CONTACT TRANSFORMATIONS AND DETERMINABLE PARAMETERS IN SPECTROSCOPIC FITTING HAMILTONIANS

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In recent least-squares fits of torsion-rotation spectra of acetaldehyde and methanol it was found possible to adjust more fourth-order parameters than would be expected from traditional contact-transformation considerations. To investigate this discrepancy between theory and practice we have carried out numerical fitting experiments on the simpler three-dimensional asymmetric rotor problem, using $J \leq 20$ energy levels generated artificially from a full orthorhombic Hamiltonian with quadratic through octic operators in the angular momentum components. Results are analyzed using the condition number $\kappa$ of the least-squares matrix, which is a measure of its invertibility in the presence of round-off and other errors. When $\kappa$ is very large, parameters must be removed from the fit until $\kappa$ becomes acceptably small, corresponding to procedures which lead to reduced Hamiltonians in molecular spectroscopy. We find that under certain circumstances $\kappa$ can be decreased to an acceptable level for Hamiltonians which are only partially reduced when compared to Watson $A$ and $S$ reductions. Some insight into this behavior is obtained from classical mechanics and from the concept of delayed contact transformations. Our attempts to transfer this understanding to the four-dimensional methyl-top internal rotor problem are complicated by the fact that both order-of-magnitude considerations and commutation relations are somewhat different.