EXTENDING DIFFUSION MONTE CARLO TO INTERNAL COORDINATES

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Diffusion Monte Carlo (DMC) is a powerful technique for studying the properties of molecules and clusters that undergo large-amplitude, zero-point vibrational motions. However, the overall applicability of the method is limited by the need to work in Cartesian coordinates and therefore have available a full-dimensional potential energy surface (PES). As a result, the development of a reduced-dimensional DMC methodology has the potential to significantly extend the range of problems that DMC can address by allowing the calculations to be performed in the subset of coordinates that is physically relevant to the questions being asked, thereby eliminating the need for a full-dimensional PES.

As a first step towards this goal, we describe here an internal coordinate extension of DMC that places no constraints on the choice of internal coordinates other than requiring them all to be independent. Using H_3^+ and its isotopologues as model systems, we demonstrate that the methodology is capable of successfully describing the ground state properties of highly fluxional molecules as well as, in conjunction with the fixed-node approximation, the $\nu = 1$ vibrationally excited states.

The calculations of the fundamentals of H_3^+ and its isotopologues provided general insights into the properties of the nodal surfaces of vibrationally excited states. Specifically, we will demonstrate that analysis of ground state probability distributions can point to the set of coordinates that are less strongly coupled and therefore more suitable for use as nodal coordinates in the fixed-node approximation. In particular, we show that nodal surfaces defined in terms of the curvilinear normal mode coordinates are reasonable for the fundamentals of H_2D^+ and D_2H^+ despite both molecules being highly fluxional.