Tensor decomposition in potential energy surface representations

G. Rauhut

Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany; rauhut@theochem.uni-stuttgart.de

Sum-of-products representations of multidimensional potential energy surfaces (PES) allow for the fast evaluation of integrals within variational vibrational structure calculations, e.g. vibrational configuration interaction theory (VCI). A new approach for generating such representations using global (polynomal) and local (B-splines, distributed Gaussians) bases relying on a repeated use of Kronecker products will be presented [1].
Once an analytical representation of the potential energy surface is available, the expansion coefficients of high-order coupling terms within multimode expansions of the PES can be decomposed by an alternating least squares approach (CP-ALS). This allows for computational savings in vibration correlation calculations once the rank of the factor matrices can be kept small [2].
Benchmark calculations are provided for single-reference and multi-reference vibrational structure methods.

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References

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[2] L. Ostrowski, B. Ziegler and G. Rauhut, *J. Chem. Phys.* 2016, in press.