

**Calculation of global,
high-dimensional Potential Energy
Surface fits in canonical
decomposition form using
Monte-Carlo Methods: application to
the Eigen cation**

Markus Schröder and Hans-Dieter Meyer

Physikalisch Chemisches Institut, Universität Heidelberg



Stuttgart, October 8, 2020

Quantum dynamics for molecular vibrations

Time-dependent Schrödinger Equation

$$i\hbar \frac{\partial}{\partial t} \Psi(q_1, \dots, q_p, t) = \hat{H}(q_1, \dots, q_p) \Psi(q_1, \dots, q_p, t)$$

- Ψ : state of the molecule depending on internal coordinates q_κ
- $\hat{H} = \hat{T} + \hat{V}$: Hamiltonian with kinetic energy \hat{T} and potential \hat{V}
- Kinetic energy \hat{T} usually consists of derivative operators and elementary functions
- Potential \hat{V} is usually a high-dimensional function that is not analytically available (like \hat{T}) but is a result of quantum chemistry calculations

Quantum dynamics for molecular vibrations

Multi-dimensional wavefunction in MCTDH form

$$\begin{aligned}\Psi(q_1, \dots, q_p, t) &= \sum_{j_1 \dots j_p} A_{j_1 \dots j_p} \prod_{\kappa} \phi_{j_{\kappa}}^{(\kappa)}(q_{\kappa}, t) \\ i\dot{A}_J &= \sum_L \langle \Phi_J | \hat{H} | \Phi_L \rangle A_L \\ i\dot{\phi}^{(\kappa)} &= (1 - P^{\kappa}) \left(\rho^{(\kappa)} \right)^{-1} \langle \hat{H} \rangle^{(\kappa)} \phi^{(\kappa)}\end{aligned}$$

- Matrix elements computed as high dimensional integrals, for instance: $\langle \Phi_J | \hat{H} | \Phi_L \rangle$
- Integrals reduce to a sum of products of one-dimensional integrals if the Hamiltonian is a sum of products:

$$\hat{H} = \sum_r c_r \prod_{\kappa} h_r^{(\kappa)}(q_{\kappa})$$

$$\langle \Phi_J | \hat{H} | \Phi_L \rangle = \sum_r c_r \prod_{\kappa} \langle \phi_j^{\kappa} | h_r^{(\kappa)} | \phi_l^{\kappa} \rangle$$

Canonical Polyadic Decomposition

Canonical Polyadic Decomposition ("CANDECOMP")

Express potential as a sum of products of low dimensional terms:

$$V(\vec{q}) \approx \sum_r^R c_r \prod_{\kappa}^p v_r^{(\kappa)}(q_{\kappa}) \quad \text{Tucker : } \sum_{j_1 \dots j_p} c_{j_1 \dots j_p} \prod_{\kappa} \nu_{j_{\kappa}}^{(\kappa)}(q_{\kappa})$$

General properties

- **CANDECOMP**: Large reduction of terms compared to **Tucker**
- Basis functions $v_r^{(\kappa)}(q_{\kappa})$ are normalized but not orthogonal
- The decomposition is not unique
- Poses a highly non-linear problem
- There is no way to a priori know the number of terms R to achieve a given upper error bound

Very difficult to find an optimal solution

Finding a near optimal decomposition

- Minimize a cost functional

$$J = \int d\vec{q} \left(V(\vec{q}) - \sum_r c_r \prod_{\kappa} v_r^{(\kappa)}(q_{\kappa}) \right)^2$$

- Variation wrt. $c_r v_r^{(\kappa)}(q_{\kappa})$

$$\underbrace{\int d\vec{q}^{\{\kappa\}} V(\vec{q}) \prod_{\kappa' \neq \kappa} v_r^{(\kappa')}(q_{\kappa'})}_{b_r(q_{\kappa})} = \sum_{r'} \underbrace{c_{r'} v_{r'}^{(\kappa)}}_{x_{r'}(q_{\kappa})} \underbrace{\int d\vec{q}^{\{\kappa\}} \prod_{\kappa' \neq \kappa} v_r^{(\kappa')}(q_{\kappa'}) v_{r'}^{(\kappa')}(q_{\kappa'})}_{a_{rr'}^{(\kappa)}}$$

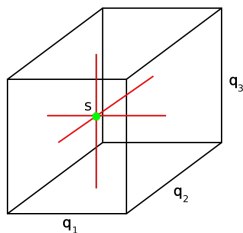
- Simple linear equation $\vec{b} = A\vec{x}$
- However: vectors \vec{b} and the matrices A depend on the solutions of the same equations of all other modes
- Solve iteratively (Alternating Least Squares)

Avoiding high-dimensional integrals

- Evaluate integrals with Monte-Carlo techniques
- → Massive reduction of PES evaluations
- → Importance sampling helps convergence

$$\begin{aligned} & \sum_s V_s(q_\kappa) \prod_{\kappa' \neq \kappa}^p \nu_r^{(\kappa')} (q'_\kappa, s) \\ &= \sum_{r'}^R c_{r'} \nu_{r'}^{(\kappa)} (q_\kappa) \sum_s \prod_{\kappa' \neq \kappa}^p \nu_r^{(\kappa)} (q_{\kappa'}, s) \nu_{r'}^{(\kappa')} (q_{\kappa'}, s) \end{aligned}$$

- No random sampling on q_κ , only on all other coordinates, but q_κ discretized.



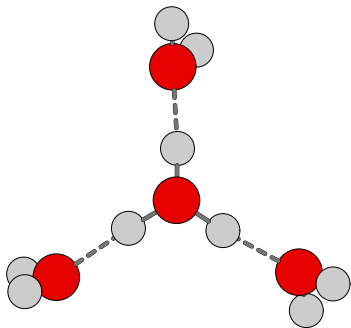
*Potential is probed
along 1D cuts through
sampling points*

Creating the fit

Four tasks:

- 1 Create a suitable sampling (e.g. Metropolis-Hastings, Path-Integral Monte-Carlo, Diffusion Monte-Carlo, etc.)
- 2 Calculate 1-D cuts ("fibers") on a regular grid along each coordinate through each sampling point
→ embarrassingly parallel as all fibers are independent
- 3 Optimize the fit on the fibers (iteratively solve Eq. on previous slide)
→ building matrices and vectors also embarrassingly parallel
- 4 Test the fit on an independent set of sampling points.

Eigen cation $H_9O_4^+$



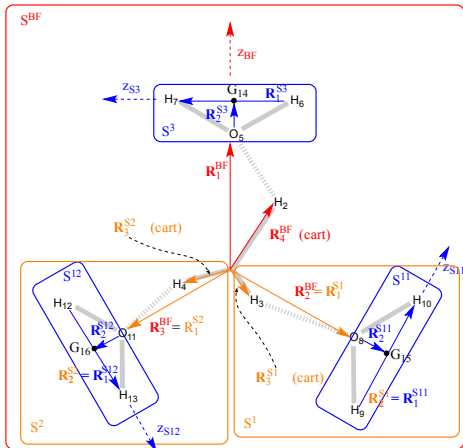
- Three water molecules around a central hydronium
- 33-D, highly correlated and very floppy molecule
- Global description of the potential and dipoles are available^[1]

[1] PES by Yu et al., J. Phys. Chem. A 123, 1399 (2019)

Eigen cation $H_9O_4^+$

33 Internal coordinates:

- 3 times Water internal (9)
- 3 times wagging of Water (3)
- 3 times rocking of Water (3)
- 3 times O-O distance (3)
- 3 times Water rotation around O-O (3)
- Cartesian coordinates for inner H's (9)
- 2 Angles between O-O vectors (2)
- 1 Umbrella (1)



In the following: restriction of the umbrella motion to one side of the double well.

Results: Calculation of the PES fit

Boltzmann distributed sampling points

- 10^6 points at $k_B T = 1500 \text{ cm}^{-1}$ plus
- 1.25×10^6 points at $k_B T = 4000 \text{ cm}^{-1}$

Organized the 33 DOF into 13 logical coordinates

	Product grid	MC-CPD
No. Potential evaluations	1.7×10^{33}	1.8×10^{10}
Memory	1.2×10^{22} TB	138 GB

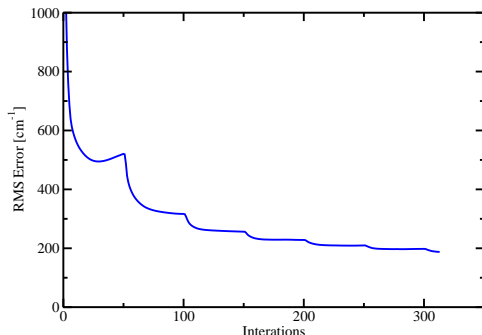
2048 terms (R) in CPD; file size: 95 MB

RMS Error tested on 10^6 Boltzmann distributed sampling points

- RMS = 124 cm^{-1} at $k_B T = 1500 \text{ cm}^{-1}$
- RMS = 253 cm^{-1} at $k_B T = 4000 \text{ cm}^{-1}$
- RMS = 308 cm^{-1} at $k_B T = 5000 \text{ cm}^{-1}$

Speeding up convergence

- Grow rank of the fit



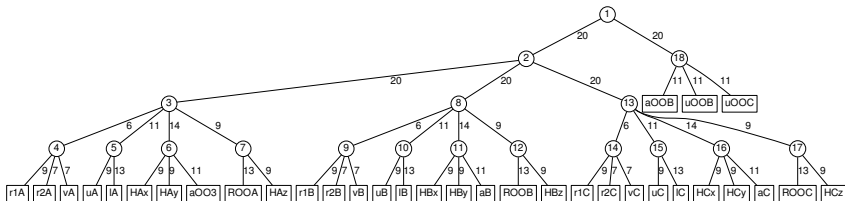
- Small initial guess
 - Iterate a number of times
 - Add terms with zero coefficient but random numbers as basis functions
 - Repeat...
-
- Fit calculated on 19200 cores on Hazel-Hen in approximately 4 hours.
 - Several runs with different initial guess but same cuts and samplings necessary

Results: Linear absorption spectrum

$$\alpha(\omega) \propto \omega I(\omega)$$

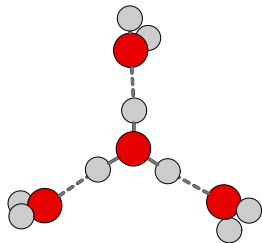
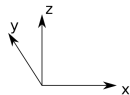
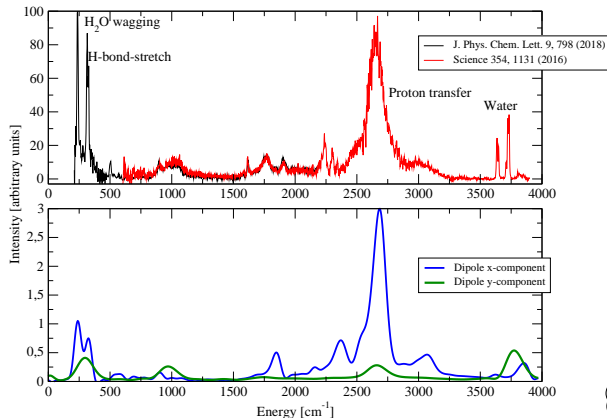
- $I(\omega)$: half-sided Fourier transform of the dipole-dipole correlation function $C(t)$
- \rightarrow Propagation of the dipole-operated ground state wavefunction

Multi-Layer MCTDH



Results: Linear absorption spectrum

Linear absorption spectrum $\alpha(\omega)$ as FFT of the dipole-dipole correlation function



Summary

Algorithm

- Working method to obtain high-dimensional PESs in CPD form
- Based on iterative optimizer with integrals replaced by Monte-Carlo
- Shown with preliminary results for $H_9O_4^+$

Preliminary IR spectra of the Eigen Cation

- Preliminary spectrum in good agreement with experiments
- Peaks are not all at the correct position (water)
- Improvements needed (ML-Tree, CANDECAMP, grids...)