Cross-Contamination of the Fitting Parameters in Multidimensional Tunneling Treatments

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In this talk we examine the two-dimensional tunneling formalism used previously to fit the hydrogen-transfer and internal-rotation splittings in the microwave spectrum of 2-methylmalonaldehyde in an effort to determine the origin of various counterintuitive results concerning the isotopic dependence of the internal-rotation splittings in that molecule. We find that the cause of the problem lies in a "parameter contamination" phenomenon, where some of the numerical magnitude of splitting parameters from modes with large tunneling splittings "leaks into" the parameters of modes with smaller tunneling splittings. We find that such parameter contamination, which greatly complicates the determination of barrier heights from the least-squares-fitted splitting parameters, will be a general problem in spectral fits using the multi-dimensional tunneling formalism, since it arises from subtle mathematical features of the non-orthogonal framework functions used to set up the tunneling Hamiltonian. Transforming to a physically less intuitive orthonormal set of basis functions allows us to give an approximate numerical estimate of the contamination of tunneling parameters for 2-methylmalonaldehyde by combining a dominant tunneling path hypothesis with results recently given for the hydrogen-transfer--internal-rotation potential function for this molecule.