USING DIFFUSION MONTE CARLO TO PROBE ROTATIONAL EXCITED STATES

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Since its inception in 1975 by Anderson,[a] Diffusion Monte Carlo (DMC) has been successfully applied to a wide range of electronic and vibrational problems. In the latter case, it has been shown to be a powerful method for studying highly fluxional systems exhibiting large amplitude vibrational motions. We report here our recent work developing a new DMC algorithm capable of treating rotational excited states. We first develop the appropriate coordinates, nodal structures, and re-crossing corrections for this problem. Then, using H_3O^+ and D_3O^+ as model systems,[b] we show that our method can successfully describe a range of rotational states from $|0,0,0\rangle$ to $\frac{1}{\sqrt{2}}\left(|10,10,0\rangle+|10,-10,0\rangle\right)$. In particular, we examine the combined effects of rotational and zero-point vibrational motion on the geometric structure of the molecules. Finally, we find the $|10,0,0\rangle$ state to be somewhat problematic but show that the problem is straightforward to identify and has a well-defined solution.

[a] J. B. Anderson, *J. Chem. Phys.*, 63, 1499 (1975).

[b] X. Huang, S. Carter, and J. Bowman, *J. Chem. Phys.*, 118, 5431 (2003).