THREE-STATE CONICAL INTERSECTIONS IN BIOLOGICALLY RELEVANT MOLECULES

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Three-state conical intersections, actual degeneracies between three electronic states that are not imposed by symmetry, have been shown in recent years to be present in many polyatomic molecules. These features may exist when there are at least five degrees of freedom present in the molecule. Their importance and effect on nonadiabatic dynamics, however, are not well understood. We have investigated the importance of two- and three-state conical intersections in photoinitiated processes of biologically relevant systems, and particularly the nucleic acid bases and their analogs. Three-state conical intersections have been located using multi-reference configuration-interaction ab initio methods. The potential energy surfaces for each base contain many different seams of three-state intersections. Paths along seams from these intersections are shown to be connected to well characterized stationary points involved in radiationless decay pathways. Nonadiabatic coupling terms have also been calculated, and the effects of the proximal third state on these quantities are detailed. In particular, it is shown that when one of these loops incorporates more than one seam point there is a profound and predictable effect on the phase of the nonadiabatic coupling terms, and as such provides a diagnostic for the presence and location of additional seams.