A DMRG-based framework for large-scale anharmonic vibrational calculations

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As countless chemical processes are influenced by molecular vibrations, methods that provide an accurate description of the correlated nuclear wave function are sought-after for a reliable characterization of strongly anharmonic molecules. Towards this end, we present a versatile framework based on the density matrix renormalization group (DMRG) algorithm for anharmonic *ab initio* vibrational calculations [1,2]. Our framework builds upon modal basis functions which are optimized with the vibrational self-consistent field (VSCF) method in conjunction with an on-the-fly calculated potential energy surface (PES) in the n-mode format. The obtained anharmonic modals form a compact basis set for vibrational configuration interaction (VCI)-type methods. As systems with more than 15 correlated vibrational degrees of freedom are extremely challenging for conventional VCI algorithms, we introduce a new VSCF-based formulation of the vibrational DMRG (vDMRG) theory applicable to general n-mode PES [3]. By expressing the VCI wave function as a matrix product state, n-mode vDMRG can target systems with up to 30 coupled vibrational modes. Hence, the combined VSCF/vDMRG approach allows for large-scale vibrational calculations of strongly anharmonic molecules through the proper inclusion of vibrational correlation effects.
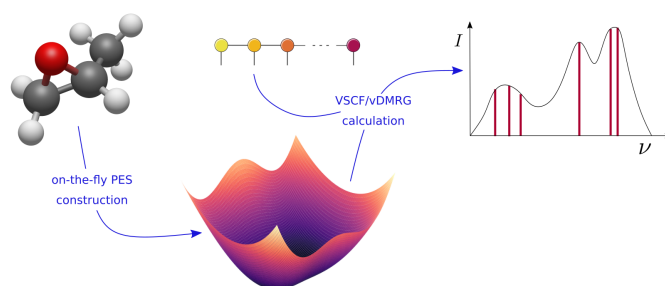
Figure 1: Illustration of the computational workflow of a VSCF/vDMRG calculation

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[2] N. Glaser, A. Baiardi, M. Reiher, in "Vibrational Dynamics of Molecules" J. M. Bowman, Ed. World Scientific, (2022), 80.
[3] N. Glaser, A. Baiardi, M. Reiher, manuscript in preparation.