

Abstract Submitted
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Non-adiabatic effects in photoelectron spectroscopy MICHAEL SCHUURMAN, DAVID YARKONY, Johns Hopkins University — Recent developments in the construction of approximately diabatic second-order Hamiltonians in the vicinity of conical intersections have been employed to study photoelectron spectra of molecules in which nonadiabatic effects are preeminent. Our current approach explicitly includes all non-adiabatic coupling terms through second order, while requiring ab initio data at only $(N_{\text{int}} + 3)$ or $(N_{\text{int}} + 15)$ points for two and three-state intersections, respectively, where N_{int} is the number of internal coordinates. This scaling allows very accurate wave functions to be used. Since the Hamiltonian is determined at a point of conical intersection, the method is “self-policing” in that the ability of the resultant surfaces to reproduce the vicinity of seams of intersection, as well as energy minima and the Franck-Condon region, is easily verified. We will report photoelectron spectra determined from these diabatic representations employing a harmonic oscillator basis and a Lanczos solver algorithm to diagonalize the resultant vibronic Hamiltonian matrices. The results of some initial applications will be discussed, with emphasis on the previously studied five membered heterogeneous ring systems, pyrazolyl ($\text{C}_3\text{H}_3\text{N}_2$) and pyrrolyl ($\text{C}_4\text{H}_4\text{N}$) doublet radicals. These systems are of particular interest since they display low-lying conical intersections adjacent to both the neutral ground state geometries and the Franck-Condon region.

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