

COMPUTING THE VIBRATIONAL ENERGIES OF CH₂O AND CH₃CN WITH PHASE-SPACED LOCALIZED FUNCTIONS AND AN ITERATIVE EIGENSOLVER

JAMES BROWN, TUCKER CARRINGTON, *Department of Chemistry, Queen's University, Kingston, ON, Canada.*

For decades scientists have attempted to use ideas of classical mechanics to choose basis functions for calculating spectra. The hope is that a classically-motivated basis set will be small because it covers only the dynamically important part of phase space. One popular idea is to use phase-space localized (PSL) basis functions. Because the overlap matrix, in the matrix eigenvalue problem obtained by using PSL functions with the variational method, is not an identity, it is costly to use iterative methods to solve the matrix eigenvalue problem. Iterative methods are imperative if one wishes to avoid storing matrices which is important for larger molecules. Recently^a we showed it was possible to circumvent the orthogonality (overlap) problem and use iterative eigensolvers. Here, we present calculated vibrational energies of CH₂O and CH₃CN using the iterative Arnoldi algorithm and PSL functions, and show that our PSL basis is competitive with other previously used basis sets for these molecules.

^aJ. Brown and T. Carrington Jr., Phys. Rev. Lett. **114**, 058901 (2015).