Quantum dynamics at conical intersections

Stuart C. Althorpe
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW.

A conical intersection is a funnel-shaped object, produced where two electronic potential energy surfaces cross. The Born-Oppenheimer approximation breaks down near the intersection, with the result that the system can relax from the upper to the lower state on a timescale of tens of femtoseconds. Much is now understood about the electronic structure that gives rise to conical intersections, but much less is known about the quantum effects experienced by the atomic nuclei in the vicinity of an intersection. This talk will present recent findings about the properties of the nuclear wave function that describes the dynamics of the nuclei in the vicinity of a conical intersection. Specifically, we will build on recent topological results, which show that a nuclear wave function confined to the ground state surface can be split into contributions from reaction paths that loop in opposite senses about the intersection [1, 2]. We will explain how these results can be generalised to analyse a nuclear wave function describing coupled dynamics on two potential energy surfaces.

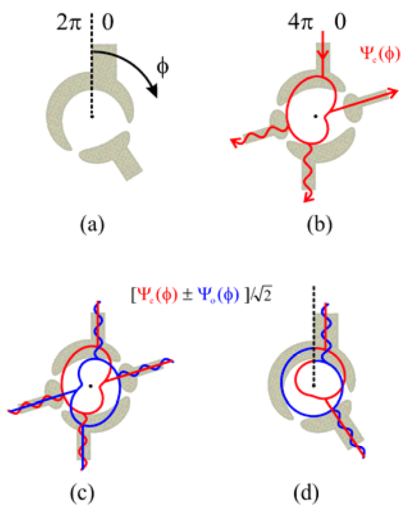

Fig. 1 Schematic diagram (taken from ref. 1), showing how a nuclear wave function confined to one potential surface can be decomposed into contributions from paths that loop in clockwise and anti-clockwise senses around the conical intersection.

1. J.C. Juanes-Marcos, S.C. Althorpe and E. Wrede, *Science* 309, 1227 (2005).
2. S.C. Althorpe, *J. Chem. Phys.* 124, 084105 (2006).
3. S.C. Althorpe, J.C. Juanes-Marcos and E. Wrede, *Adv. Chem. Phys.* 138, 1 (2008).