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Representing Adiabatic Potential Energy Surfaces Coupled by Conical Intersections in their Full Dimensionality Using Coupled Quasi-Diabatic States

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The construction of fit single state potential energy surfaces (PESs), analytic representations of *ab initio* electronic energies and energy gradients, is now well established. These single state PESs, which are essential for accurate quantum dynamics and have found wide application in more approximate quasi-classical treatments, have revolutionized adiabatic dynamics. The situation for nonadiabatic processes involving dissociative and large amplitude motion is less sanguine. In these cases, compared to single electronic state dynamics, both the electronic structure data and the representation are more challenging to determine. We describe the recent development and applications of algorithms that enable description of multiple adiabatic electronic potential energy surfaces coupled by conical intersections in their full dimensionality using coupled quasi-diabatic states. These representations are demonstrably quasi-diabatic, provide accurate representations of conical intersection seams and can smooth out the discontinuities in electronic structure energies due to changing active orbital spaces that routinely afflict global multistate representations.