STEALING IDEAS FROM ELECTRONIC STRUCTURE THEORY TO IMPROVE VIBRATIONAL CALCULATIONS. PART I - THE HAMILTONIAN

JAMES H. THORPE, *Department of Chemistry, Southern Methodist University, Dallas, TX, USA*.

The fields of electronic and vibrational structure theory have largely evolved independently over the years. Demonstrative of this is the fact that the electronic structure community has generally embraced coupled-cluster wavefunctions as the gold standard for small, well-behaved systems, while vibrational structure practitioners tend to prefer treatments based on vibrational perturbation theory or vibrational configuration interaction. While this is not surprising — the two fields face dramatically different challenges and goals — one does wonder if ideas from one can be used to improve or inform the other.

To this point, Part I of this presentation borrows the concept of normal-ordered strings of creation/annihilation operators from electronic coupled-cluster to develop a new form of the vibrational Hamiltonian which is amenable to vibrational many-body (VMP,VCI,VCC) calculations. This "GEN" Hamiltonian generates greatly simplified equations to be implemented in black-box software, and folds-in higher-order many-body effects into lower-order treatments. The goal is to present these (somewhat complicated) concepts in a way accessible to theorists from both communities, as well as to the broader field of spectroscopists as a whole.