ACTA PHYSICA DEBRECENIENSIS XLI, 113 (2007)

CONICAL INTERSECTIONS INDUCED BY THE RENNER EFFECT IN POLYATOMIC MOLECULES

Á. Vibók[1], G. J. Halász[2]

[1] Department of Theoretical Physics, University of Debrecen, H-40410 Debrecen, PO Box 5, Hungary
[2] Department of Information Technology, University of Debrecen, H-4010 Debrecen, PO Box 12, Hungary

Abstract

Characterizing and localizing electronic energy degeneracies is important for describing and controlling electronic energy flow in molecules. We show [1], using topological phase considerations, that the Renner effect in polyatomic molecules with more than three nuclei is necessarily accompanied by 'satellite' conical intersections. In these intersections the non-adiabatic coupling term is on average half an integer.

The dynamics triggered in a molecule after absorbing a photon is usually discussed in terms of the Born-Oppenheimer theory [2], where the fast electronic degrees of freedom are treated separately from the slow nuclei. In this picture, electrons and nuclei do not easily exchange energy. Yet, in some nuclear configurations called conical intersections (CIs) energy exchange can become significant [2]-[7]. It is widely recognized today that were it not for CIs, important photo-biochemical processes such as vision [8]-[10] and photosynthesis of vitamin D [11] could not take place. CIs affect other important processes as well, such as photosynthesis in plants [12], photochemistry of DNA [13], fluorescence of proteins [14, 15], molecular electronics [16, 17] and chemical dynamics [5],[18]-[20]. A major theoretical effort for the research of photochemistry and molecular light-harvesting

processes is invested in the identification and localization of CIs [15],[20]-[26]. While numerical work is indispensable, there is still a fundamental need for understanding more on the ways CIs form. In few known cases CIs can be attributed to simple symmetry considerations [26]. Still, most CIs identified numerically seem to appear accidentally. In this communication, we report for the first time an unexpected connection between CIs and another type of electronic intersection, namely the Renner or Renner-Teller (RT) intersection [27]. We show, using their unique topological characteristics, that certain CIs must exist in a polyatomic molecule exhibiting the RT effect when these molecules are distorted from a linear configuration so that they lose both their axis and their plane of symmetry. These topological features can be revealed by considering a computationally accessible quantity, namely the line integral of the non-adiabatic coupling (NACT) vector along a closed contour in nuclear configuration space.

References

[1] G.J. Halász, Á. Vibók, R. Baer and M. Baer, J. Phys. A: Math.Theor. **40**, 267 (2007).

[2] M. Baer. *Beyond Born-Oppenheimer: Electronic Non-Adiabatic Coupling Terms and Conical Intersections* (Hoboken, NJ: Wiley, 2006).

[3] J. Michl and V. Bonacic-Koutecky, *Electronic Aspects of Organic Photochemistry* (New York: Wiley, 1990).

[4] W. Domcke, D. R. Yarkony and H. Koppel, *Advanced Series in Physical Chemistry vol 15* (Singapore: World Scientific, 2004).

[5] M. Ben-Nun and T. J. Martinez, Chem. Phys. **259**, 237 (2000)

[6] I. B. Bersuker, Chem. Rev. **101**, 1067 (2001).

[7] R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (London: Wiley-Interscience, 1972).

[8] P. Kukura et al, Science **310**, 1006 (2005).

[9] S. Hahn and G. Stock, J. Phys. Chem. B **104**, 1146 (2000).

[10] T. Andruniow, N. Ferre and M. Olivucci, Proc. Natl. Acad. Sci. USA **101**, 17908 (2004).

[11] F. Bernardi, M. Olivucci and M. Robb, Isr. J. Chem. **33**, 265 (1993).

[12] E. Papagiannakis et al, Proc. Natl. Acad. Sci. USA **99**, 6017 (2002).

[13] T. Schultz et al, Science **306**, 1765 (2004).

[14] O. Weingart, V. Buss and M. A. Robb, Phase Transit. **78**, 17 (2005).

[15] C. Ko et al, J. Am. Chem. Soc. **125**, 12710 (2003).

[16] K. L. Kompa and R.D. Levine, Proc. Natl. Acad. Sci. USA **98**, 410 (2001).

[17] D. Geppert, L. Seyfarth and R. de Vivie-Riedle R, Appl. Phys. B **79**, 987 (2004).

[18] A. Kuppermann and R. Abrol, Role of Degenerate States in Chemistry, ed M Baer and G D Billing **124**, 283 (2002).

[19] R. Baer et al, J. Chem. Phys. **105**, 9141 (1996).

[20] D.R. Yarkony, J. Chem. Phys. **105**, 10456 (1996).

[21] I. Ryb and R. Baer, J. Chem. Phys. **121**, 10370 (2004).

[22] I.N. Ragazos et al, Chem. Phys. Lett. **197**, 217 (1992).

[23] R. Izzo and M. Klessinger, J. Comput. Chem. **21**, 52 (2000).

[24] T. Pacher, L.S. Cederbaum and H. Koppel, Adv. Chem. Phys. **84**, 293 (1993).

[25] M. Baer M, T. Vértesi, G.J. Halász and Á. Vibók, Faraday Discuss. **127**, 337 (2004).

[26] G. Herzberg and H.C. Longuet-Higgins, Discuss. Faraday Soc. **35**, 77 (1963).

[27] G.J. Halász, Á. Vibók et al, J. Chem. Phys. **125**, 094102 (2006).

[28] M. Baer, Chem. Phys. Lett. **35**, 112 (1975).