CALCULATING RO-VIBRATIONAL SPECTRA USING AN ECKART FRAME

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Using normal coordinates and an Eckart molecule-fixed frame it is possible, for some molecules, to compute ro-vibrational spectra with either perturbation theory or variational methods. A compact normal coordinate Eckart kinetic energy operator (KEO) has been known for decades. The Eckart frame minimises Coriolis coupling and thereby reduces the number of basis functions required to achieve converged energy levels. It, however, is almost always used with normal coordinates which are poorly suited to the description of large amplitude vibrations. For molecules with large amplitude motion, it is common to use, as vibrational coordinates, polar coordinates associated with a set of vectors specifying the position of the atoms of the molecule. The vectors may be bond vectors, Jacobi vectors, Radau vectors etc. It would clearly be advantageous to use polar (polyspherical) coordinates and an Eckart frame. Instead, polar coordinates are generally used with a frame attached to a small number of the vectors. Unfortunately, the Eckart polyspherical KEO is complicated. It has been derived only for three-atom molecules. Using finite difference methods it is possible, without deriving a KEO, to work with polyspherical vibrational coordinates and an Eckart frame. We demonstrate that this allows us to deal with large amplitude motion and at the same time exploit the fact that an Eckart frame facilitates the choice of good basis functions.