A second-order multi-reference perturbation method for molecular vibrations

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We will present a multi-reference method in vibrational structure theory. Quantum nature of molecular vibrations plays important roles in a variety of chemical phenomena. Theory for vibrational wavefunctions, so called vibrational structure theory, is thus a vital tool to understand them at atomistic level. So far, various mean-field-based (i.e. single-reference) models have been developed for a system consisting of weakly-correlated vibrational motions. [1] These methods are capable of efficiently describing quantum dynamics when a targeted system or phenomenon includes no strongly-coupled motions. There exist, however, many chemical phenomena that contain strongly-coupled motions such as floppy hydrogen stretching and wide-amplitude motions. We develop a multi-reference vibrational wavefunction model to obtain accurate descriptions of small to medium size molecules with such motions.

Our approach is based on a mixed configuration-interactions (CI) and mean-field (SCF) wavefunction ansatz. In this scheme, vibrational coordinates are divided into active and bath space: active space includes a targeted strongly-coupled modes and bath space consists of the other modes; CI wavefunction is used for active space and SCF wavefunction for bath space; a system's wavefunction is defined as a direct product of active and bath wavefunctions. Although this procedure considers strong correlation within active space, it neglects weak correlation among bath modes and between bath and active modes. In order to take into account the weak correlation, we introduce a second-order perturbation to this multi-reference reference function. The method is named as Vibrational Active Space Second-Order Perturbation Theory (VASPT2). VASPT2 allows us to quantitatively evaluate vibrational energy levels of a system including either resonances or strong mode coupling in a cost effective way.

We will show some pilot applications of VASPT2 method. For example, VASPT2 has been employed to compute fundamental bands of *trans*-formic acid with a new semi-global potential energy surface at CCSD(T)(F12*)/cc-pVTZ-F12 level of theory; [2] the results exhibit that the root mean squared deviation of VASPT2 from experimental values is 7 cm^{-1}, while that of the widely-used vibrational MP2 method is 20 cm^{-1}.

[1] Christiansen O., *Phys. Chem. Chem. Phys.*, 14:6672-6687 2012.

[2] Hättig C., Tew D.P., Köhn A., *J. Chem. Phys.*, 132:231102 2010.