

Ongoing work to devise a form capable of accurately modeling the three C_{2v} disjoint seams, in addition to the D_{3h} one, will also be briefly addressed. It also includes, a simplified version of the multiple energy switching scheme (ES) [5] to improve the PES in the vicinity of its linear global minima such as to attain near spectroscopic accuracy. The global form so obtained will then be commended for both spectroscopic and reaction dynamics.

Acknowledgments: This work has the support of Fundação para a Ciência e Tecnologia, Portugal, under Contract Nos. PTDC/CEQCOM3249/2012 and PTDC/AAG-MAA/4657/2012, as well as the support to the Coimbra Chemistry Centre through the Project No. PEst-OE/QUI/UI0313/2014. C.M. thanks also the CAPES Foundation (Ministry of Education of Brazil) for a scholarship (Process No. BEX 0417/13-0).

References

[1] I. B. Bersuker, *Chem. Rev.* 2001, **101**, 1067-1114.
[2] J. W. Zwanziger and E. R. Grant, *J. Chem. Phys.* 1987, **87**, 2954-2964.
[3] C. M. R. Rocha and A. J. C. Varandas, *J. Chem. Phys.* 2016, **144**, 064309-064314.
[4] C. M. R. Rocha and A. J. C. Varandas, *J. Chem. Phys.* 2015, **143**, 074302-074318.
[5] A. J. C. Varandas, *J. Chem. Phys.* 2003, **119**, 2596-2613.