

Towards Polanyi rules for polyatomics: Vibrational dynamics at Conical Intersections

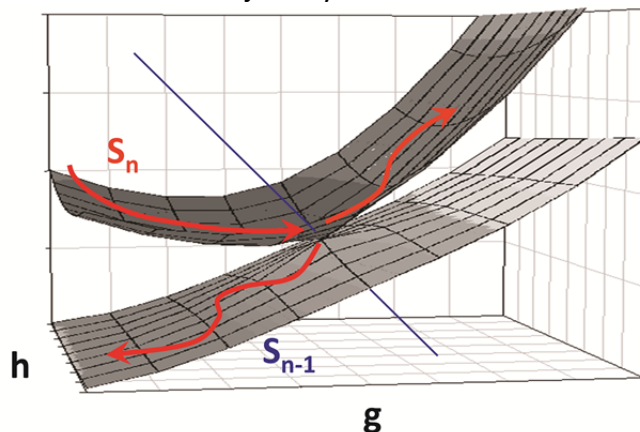
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Conical intersections play a role in excited state reaction dynamics very similar to that of the transition state in ground state dynamics. As such, one might hope that there should emerge, for excited state polyatomic dynamics, a set of notions analogous to the Polanyi rules for ground states which guide our thinking about the topography and location of conical intersections relative to potential gradients, barriers and thresholds. Will there be notions such as "early" or "late"? Do the "velocity" and "direction" of passage through a conical intersection affect diabatic versus adiabatic branching? We experimentally probe excited state dynamics using time-resolved photoelectron spectroscopy ^[1] (TRPES), a method sensitive to both vibrational and electronic degrees of freedom. We combine TRPES with 'on the fly' ab initio Full Multiple Spawning (FMS) trajectory calculations wherein we additionally compute the excited state photoelectron spectrum 'on the fly' during each trajectory. Using a phenomenological approach, we vary methyl substitution on unsaturated hydrocarbons ^{[2]-[6]} so as to 'tune' trajectory motions near conical intersections.



References

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