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Electronically Excited States and Conical Intersections in Cytosine and its Analogs

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Conical intersections between two and three electronic states of the same symmetry have been found to play a key role in nonadiabatic processes. In recent years many studies have shown that conical intersections are important in the photophysics of nucleobases and facilitate radiationless decay to the ground state. Interestingly, there are molecules very similar in structure to the nucleobases which show very different photophysical behavior, i.e., longer excited state lifetimes and high quantum yields of fluorescence. An important question that arises is what causes the different behavior between nucleobases and their fluorescent analogs. In this work we present studies of cytosine and several of its analogs in an effort to correlate the molecular structure to the photophysical behavior. Large scale ab initio multireference configuration interaction methods (MRCI) are being used. Our results show the presence of many seams of two- or three-state conical intersections in both types of systems and energetic differences seem to be the cause of the different photophysical behavior. A mixed quantum mechanical/ classical mechanical (QM/MM) approach where the solute is described with the MRCI method will also be presented as a means to study the effect of the solvent on excited states.