Efficient approaches to multidimensional quantum dynamics: Dynamical pruning in phase, position and configuration space

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How to do molecular quantum dynamics simulations?

$|\Psi(t)\rangle = \sum_I A_I(t) |I\rangle$

$I \equiv \{i_1, i_2, \ldots, i_D\}, i_\kappa \in [1, N_\kappa]$

HUGE tensor $A$, size $\prod_{\kappa=1}^D N_\kappa = H \times A_H$

$\hat{H}_{IJ} = \langle I | \hat{H} | J \rangle$

$\frac{\partial}{\partial t} |\Psi(t)\rangle$

$\text{TD-FCI: Standard approach in mol. quantum dynamics}$

$\text{Problem: Curse of dimensionality (exponential scaling)}$

$\text{Possible loophole: Employ bases that lead to sparse tensors}$

$\text{Dynamical Pruning (DP)}$
How to do molecular quantum dynamics simulations?

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- **TD-FCI:** *Standard* approach in mol. quantum dynamics
- **Problem:** Curse of dimensionality (exponential scaling)

**Direct-product basis**
\[ |I\rangle \equiv \bigotimes_{\kappa=1}^D |\chi_{j_\kappa}^\kappa\rangle \]
How to do molecular quantum dynamics simulations?

Wave function $|\Psi(t)\rangle$

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HUGE tensor $A$, size $\prod_{\kappa=1}^{D} N_\kappa$

$\sum_{I} A_{I}(t) |I\rangle$

Direct-product basis

$|I\rangle \equiv \bigotimes_{\kappa=1}^{D} |\chi_{j_\kappa}^{\kappa}\rangle$

$i\partial_t |\Psi(t)\rangle$

$H \times A$

$H_{IJ} = \langle I|\hat{H}|J\rangle$

- TD-FCI: Standard approach in mol. quantum dynamics
- Problem: Curse of dimensionality (exponential scaling)
- Possible loophole: Employ bases that lead to sparse tensors $A$

 Dynamical Pruning (DP)
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TD-FCI

phase space bases

PvB

pW

DVR

FGH

Gauß-Grid

MCTDH

primitive basis (SPF representation)

SPF (A tensor)
- Exploit *locality* of $|\Psi\rangle$ in position space:

- Add/remove neighbors if $|A_i| > \theta$ / $|A_i| < \theta$
- Used by Hartke\(^1\), Wyatt\(^2\) and others.
- Easiest to use: DVR/pseudospectral functions
- Bonus: Potential is diagonal $V_{ij} = \delta_{ij} V(x_i)$

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Phase-space-localised von Neumann basis

\[ \langle x | \tilde{g}_{n,l} \rangle = \left( \frac{2\alpha}{\pi} \right)^{\frac{1}{4}} \exp \left( -\alpha (x - x_n)^2 + i \cdot p_l \cdot (x - x_n) \right), \quad \alpha = \frac{\sigma_p}{2\sigma_x} \]

- Basis is localised at \((x_n, p_l)\).
- Problem: Poor convergence.
Phase-space-localised von Neumann basis

\[
\langle x | \tilde{g}_{n,l} \rangle = \left( \frac{2\alpha}{\pi} \right)^{\frac{1}{4}} \exp \left( -\alpha(x - x_n)^2 + i \cdot p_l \cdot (x - x_n) \right), \quad \alpha = \frac{\sigma_p}{2\sigma_x}
\]

- Basis is localised at \((x_n, p_l)\).
- Problem: Poor convergence.
- **Solution 1:**
  
  Projected von Neumann (PvN/PvB):
  \[ |g_i\rangle = \sum_j |\chi_j\rangle \langle \chi_j | \tilde{g}_i \rangle; \quad \{\chi_i\}: \text{DVR} \]
  Non-Orthogonal! (PvB: biorthogonal basis)

\[\text{PvN (} \sqrt{N} \times \sqrt{N} \text{ points)} \quad \text{FGH (} N \text{ points)}\]

\[\text{vN} \quad \Delta x \quad x\]

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Phase-space-localised von Neumann basis

\[ \langle x | \tilde{g}_{n,l} \rangle = \left( \frac{2\alpha}{\pi} \right)^{\frac{1}{4}} \exp \left( -\alpha (x - x_n)^2 + i \cdot p_l \cdot (x - x_n) \right), \quad \alpha = \frac{\sigma_p}{2\sigma_x} \]

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  Non-Orthogonal! (PvB: biorthogonal basis)

- Solution 2:\(^4\) Projected Weylets (pW):
  \[ \langle x | \tilde{\phi}_{nl} \rangle = \left( \frac{8\alpha}{\pi} \right)^{\frac{1}{4}} \exp \left[ -\alpha (x - x_n)^2 \right] \sin \left[ p_l \left( x - x_n - \sqrt{\frac{\pi}{8\alpha}} \right) \right] \]
  Orthogonal! Less sparse than PvB!


Example of a PvB propagation
Multidimensions: Hamiltonian times state: $H \cdot A$

<table>
<thead>
<tr>
<th>Unpruned case</th>
</tr>
</thead>
<tbody>
<tr>
<td>▪ Assume a SoP Hamilton-Tensor: $H = h^{(1)} \otimes h^{(2)} + \ldots$</td>
</tr>
<tr>
<td>▪ $D$: dimension, $n$: 1D basis size, $n^{2D}$: size of $H$; $n^D$: size of $A$</td>
</tr>
<tr>
<td>▪ Scaling of $H \cdot A$: $O(n^{D+1})$ by sequential summation</td>
</tr>
<tr>
<td>▪ (as done in electronic integral transformations)</td>
</tr>
</tbody>
</table>

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### Multidimensions: Hamiltonian times state: $H \cdot A$

#### Unpruned case

- Assume a SoP Hamilton-Tensor: $H = h^{(1)} \otimes h^{(2)} + \ldots$
- $D$: dimension, $n$: 1D basis size, $n^{2D}$: size of $H$; $n^D$: size of $A$
- Scaling of $H \cdot A$: $\mathcal{O}(n^{D+1})$ by sequential summation (as done in electronic integral transformations)

#### Pruned case

- Pruning: $n^D \rightarrow \tilde{n}^D$
- $\mathcal{O}(\tilde{n}^{D+1})$ scaling possible with new algorithm
- ONLY for orthogonal basis
- Nonorthogonal basis: $S_{PvB}^{-1} H_{PvB}^{} A$
- Pruned $S^{-1}$ not of SoP form: $\mathcal{O}(\tilde{n}^{2D})$ scaling

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Application: 2D double well

- Testing a pruned DVR (FGH), PvB and pW
Application: 2D double well

- Testing a pruned DVR (FGH), PvB and pW
- Accuracy versus basis size?

![Graph showing infidelity of the autocorrelation and mean number of used basis functions]
**Application: 2D double well**

- Testing a pruned DVR (FGH), PvB and pW
- Accuracy versus basis size?
- Timing?

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**Infidelity of the autocorrelation**
- Mean number of used basis functions / %
  - pW
  - FGH
  - PvB

**Needed time / s**
- full FGH time
  - pW
  - FGH
  - PvB

FGH/DVR: Potential diagonal, pW: Non-diagonal
Vibr. resonance dynamics of DCO$^4$

- DP-DVR with filter diagonalization + CAP
- Controlled accuracy of pruning for energies and widths
- Decay dynamics up to 200 ps with DP-DVR: Confirms polyad model
- Comparison with velocity mapped images from Temps Group @ Kiel

\[ \Delta E = 8902 \text{ cm}^{-1}; \quad (2,2,2) \quad \text{v} = 0 \]

\[ \Delta E = 8942 \text{ cm}^{-1}; \quad (0,5,0) \quad \text{v} = 0 \]

\[ \Delta E = 9896 \text{ cm}^{-1}; \quad (2,3,1) \quad \text{v} = 2 \]

\[ \Delta E = 10065 \text{ cm}^{-1}; \quad (1,4,1) \quad \text{v} = 0 \]

<table>
<thead>
<tr>
<th>P</th>
<th>label</th>
<th>$\Delta E$/cm$^{-1}$</th>
<th>$\Gamma$/cm$^{-1}$</th>
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<tbody>
<tr>
<td>5</td>
<td>(034)</td>
<td>8778</td>
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<td>(042)</td>
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<td>(230)</td>
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<td>(140)</td>
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<td>(051)</td>
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<td>(133)</td>
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<tr>
<td>5.5</td>
<td>(231)</td>
<td>9896</td>
<td>9891</td>
</tr>
<tr>
<td>5.5</td>
<td>(141)</td>
<td>10065</td>
<td>10044</td>
</tr>
</tbody>
</table>

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. . .

MCTDH

primitive basis (SPF representation)

SPF (A tensor)
Multi-Configurational Time-Dependent Hartree (MCTDH)

∼ TD-CAS-SCF for nuclei
- Single Particle Functions (SPF) $|\phi\rangle$: time-dependent, variationally optimised direct-product basis
- Configurations $|l\rangle$: Hartree-Product of SPFs

![Diagram](https://via.placeholder.com/150)

- Wave function $|\psi(t)\rangle$
  - $\sum_{l} A_{l}(t) |l(t)\rangle$
  - $i_\kappa \in [1, n_\kappa]$
  - Tensor size $\prod_{i}^{D} n_{i}$, $n_{i} \leq N_{i}$

- Single particle functions (SPF), $|l(t)\rangle \equiv \bigotimes_{k=1}^{D} |\phi_{j_\kappa}^{k}(t)\rangle$
Multi-Configurational Time-Dependent Hartree (MCTDH)

~ TD-CAS-SCF for nuclei
- Single Particle Functions (SPF) $|\phi\rangle$: time-dependent, variationally optimised direct-product basis
- Configurations $|I\rangle$: Hartree-Product of SPFs

- Mode combination: Combine strongly coupled modes to propagate multidimensional SPFs.
- Shifts both computational effort and storage requirement
Multi-Configurational Time-Dependent Hartree (MCTDH)

≈ TD-CAS-SCF for nuclei
- **Single Particle Functions (SPF)** $|\phi\rangle$: time-dependent, variationally optimised direct-product basis
- **Configurations** $|I\rangle$: Hartree-Product of SPFs

\[
|\Psi(t)\rangle = \sum_I A_I(t) |I(t)\rangle \\
i_\kappa \in [1, n_\kappa] \\
\text{tensor size } \prod_i n_i, n_i \leq N_i
\]

- Mode combination: Combine strongly coupled modes to propagate multidimensional SPFs.
- Shifts both computational effort and storage requirement
- Multilayer MCTDH: Propagate multidimensional SPFs with MCTDH (recursively) ≈ Tree Tensor Network States
How to prune MCTDH?

- Prune SPFs (configuration space)
- Related to selected CI/MCTDH... \(^5\)
- but here \textit{dynamically} for TDSE!\(^6\)
- Use natural orbitals

\[ \Rightarrow \text{MCTDH with one parameter!} \]

---


\(^6\) H. R. Larsson and D. J. Tannor, \textit{J. Chem. Phys.}, 2017, 147, 044103
How to prune MCTDH?

**Wave function**

\[ |\Psi(t)\rangle \]

\[ \sum_i A_i(t) |l(t)\rangle \]

\[ i_\kappa \in [1, n_\kappa] \]

tensor size \[ \prod_i D_i n_i, \; n_i \leq N_i \]

- Prune SPF representations (configuration space)
- Related to selected CI/MCTDH...\(^5\)
- but here *dynamically* for TDSE!\(^6\)
- Use natural orbitals

\[ \Rightarrow \text{MCTDH with one parameter!} \]

**Single particle functions (SPF),**

\[ |l(t)\rangle \equiv \bigotimes_{\kappa=1}^D |\phi_{j_{\kappa}}^\kappa(t)\rangle \]

- Prune SPF representation:
  \[ |\phi_{i}^\kappa\rangle = \sum_{a=1}^{N_\kappa} U_{a_i}^{\kappa} |\chi_{i}^{\kappa}\rangle \]
  - \[ |\chi_{i}^{\kappa}\rangle \]: Primitive basis
  \[ \Rightarrow \text{High-dim. mode comb.} \]
  \[ \Rightarrow \text{Relaxes requirement of SoP form of } \hat{H} \]

---


Example: 24D pyrazine/ 9D A tensor: Spectrum

- Pruning with restricted number of SPF

- Speed-ups of up to 50!
- Comparable or faster than ML-MCTDH!
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primitive basis (SPF representation)

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Example: 24D pyrazine: More mode combination

Based on variant with fewer SPFs. Mode combination unfavorable (36 vs 59 h); one prim. basis size as large as A

Pruning as fast as unpruned variant without unfavorable mode combination!
Thanks!

You!

Hartke Group
Christian-Albrechts-Universität zu Kiel

Tannor Group
WEIZMANN INSTITUTE OF SCIENCE

FCI
FONDS DER
CHEMISCHEN
INDUSTRIE

Studienstiftung
des deutschen Volkes

DAAD
### Summary

**Pruning TD-FCI:**

<table>
<thead>
<tr>
<th></th>
<th>DVR</th>
<th>PvB</th>
<th>pW</th>
</tr>
</thead>
<tbody>
<tr>
<td>sparsity</td>
<td>😞</td>
<td>😊</td>
<td>😊</td>
</tr>
<tr>
<td>$V$ diagonal?</td>
<td>😊</td>
<td>😞</td>
<td>😞</td>
</tr>
<tr>
<td>orthogonal?</td>
<td>😊</td>
<td>😞</td>
<td>😊</td>
</tr>
<tr>
<td>$O(\tilde{n}^{D+1})$ scaling?</td>
<td>😊</td>
<td>😞</td>
<td>😊</td>
</tr>
<tr>
<td>actual runtime</td>
<td>😊</td>
<td>😞</td>
<td>😊</td>
</tr>
</tbody>
</table>

**Pruning MCTDH:**

**Pruning coefficient tensor $A$**
- Most important
- MCTDH with one parameter
- Speedups between 5 and 50
- Competitive with ML-MCTDH but much simpler

**Pruning primitive basis**
- Makes unfavorable mode combination favorable
- Relaxes requirements regarding SoP form of $\hat{H}$
- Treats highly correlated modes

**Not shown**
Applications to electron dynamics in strong fields