Author Richardson JO. Althorpe SC. Wales DJ. Tittle Instanton calculations of tunneling splittings for water dimer and trimer Source JOURNAL OF CHEMICAL PHYSICS vol.135 no.12 124109 DOI: 10.1063/1.3640429

SEP 28 2011

Abstract

We investigate the ability of the recently developed ring-polymer instanton (RPI) method [J. O. Richardson and S. C. Althorpe, J. Chem. Phys. 134, 054109 (2011)] to treat tunneling in water clusters. We show that the RPI method is easy to extend to treat tunneling between more than two minima, using elementary graph theory. Tests of the method on water dimer and trimer yield a set of instanton periodic orbits which correspond to all known tunneling pathways in these systems. Splitting patterns obtained from the orbits are in good overall agreement with experiment. The agreement is closer for the deuterated than for the protonated clusters, almost certainly because the main approximation in the calculations is neglect of anharmonicity perpendicular to the tunneling path. All the calculations were performed on a desktop computer, which suggests that similar calculations will be possible on much larger clusters. (C) 2011 American Institute of Physics.

557.