STUDYING ROTATION/TORSION COUPLING IN H_5^+ USING DIFFUSION MONTE CARLO

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H_5^+ is a highly fluxional intermediate found in interstellar clouds. The rotational/torsional couplings in this molecule are of great interest due to the unusually large coupling between these modes. However, theoretical studies of highly fluxional molecules like H_5^+ are challenging due to the lack of a good zero-order model. In order to better understand the rotation/vibration interaction, a method has been developed to model the rotational/torsional motions. This method is based upon diffusion Monte Carlo (DMC). In this approach, the vibrational contribution to the wavefunction is modeled using standard DMC approaches, while the rotational/torsional contribution is treated as a set of coefficients that are assigned to the various rotational/torsional state vectors. The potential portion of the Hamiltonian is expressed as a low-order expansion in terms of the torsion angle between the two outer H_2 units. The expansion coefficients are evaluated at each time step for each walker and depend on the $3N-7$ other internal coordinates. The transition frequencies obtained from this method for $J \leq 1$ agree well with results obtained using other methods such as fixed-node diffusion Monte Carlo.[a] This new method is advantageous over the fixed-node approach because it allows for multiple state calculations at once which saves on computation time.

[a]Sarka, J.; Fábri, C.; Szidarovszky, T.; Császár, A.G.; Lin Z.; McCoy, A.B., "Modeling Rotations, Vibrations, and Rovibrational Couplings in Astructural Molecules - A Case Study Based on the H_5^+ Molecular Ion.", accepted by Mol. Phys.