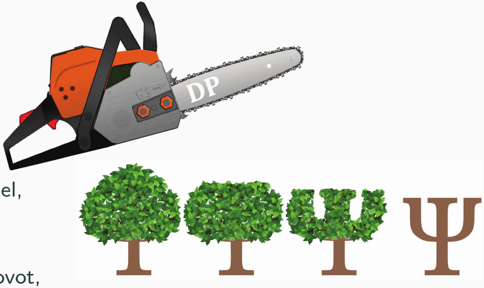
Efficient approaches to multidimensional quantum dynamics: Dynamical pruning in phase, position and configuration space

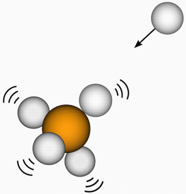
Henrik R. Larsson

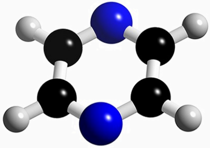
April 20, 2018



Group Prof. Hartke /
Christiana Albertina University of Kiel, Germany
Group Prof. Tannor /
Weizmann Institute of Science, Rehovot, Israel

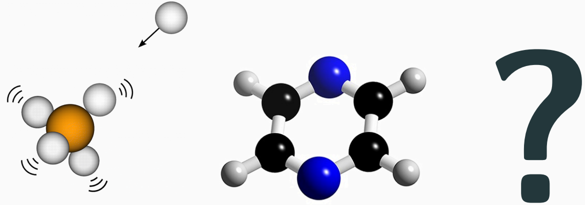
How to do molecular quantum dynamics simulations?

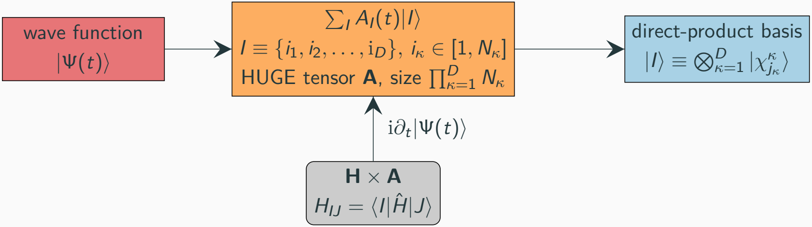




?

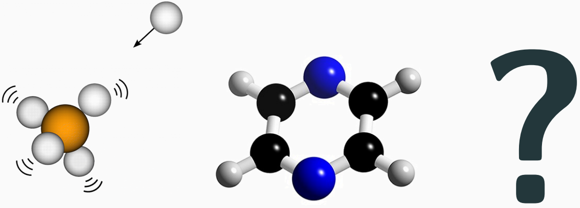
How to do molecular quantum dynamics simulations?

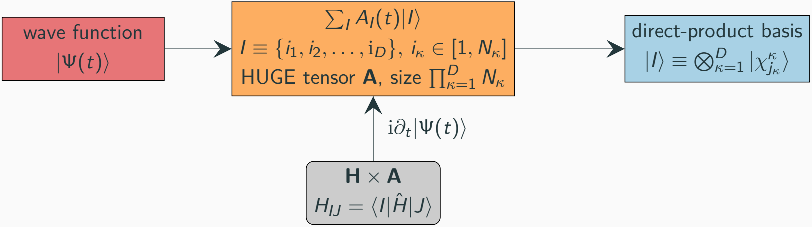




- TD-FCI: *Standard* approach in mol. quantum dynamics
- Problem: Curse of dimensionality (exponential scaling)

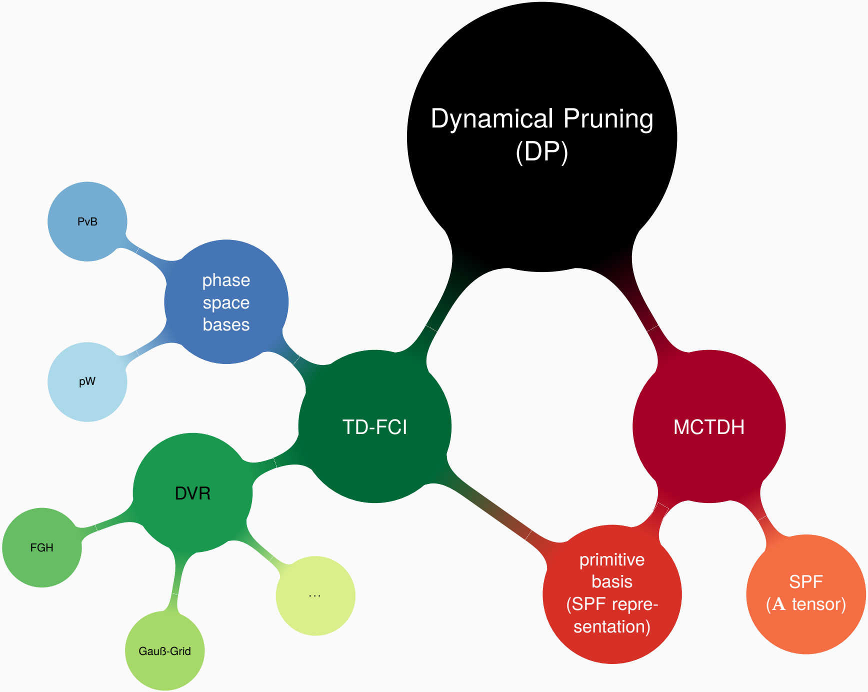
How to do molecular quantum dynamics simulations?



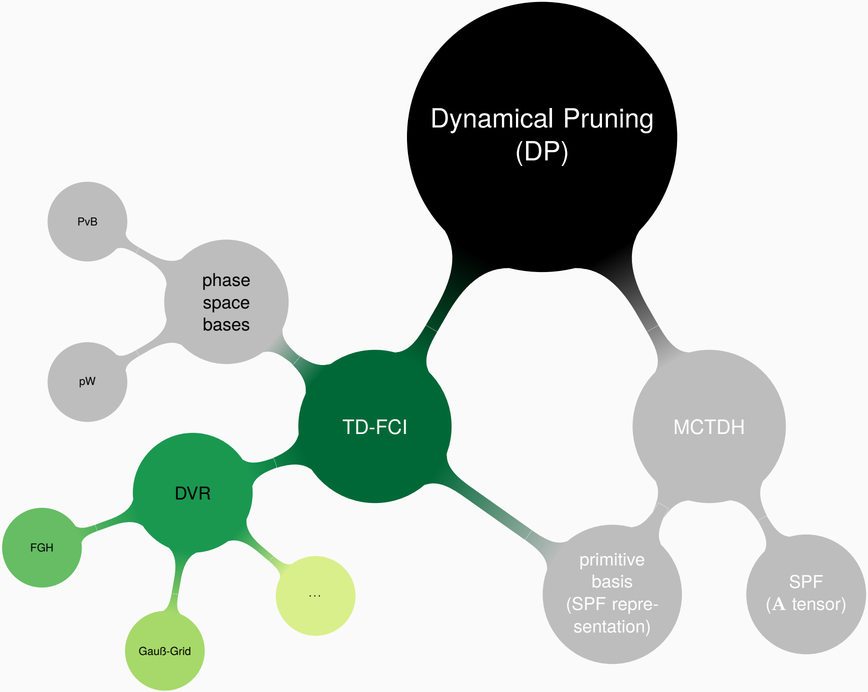


- TD-FCI: *Standard* approach in mol. quantum dynamics
- Problem: Curse of dimensionality (exponential scaling)
- Possible loophole: Employ bases that lead to **sparse** tensors **A**

↷ **Dynamical Pruning (DP)**



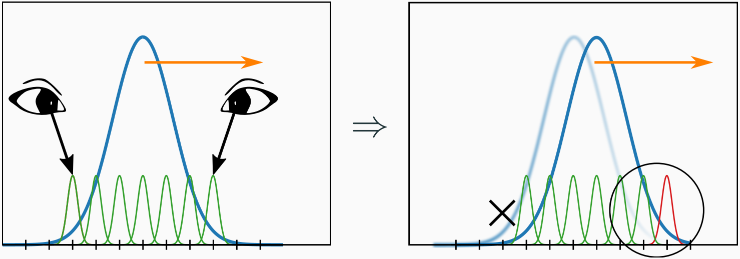
Dynamical Pruning (DP)
phase space bases
PvB
pW
TD-FCI
MCTDH
DVR
FGH
Gauß-Grid
…
primitive basis (SPF repre-sentation)
SPF ($\mathbf{A}$ tensor)



Dynamical Pruning (DP)
phase space bases
PvB
pW
TD-FCI
DVR
FGH
Gauß-Grid
...
MCTDH
primitive basis (SPF representation)
SPF ($\mathbf{A}$ tensor)

DVR/Coordinate-space-localised functions

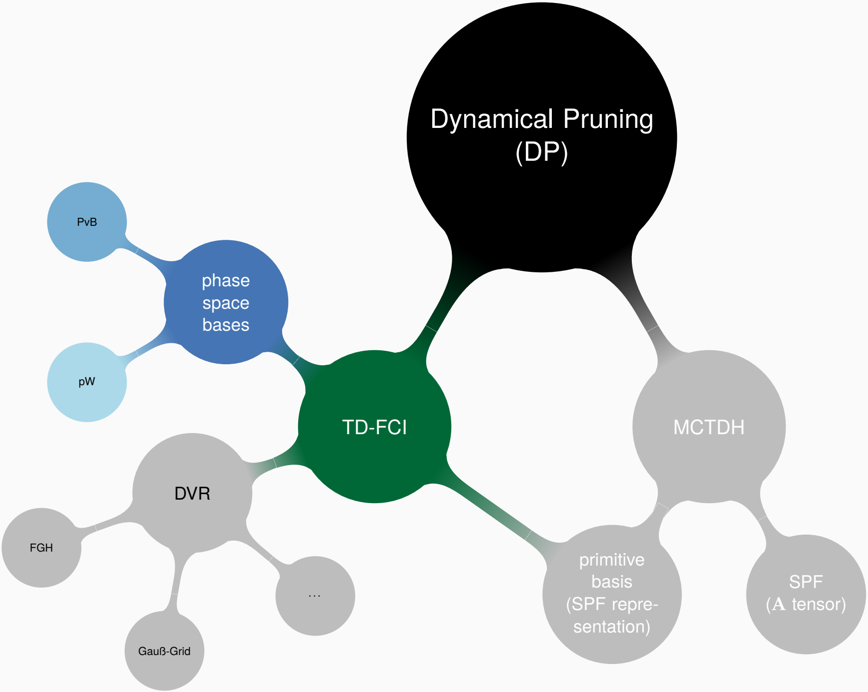
- Exploit *locality* of $|\Psi\rangle$ in position space:



- 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 $V_{ij} = \delta_{ij} V(x_i)$

[1] B. Hartke, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3627, J. Sielk et al., *Phys. Chem. Chem. Phys.*, 2009, **11**, 463–475.

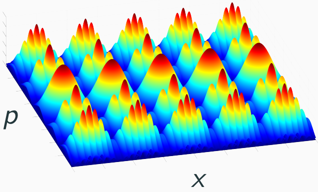
[2] L. R. Pettey and R. E. Wyatt, *Chem. Phys. Lett.*, 2006, **424**, 443 –448, L. R. Pettey and R. E. Wyatt, *Int. J. Quantum Chem.*, 2007, **107**, 1566–1573.


Dynamical Pruning (DP)
TD-FCI
phase space bases
PvB
pW
DVR
FGH
Gauß-Grid
...
MCTDH
primitive basis (SPF repre-sentation)
SPF (A tensor)

Phase-space-localised von Neumann basis

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

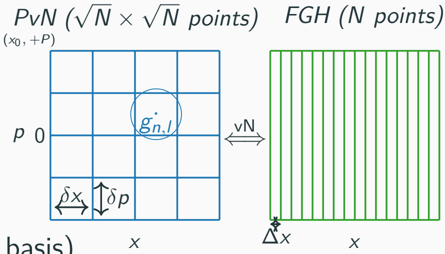
- Basis is localised at (x_n, p_l).
- Problem: Poor convergence.



Phase-space-localised von Neumann basis

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

- Basis is localised at (x_n, p_l).
- Problem: Poor convergence.
- Solution 1:[3]
  Projected von Neumann (PvN/PvB):
  $|g_i\rangle = \sum_j |\chi_j\rangle\langle\chi_j|\,\tilde{g}_i\rangle$; $\{\chi_i\}$: DVR
  Non-Orthogonal! (PvB: biorthogonal basis)

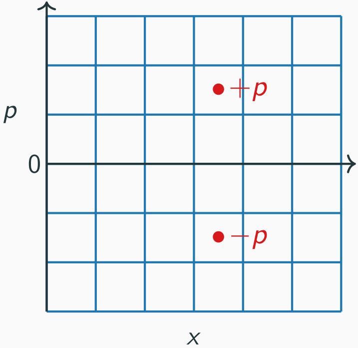


[3] A. Shimshovitz and D. J. Tannor, *Phys. Rev. Lett.*, 2012, **109**, 070402, D. J. Tannor et al., *Adv. Chem. Phys.*, 2018, **163**, in press

Phase-space-localised von Neumann basis

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

- Basis is localised at (x_n, p_l).
- Problem: Poor convergence.
- Solution 1:[3]
  Projected von Neumann (PvN/PvB):
  $|g_i\rangle = \sum_j |\chi_j\rangle\langle\chi_j|\tilde{g}_i\rangle$; $\{\chi_i\}$: DVR
  Non-Orthogonal! (PvB: biorthogonal basis)

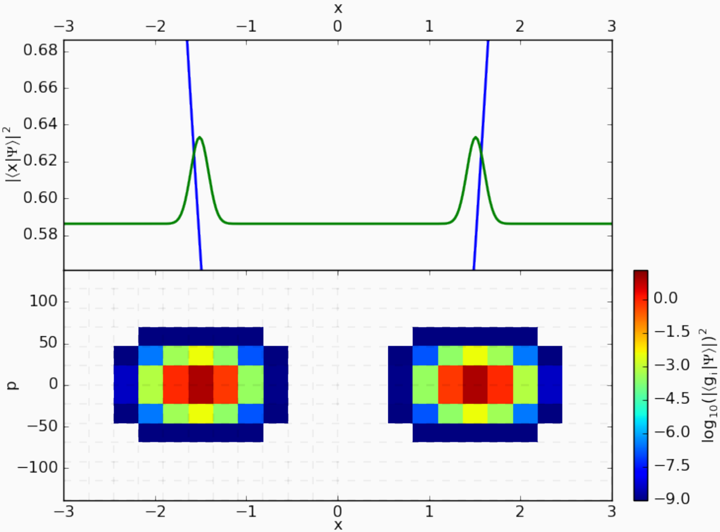


- Solution 2:[4]
  Projected Weylets (pW):
  $\langle x|\widetilde{\phi}_{nl}\rangle = \left(\frac{8\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left[-\alpha(x-x_n)^2\right] \sin\left[p_l\left(x - x_n - \sqrt{\frac{\pi}{8\alpha}}\right)\right]$
  Orthogonal! Less sparse than PvB!

[3] A. Shimshovitz and D. J. Tannor, *Phys. Rev. Lett.*, 2012, **109**, 070402, D. J. Tannor et al., *Adv. Chem. Phys.*, 2018, **163**, in press

[4] B. Poirier and A. Salam, *J. Chem. Phys.*, 2004, **121**, 1690, H. R. Larsson et al., *J. Chem. Phys.*, 2016, **145**, 204108

Example of a PvB propagation



Multidimensions: Hamiltonian times state: $\mathbf{H} \cdot \mathbf{A}$

Unpruned case

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

[3] D. J. Tannor et al., *Adv. Chem. Phys.*, 2018, **163**, in press, H. R. Larsson et al., *J. Chem. Phys.*, 2016, **145**, 204108.

Multidimensions: Hamiltonian times state: $\mathbf{H} \cdot \mathbf{A}$

Unpruned case

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

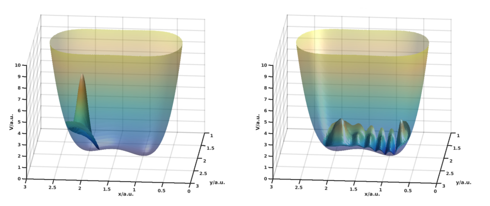
Pruned case

- Pruning: $n^D \longrightarrow \tilde{n}^D$
- $\mathcal{O}(\tilde{n}^{D+1})$ scaling possible with new algorithm[3]
- ONLY for orthogonal basis
- Nonorthogonal basis: $\mathbf{S}_{\mathrm{PvB}}^{-1}\mathbf{H}^{\mathrm{PvB}}\mathbf{A}$
- Pruned $\mathbf{S}^{-1}$ not of SoP form: $\mathcal{O}(\tilde{n}^{2D})$ scaling

[3] D. J. Tannor et al., *Adv. Chem. Phys.*, 2018, **163**, in press, H. R. Larsson et al., *J. Chem. Phys.*, 2016, **145**, 204108.

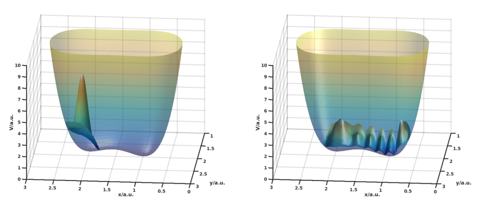
Application: 2D double well

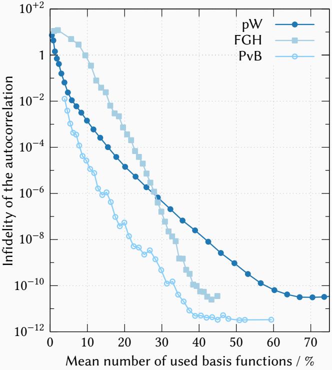
- Testing a pruned DVR (FGH), PvB and pW



Application: 2D double well

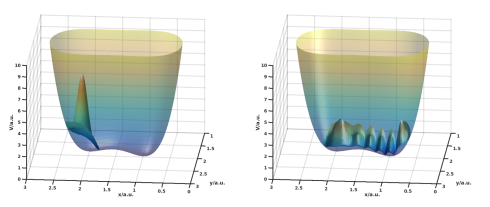
- Testing a pruned DVR (FGH), PvB and pW
- Accuracy versus basis size?

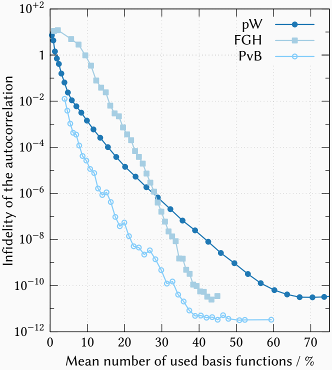


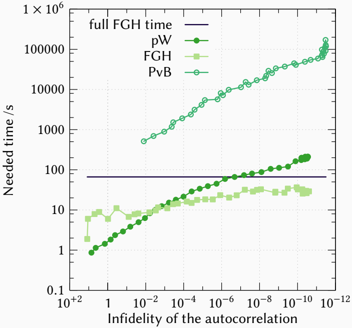


Application: 2D double well

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



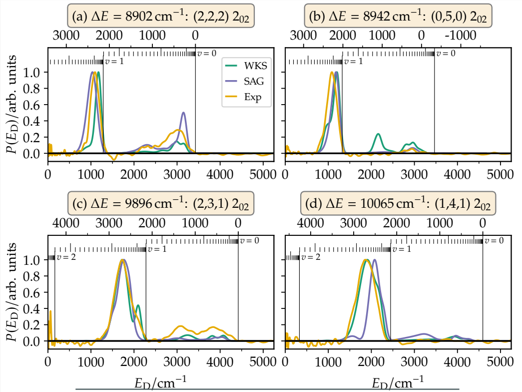




FGH/DVR: Potential diagonal, pW: Non-diagonal

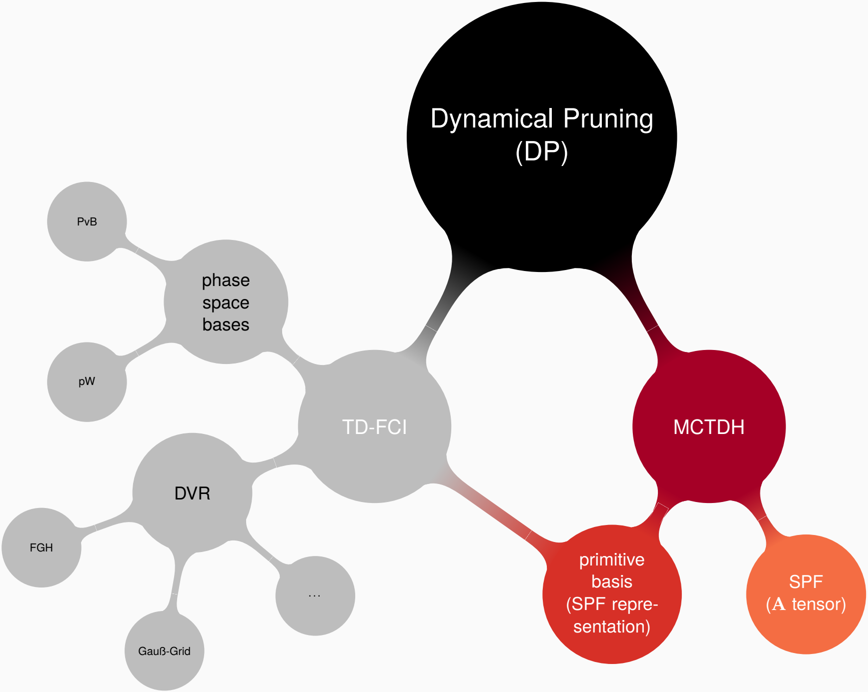
Vibr. resonance dynamics of DCO[4]

- 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



P	label	$\Delta E/\mathrm{cm}^{-1}$ Expt.	$\Delta E/\mathrm{cm}^{-1}$ DP	Γ/cm^{-1} Expt.	Γ/cm^{-1} DP
5	((034))	8778	8775	3.50	5.6
5	((042))	8821	8830	<2.00	1.1
5	((222))	8902	8895	1.06	1.2
5	(050)	8942	8950	1.79	0.13
5	(132)	9050	9029	0.34	0.28
5	(230)	9099	9096	0.20	0.32
5.5	027	—	9234	—	13
5	((140))	9272	9248	0.29	0.31
5.5	((321))	—	9494	—	17
5.5	(043)	9614	9629	2.30	1.4
5.5	(223)	9686	9688	<5.00	5.5
5.5	((051))	9757	9762	0.83	0.64
5.5	((133))	9819	9805	<3.00	1.8
5.5	(231)	9896	9891	1.22	1.6
5.5	((141))	10065	10044	6.00	3.9

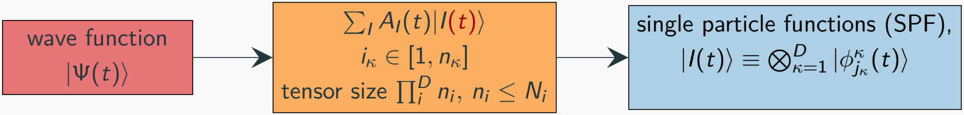
[4] H. R. Larsson et al., arXiv:1802.07050; submitted to J. Chem. Phys, 2018.


Dynamical Pruning (DP)
TD-FCI
MCTDH
phase space bases
PvB
pW
DVR
FGH
Gauß-Grid
...
primitive basis (SPF representation)
SPF (A tensor)

Multi-Configurational Time-Dependent Hartree (MCTDH)

$\sim$ TD-CAS-SCF for nuclei

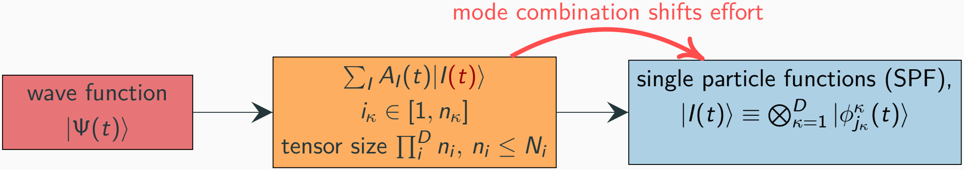
- Single Particle Functions (SPF) $|\phi\rangle$: time-dependent, variationally optimised direct-product basis
- Configurations $|I\rangle$: Hartree-Product of SPFs



Multi-Configurational Time-Dependent Hartree (MCTDH)

$\sim$ 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

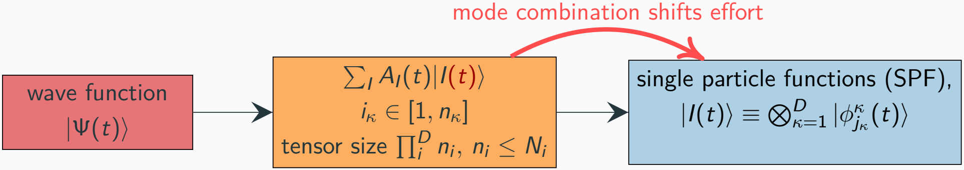


- Mode combination: Combine strongly coupled modes to propagate multidimensional SPFs.
- Shifts both computational effort and storage requirement

Multi-Configurational Time-Dependent Hartree (MCTDH)

$\sim$ 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
- Multilayer MCTDH: Propagate multidimensional SPFs with MCTDH (recursively) $\sim$ Tree Tensor Network States

How to prune MCTDH?

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

↓

$\sum_I A_I(t)|I(t)\rangle$
$i_\kappa \in [1, n_\kappa]$
tensor size $\prod_i^D n_i$, $n_i \leq N_i$

→

single particle functions (SPF),
$|I(t)\rangle \equiv \bigotimes_{\kappa=1}^{D} |\phi^\kappa_{j_\kappa}(t)\rangle$

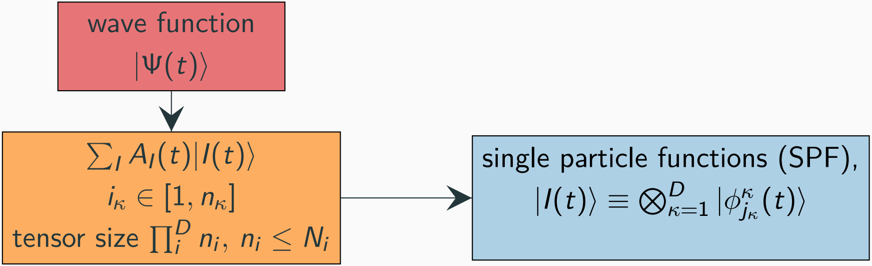
- Prune SPFs (configuration space)
- Related to selected CI/MCTDH. . .[5]
- but here *dynamically* for TDSE![6]
- Use natural orbitals

⇒ MCTDH with *one* parameter!

[5] G. A. Worth, *J. Chem. Phys.*, 2000, **112**, 8322–8329, R. Wodraszka and T. Carrington, *J. Chem. Phys.*, 2016, **145**

[6] H. R. Larsson and D. J. Tannor, *J. Chem. Phys.*, 2017, **147**, 044103

How to prune MCTDH?



- Prune SPFs (configuration space)
- Related to selected CI/MCTDH. . . [5]
- but here *dynamically* for TDSE![6]
- Use natural orbitals

⇒ MCTDH with *one* parameter!

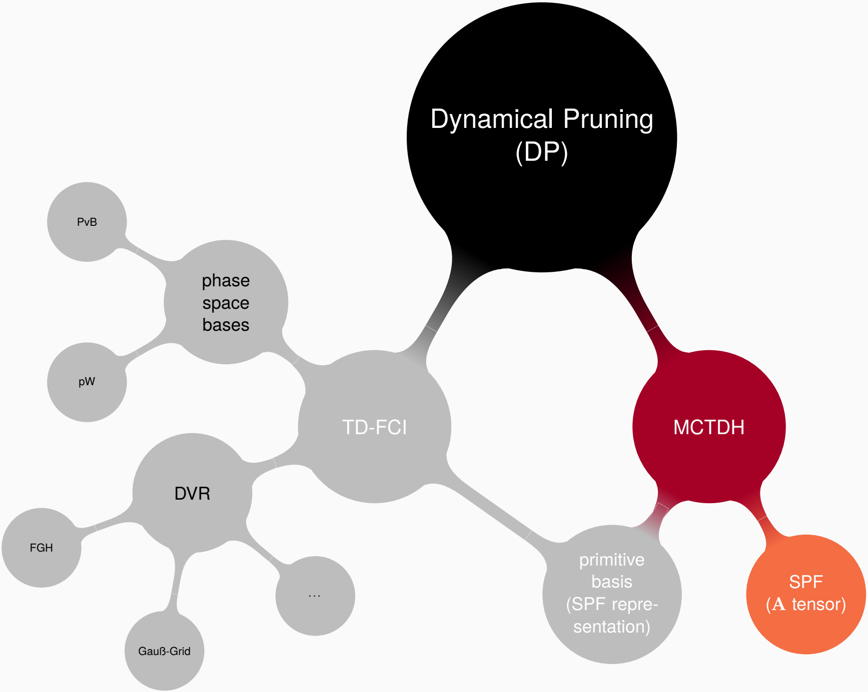
- Prune SPF representation: $|\phi_i^\kappa\rangle = \sum_{a=1}^{N_\kappa} U^\kappa_{ai}|\chi_i^\kappa\rangle$
- $|\chi_i^\kappa\rangle$: Primitive basis

⇒ High-dim. mode comb.

⇒ Relaxes requirement of SoP form of $\hat{H}$

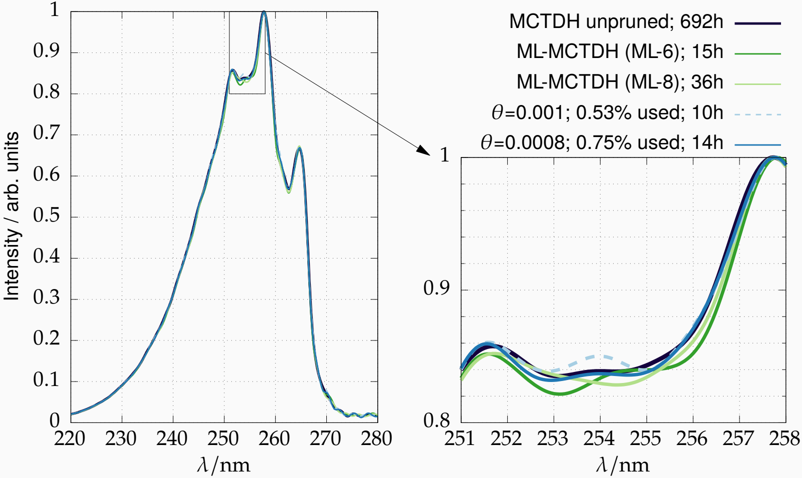
[5] G. A. Worth, *J. Chem. Phys.*, 2000, **112**, 8322–8329, R. Wodraszka and T. Carrington, *J. Chem. Phys.*, 2016, **145**

[6] H. R. Larsson and D. J. Tannor, *J. Chem. Phys.*, 2017, **147**, 044103

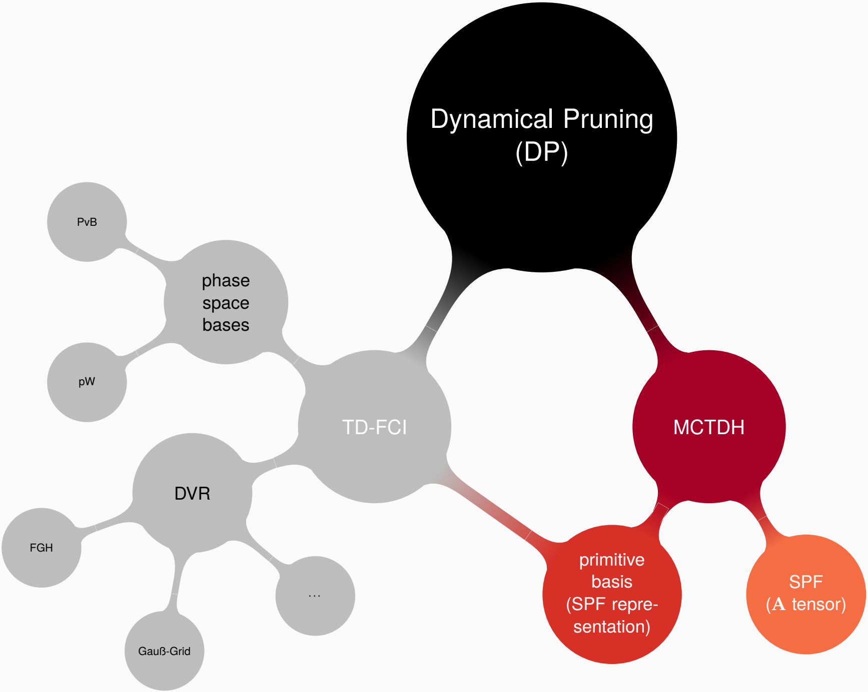

Dynamical Pruning (DP)
TD-FCI
MCTDH
phase space bases
PvB
pW
DVR
FGH
Gauß-Grid
...
primitive basis (SPF representation)
SPF (A tensor)

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

- Pruning with restricted number of SPF

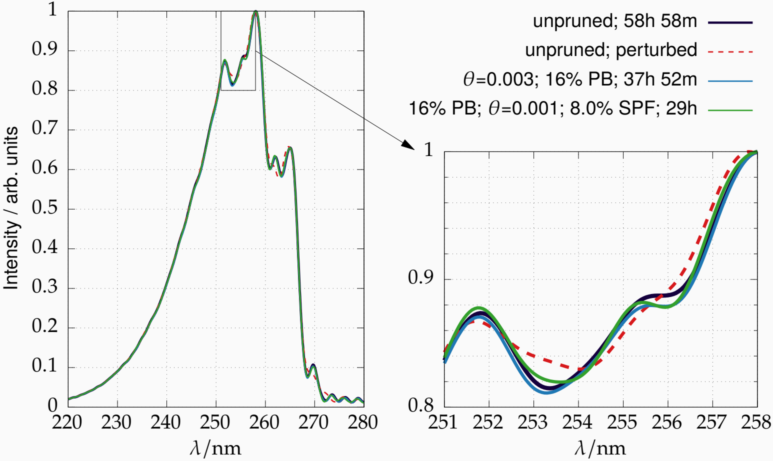


- Speed-ups of up to 50!
- Comparable or faster than ML-MCTDH!


Dynamical Pruning (DP)
MCTDH
TD-FCI
phase space bases
PvB
pW
DVR
FGH
Gauß-Grid
...
primitive basis (SPF repre- sentation)
SPF (A tensor)

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!

C A U Hartke Group
Christian-Albrechts-Universität zu Kiel

מכון ויצמן למדע Tannor Group
WEIZMANN INSTITUTE OF SCIENCE

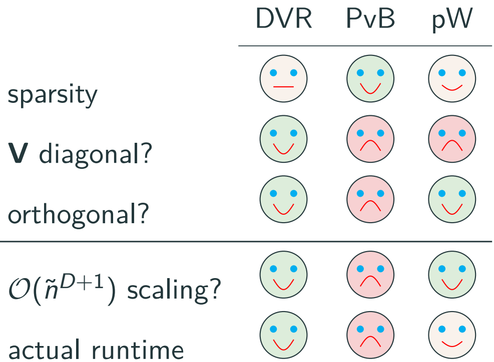
FCI FONDS DER CHEMISCHEN INDUSTRIE

Studienstiftung des deutschen Volkes

DAAD

Summary

Pruning TD-FCI:



Not shown

Applications to electron dynamics in strong fields

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