

VIBRONICALLY COUPLED STATES: COMPUTATION AND CHARACTERIZATION OF VIBRONIC AND RO-VIBRONIC SPECTROSCOPIC PARAMETERS

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The importance of the breakdown of the Born-Oppenheimer (BO) approximation in the vicinity of a conical intersection has spurred the recent development of computational approaches that involve vibronic coupling between electronic states. Computational chemistry has mainly focused on conical intersections along reaction paths. Jahn-Teller type conical intersections offer a spectroscopically accessible alternative that can be used for benchmarking these calculations. The presence of Jahn-Teller and pseudo-Jahn-Teller couplings not only leads to additional terms in the rotational Hamiltonian but also modify how well known terms like Coriolis coupling and spin-rotation coupling are computed. In this talk we build upon the general quantum chemical method pioneered by Köppel, Domcke and Cederbaum^a to tackle molecules with vibronic coupling wherein *ab initio* electronic structure calculations in the adiabatic limit are used as the starting point for calculating properties of molecules in the regime where the BO approximation breaks down. A model vibronic Hamiltonian is parameterized using derivatives of adiabatic potential energy surfaces. Vibronic eigenvectors are obtained from this model Hamiltonian that allow the calculation of parameters in the rotation-spin Hamiltonian that can be determined experimentally from high resolution spectroscopy.

^aH. KÖPPEL AND W. DOMCKE AND L. S. CEDERBAUM Multimode Molecular Dynamics Beyond the Born-Oppenheimer Approximation. *Adv. Chem. Phys.* 57, (1984), 59-246