Progress in Vibrational Coupled Cluster Theory

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Traditionally the major focus of theoretical chemistry has been on calculating electronic energies and wave functions. Today a large number of computational methods are widely available. The situation for the quantum description of molecular dynamics has, however, to a large extent been a topic for specialists and restricted to small molecules. Our overall aim is to make quantum mechanical calculations of quantum molecular dynamics more automatic and more generally applicable. Beginning with vibrational motion, we note that anharmonic molecular vibrations is an unavoidable fact, an important study in itself, and an aspect that modulates essentially all aspects of spectroscopy and reactions dynamics.

A set of recently developed theoretical methods for calculating quantum wave functions for describing anharmonic vibrational motion is described. Emphasis is put on the theory, implementation and application of vibrational coupled cluster (VCC) theory. The similarities and differences compared to electronic structure theory will be considered. A key issue the possibility of doing explicit wave function calculations for systems with many degrees of freedom. It will be demonstrated how VCC is competitive in terms of providing high accuracy relative to the number of independent parameters. Although very complicated, highly efficient implementations can be made.

Methods for constructing potential and property surfaces are also considered including new ideas allowing adaptive construction of potential energy surfaces and efficient use of derivative information.