FIRST PRINCIPLES DYNAMICS AROUND CONICAL INTERSECTIONS: THE ROLE OF THE ENVIRONMENT AND INTERSECTION TOPOGRAPHY

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We discuss some recent examples, drawn from small molecules and chromophores in solvated/protein environments, of excited state dynamics using the ab initio multiple spawning method. We explore the role of the environment in altering the energetics of conical intersections and/or their topography, e.g. sloped vs peaked. A first attempt at a rate theory incorporating these aspects will be presented and compared to dynamics results. A key question which we comment on is the number of degrees of freedom which should be required in such a rate model. Is a single reaction coordinate sufficient, or are conical intersection dynamics inextricably multi-dimensional?