

SIMULTANEOUS EVALUATION OF MULTIPLE ROTATIONALLY EXCITED STATES OF FLOPPY MOLECULES USING DIFFUSION MONTE CARLO

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In this work, an extension to diffusion Monte Carlo (DMC) is proposed, allowing for the simultaneous calculation of the energy and wave function of multiple rotationally excited states of floppy molecules.^a The total wave function is expanded into a set of Dirac δ -functions called walkers, while the rotational portion of the wave function is expanded in a symmetric top basis set. Each walker is given a rotational state vector containing coefficients for all states of interest. The positions of the atoms and the coefficients in the state vector evolve according to the split operator approximation of the quantum propagator. The method was benchmarked by comparing calculated rotation-vibration energies for H_3^+ , H_2D^+ , and H_3O^+ to experimental values. For low to moderate values of J , the resulting energies are within the statistical uncertainty of the calculation. Rotation-vibration coupling is captured through flexibility introduced in the form of the vibrational wave function. This coupling is found to increase with increasing J -values. Based on the success achieved through these systems, the method was applied to CH_5^+ and its deuterated isotopologues for $v = 0$, $J \geq 10$. Based on these calculations, the energy level structure of CH_5^+ is found to resemble that for a spherical top, and excitations up to $J = 10$ displayed insignificant rotation-vibration coupling. Extensions of this approach that explicitly account for vibrations will also be discussed.

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