PARTICLES-ON-A-SPHERE: A REDUCED DIMENSIONAL APPROACH TO LARGE-AMPLITUDE MOTION FOR POLYATOMIC HYDRIDES

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We introduce a relatively simple but computationally tractable ”particle-on-a-sphere” (POS) model for the intramolecular motion of light atoms constrained to the surface of a sphere. The model assumes independent 2D angular motion of H atoms embedded on the surface of a sphere with an arbitrary interatomic angular potential, which permits systematic evolution from ”free rotor” to ”tunneling” to ”quasi-rigid” polyatomic molecule behavior for small values of total angular momentum J. This work focuses on the simple tetratom (n=3) system as a function of interatomic potential stiffness, with explicit consideration of H_3O^+ as a test case. The particle-on-a-sphere model also establishes the necessary mathematical groundwork for calculations on dynamically much more challenging XH_n species with n>3, (e.g., reduced dimensional models of CH_5^+), where such an approach offers prospects for being quantum mechanically tractable at low J values characteristic of supersonic jet expansion conditions.