DMRG Implementation for Anharmonic Vibrational Analysis Using Discrete Variable Representation

Qian-Rui Huang[1], Jheng-Wei Li[2] and Jer-Lai Kuo[1]
[1] *Institute of Atomic and Molecular Sciences, Academia Sinica, 106319, Taiwan*
[2] *Université Grenoble Alpes, CEA, Grenoble INP, IRIG, Pheliqs, F-38000 Grenoble, France*

We present a DMRG-based implementation for solving the anharmonic vibrational Schrödinger equation formulated in discrete variable representation (DVR).[1] Plain DVR suffers from the famous "curse of dimensionality", which produces three coupled bottlenecks: (i) Scan - exponential sampling of the potential surfaces, (ii) Solve - Hamiltonians too large for direct diagonalization, and (iii) Store - dense eigenvectors with prohibitive memory / storage. Previously we adopt techniques such as n-mode representations (nMR),[2] sparse eigensolvers, and finite basis representations (FBR), which partly solved some issues, but introduces some other problems in complicated cases.

We then proposed a new implementation, which addresses all these problems simultaneously by combining tensor cross interpolation (TCI)[3] for informative PES/DMS sampling with a matrix-product operator (MPO) Hamiltonian and a DMRG variational solver over matrix-product states (MPS) using Cytnx library.[4] TCI produces a low-rank surrogate that reduces ab-initio evaluations (Scan), the MPO+DMRG formulation enables polynomial-scaling iterative solution of large DVR problems (Solve), and MPS/MPO compression provides controllable memory usage (Store). Accuracy is monitored via rank/bond-dimension schedules and residual norms, with DVR/FBR results for validation. Applications to protonated water clusters (Eigen-form hydronium) recover key mid-IR features—including Fermi and combination-band mixing. The result is a practical, accuracy-controlled pathway to anharmonic vibrational analysis that preserves the physical fidelity of DVR while extending tractability to larger, more strongly anharmonic systems.

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