The Renner Effect: An Example of the Breakdown of the Born-Oppenheimer Approximation

Per Jensen, *Physical and Theoretical Chemistry, School of Mathematics and Natural Sciences, University of Wuppertal, D-42097 Wuppertal, Germany*

When, for a chain molecule, two electronic states become degenerate at linear geometries (with the two electronic wavefunctions spanning a doubly-degenerate irreducible representation of type $\Pi, \Delta, \Phi, \ldots$ in the appropriate symmetry group $C_{\infty \mathrm{v}}$ or $D_{\infty \mathrm{h}}$) but split up at bent geometries, we call this the Renner effect.[1] By necessity, the two electronic states are close in energy and must be treated together in the calculation of the associated rovibronic energies. We have developed two program systems, RENNER[2] and DR,[3] which solve the rovibronic Schrödinger equation for Renner-degenerate electronic states of triatomic molecules. RENNER is appropriate for a "single" Renner effect; the linear geometry at which the Renner effect occurs is taken to be the only linear geometry accessible to the molecule. DR (Double Renner) considers the situation exhibited, for example, by HOO in its electronic ground state: The molecule tunnels between two linear geometries H-O-O and O-O-H, and there is a Renner degeneracy at each of these.

Since the potential energy surfaces of Renner-degenerate electronic states are "stuck" together at linear geometries, the Renner effect can be viewed as a "predestined" breakdown of the Born-Oppenheimer approximation caused by the doubly-degenerate electronic symmetry at linearity.

The talk will briefly outline the principles behind the RENNER and DR programs and give various examples of their application.

[1] R. Renner, *Z. Phys.* **92**, 172 (1934) (in German). English translation in H. Hettema, *Quantum Chemistry, Classic Scientific Papers*, World Scientific, Singapore (2000).

[2] P. Jensen, G. Osmann, and P. R. Bunker: The Renner Effect, *in:* "Computational Molecular Spectroscopy" (P. Jensen and P. R. Bunker, Eds.), Wiley, Chichester, 2000; P. Jensen, T. E. Odaka, W. P. Kraemer, T. Hirano, and P. R. Bunker, *Spectrochimica Acta Part A* **58**, 763-794 (2002).

[3] T. E. Odaka, P. Jensen, and T. Hirano, *J. Mol. Structure* **795**, 14-41 (2006); T. E. Odaka, V. V. Melnikov, P. Jensen, T. Hirano, B. Lang, and P. Langer, *J. Chem. Phys***. 126**, 094301/1-9 (2007); V. V. Melnikov, P. Jensen, and T. Hirano, *J. Chem. Phys.* **130**, 224105/1-9 (2009); R. I. Ovsyannikov, T. Hirano, and P. Jensen, *J. Phys. Chem. A* **117**, 13450–13464 (2013).