Multi-Configuration Time Dependent Hartree Theory

A Tensor Network Perspective

Xinxian Chen

September 28, 2018

Department of Chemistry, Tsinghua University

Outline

Discrete Variable Representation

Multi-Configuration Time Dependent Hartree

MCTDH vs. DMRG

Discrete Variable Representation

Discrete Variable Representation

Problem Description

Non-Relativistic Multi-Dimentional Problem

- TDSE:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\left|\Psi(\vec{q},t)\right\rangle = H\left|\Psi(\vec{q},t)\right\rangle$$

- TISE:

$$H\left|\Psi(\vec{q},t)\right\rangle = E\left|\Psi(\vec{q},t)\right\rangle$$

where

$$H = T + V$$

and $\vec{q} = (q_1, q_2, \ldots, q_d)$.

Discrete Variable Representation

Standard Procedure

Discretization: Spectral Method

Choose a set of basis functions: $\{|\Phi_I(\vec{q})\rangle\}_{I=1}^{N}$ and require

1. Orthonormal: $\langle\Phi_I|\Phi_J\rangle = \delta_{IJ}$
2. Complete: $\sum_{I=1}^{n} |\Phi_I\rangle\langle\Phi_I| = P \to 1, \quad n \to +\infty$

Therefore,

$$|\Psi\rangle \approx P|\Psi\rangle = \sum_{I}^{n} c_I |\Phi_I\rangle \quad \text{where} \quad c_I = \langle\Phi_I|\Psi\rangle$$

and

$$A \approx PAP = \sum_{IJ}^{n} |\Phi_I\rangle A_{IJ} \langle\Phi_J| \quad \text{where} \quad A_{IJ} = \langle\Phi_I|A|\Phi_J\rangle$$

---

http://www.pci.uni-heidelberg.de/tc/usr/mctdh/lit/NumericalMethods.pdf

1-D Problem

Standard procedure:

1. Choose a set of 1-D basis $\{|\varphi_i(x)\rangle\}_{i=1}^{n}$
2. Integrate

   $T_{ij} = \langle\varphi_i(x)|\, T|\varphi_j(x)\rangle = -\frac{\hbar}{2\mu}\int \varphi^*(x)\frac{\mathrm{d}}{\mathrm{d}x}\varphi(x)\,\mathrm{d}x,$

   $V_{ij} = \langle\varphi_i(x)|\, V|\varphi_j(x)\rangle = \int \varphi^*(x)\, V(x)\varphi(x)\,\mathrm{d}x,$ and

   $H_{ij} = T_{ij} + V_{ij}$
3. Solve TDSE/TISE in matrix form
   - TDSE:

     $$\mathrm{i}\hbar\dot{c}_i = \sum_j H_{ij}c_j \quad \text{or} \quad \mathrm{i}\hbar\dot{\mathbf{c}} = \mathbf{H}\mathbf{c}$$

   - TISE:

     $$\sum_j H_{ij}c_j = Ec_i \quad \text{or} \quad \mathbf{H}\mathbf{c} = E\mathbf{c}$$

d-D Problem: $\vec{q} = (q_1, \ldots, q_d)$

Standard procedure:

1. Choose a set of d-D basis $\left\{\left|\Phi_I(\vec{q})\right\rangle\right\}_{I=1}^{N}$
   - Use the direct product of d sets of 1-D basis

$$\bigotimes_{\kappa=1}^{d} \left\{\left|\varphi_i^{(\kappa)}(q_\kappa)\right\rangle\right\}_{i=1}^{n_\kappa}$$

   as the set of d-D basis, i. e.,

$$\left|\Phi_I(q_1, \ldots, q_d)\right\rangle = \prod_{\kappa=1}^{d} \left|\varphi_{i_\kappa}^{(\kappa)}(q_\kappa)\right\rangle$$

   where $I = (i_1, \ldots, i_d)$.

d-D Problem: $\vec{q} = (q_1, \ldots, q_d)$

Standard procedure:

1. Choose a set of d-D basis $\{|\Phi_I(\vec{q})\rangle\}_{I=1}^{N}$, where $|\Phi_I(\vec{q})\rangle = \prod_{\kappa=1}^{d} \left|\varphi_{i_\kappa}^{(\kappa)}(q_\kappa)\right\rangle$
2. Integrate $H_{IJ} = T_{IJ} + V_{IJ}$
3. Solve TDSE/TISE in matrix form
   - TDSE: $\mathrm{i}\hbar\dot{\mathbf{c}} = \mathbf{H}\mathbf{c}$
   - TISE: $\mathbf{H}\mathbf{c} = E\mathbf{c}$

Discrete Variable Representation

Selection of Basis

Motivation of DVR

- How to do the integral in the standard procedure?
- Kinetic energy

  In Cartesian coordinate

$$T = -\frac{\hbar}{2}\sum_{\kappa=1}^{d}\frac{1}{\mu_\kappa}\frac{\partial^2}{\partial q_\kappa^2}$$

  Therefore,

$$\mathbf{T} = \bigotimes_{\kappa=1}^{d}\mathbf{T}^{(\kappa)} \quad \text{where} \quad T_{ij}^{(\kappa)} = -\frac{\hbar}{2\mu_\kappa}\left\langle \varphi_i^{(\kappa)}\middle|\frac{\partial^2}{\partial q_\kappa^2}\middle|\varphi_j^{(\kappa)}\right\rangle$$

  which can be integrated analytically once the set of basis is determined.

Motivation of DVR

- How to do the integration in the standard procedure?
  - Kinetic energy
  - Potential energy
    Differs in different problems.
- Can we integrate some physical quantity analytically once the set of basis is determined, and transform to the potential matrix without integration?

DVR

Fact

If $\langle \Phi_I | \vec{x} | \Phi_J \rangle = \vec{x}_I \delta_{IJ}$ and $A = A(\vec{x})$,
then $\langle \Phi_I | A | \Phi_J \rangle = A(\vec{x}_I)\delta_{IJ}$.

For a given set of basis functions $\{|\Xi_I(\vec{q})\rangle\}_{I=1}^N$, let $\vec{q}_{IJ} = \langle \Xi_I | \vec{q} | \Xi_J \rangle$, then there is a set of basis functions $\{|\Phi_I(\vec{q})\rangle\}_{I=1}^N$ s. t.

1. $|\Phi_J\rangle = \sum_{I=1}^N |\Xi_I\rangle\, U_{IJ}$, where $\mathbf{U}$ is unitary, and
2. $\vec{\mathbf{Q}} = \mathbf{U}^\dagger \vec{\mathbf{q}} \mathbf{U}$, where $\vec{Q}_{IJ} := \langle \Phi_I | \vec{q} | \Phi_J \rangle = \vec{q}_I \delta_{IJ}$.

DVR

- $\{|\Xi_I(\vec{q})\rangle\}_{I=1}^N$: finite basis set representation
- $\{|\Phi_I(\vec{q})\rangle\}_{I=1}^N$: discrete variable representation

In DVR basis, $V_{IJ} = V(\vec{q}_I)\delta_{IJ}$.

- How to calculate $T|\Psi\rangle$?
- Integrate in FBR and transform in DVR ($\mathcal{O}(N^2)$)
- Use FFT and its inverse to calculate the differential ($\mathcal{O}(N \log N)$)

Example: (1-D) Sine-DVR Basis

Choose the n-th lowest eigenstates of 1-D infinite square well as FBR:

$$\xi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin(n\pi x/L), & \text{if} \quad 0 \leqslant x \leqslant L \\ 0, & \text{else} \end{cases}$$

and in FBR, we have

$$T_{ij}^{(\mathrm{FBR})} = -\frac{\hbar^2}{2\mu} \left(\frac{i\pi}{L} \right)^2 \delta_{ij}$$

Example: (1-D) Sine-DVR Basis

Let $q = \cos(\pi x/L)$, then $\mathbf{q}$ could be diagonalized analytically:

$$U_{ij} = \sqrt{\frac{2}{n+1}} \sin\left(\frac{ij\pi}{n+1}\right)$$

$$Q_{ij} = q_i \delta_{ij} \quad \text{where} \quad q_i = \frac{iL}{n+1}$$

and $\mathbf{Q} = \mathbf{U}^\dagger \mathbf{q} \mathbf{U}$.

Example: (1-D) Sine-DVR Basis

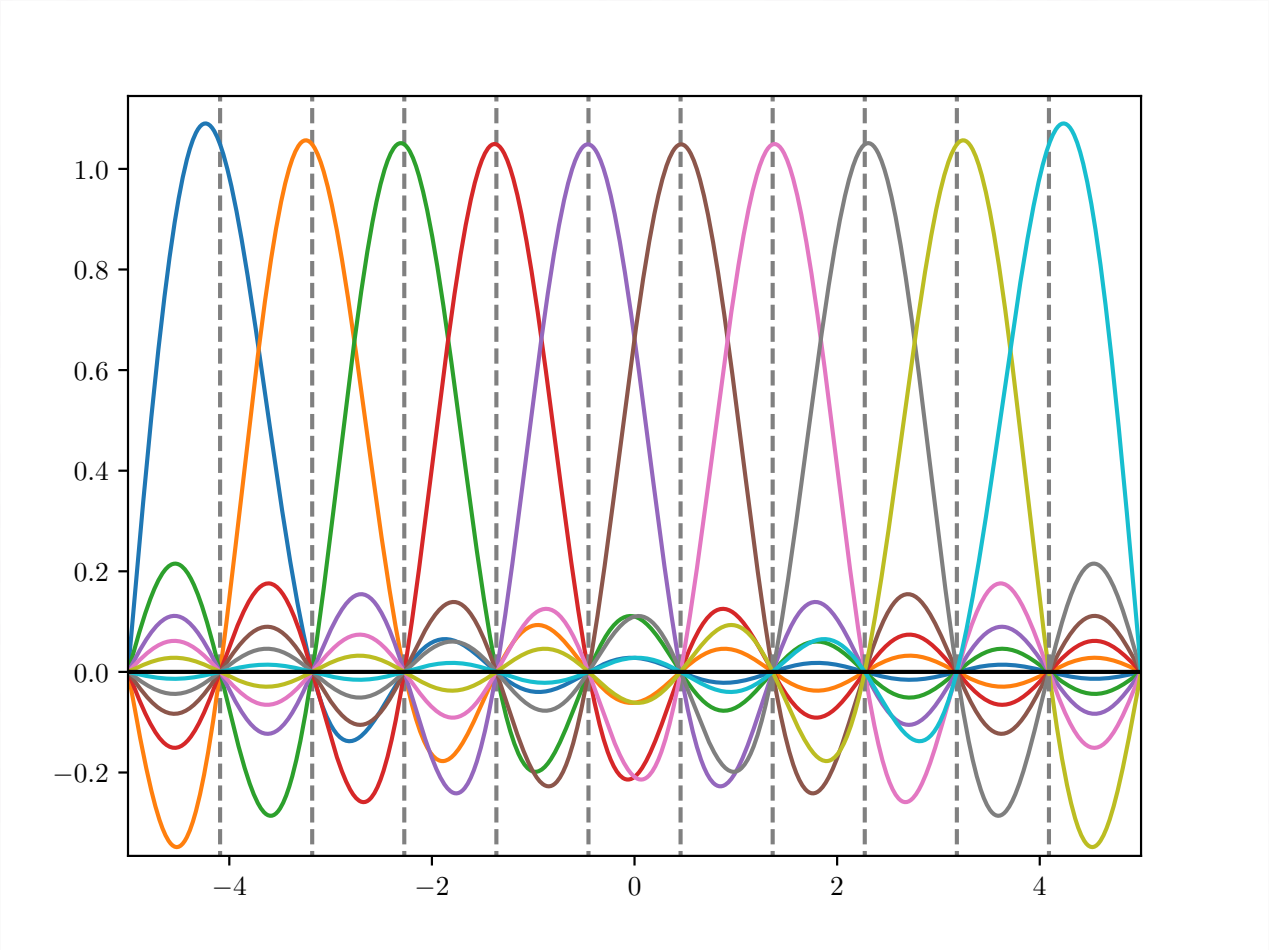


Figure 1: Sine-DVR basis functions ($L = 10$ a. u., $n = 10$)

Example: 1-D Double Well

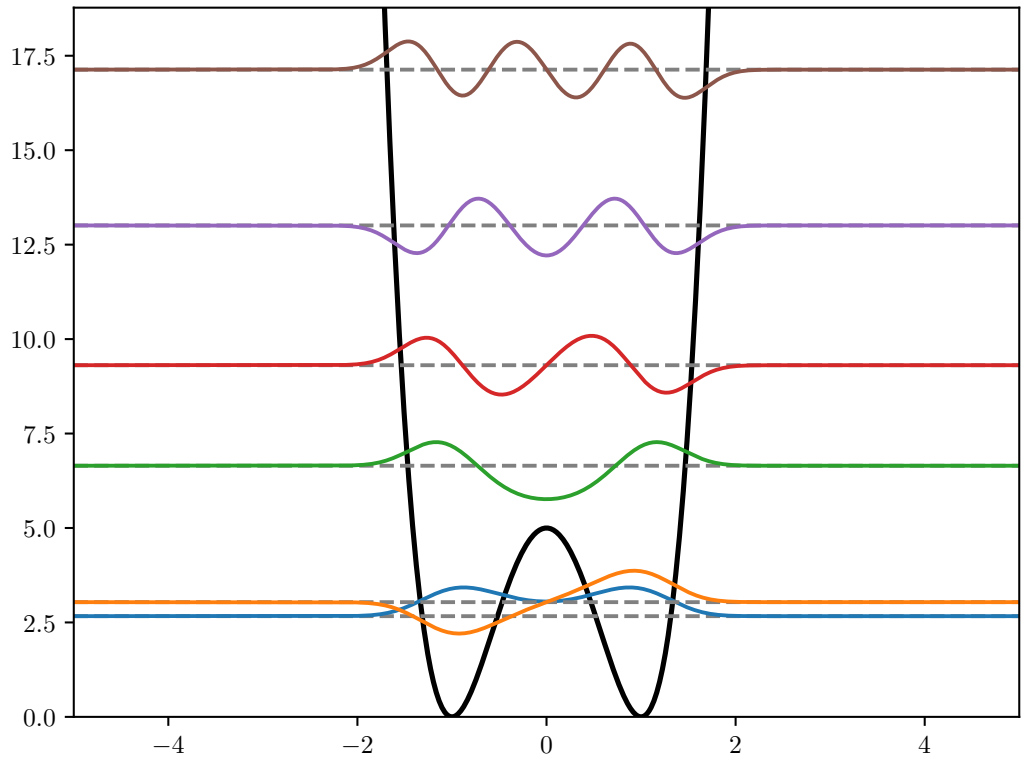


Figure 2: Potential curve and eigenstates

$$V = 5(x^2 - 1)^2,\ L = 10,\ n = 400 \text{ (in a. u.)}$$

Example: 1-D Double Well

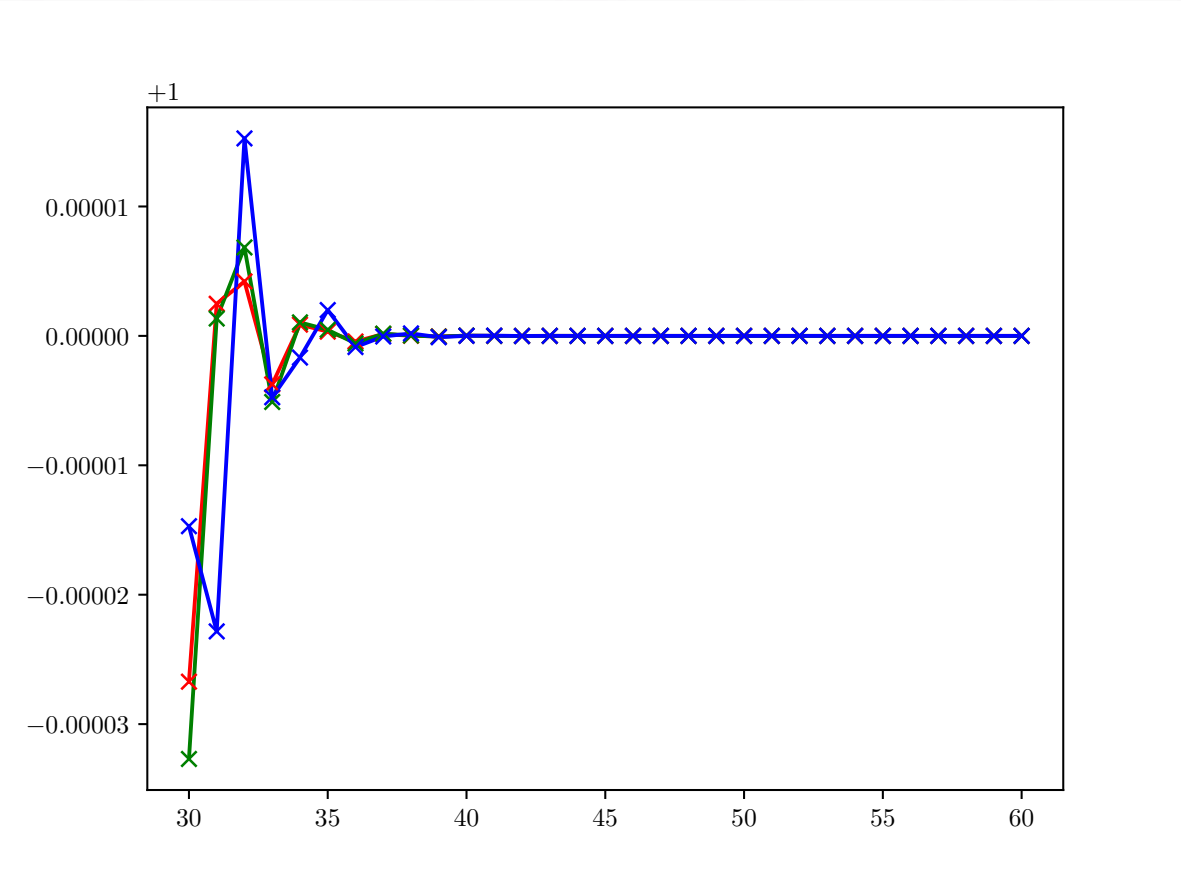


Figure 3: Relative energy to n

Red: ground state; green: 1st excited state; blue: 2nd excited state.
Relative to when $L = 10$, $n = 400$

Example: 1-D Double Well

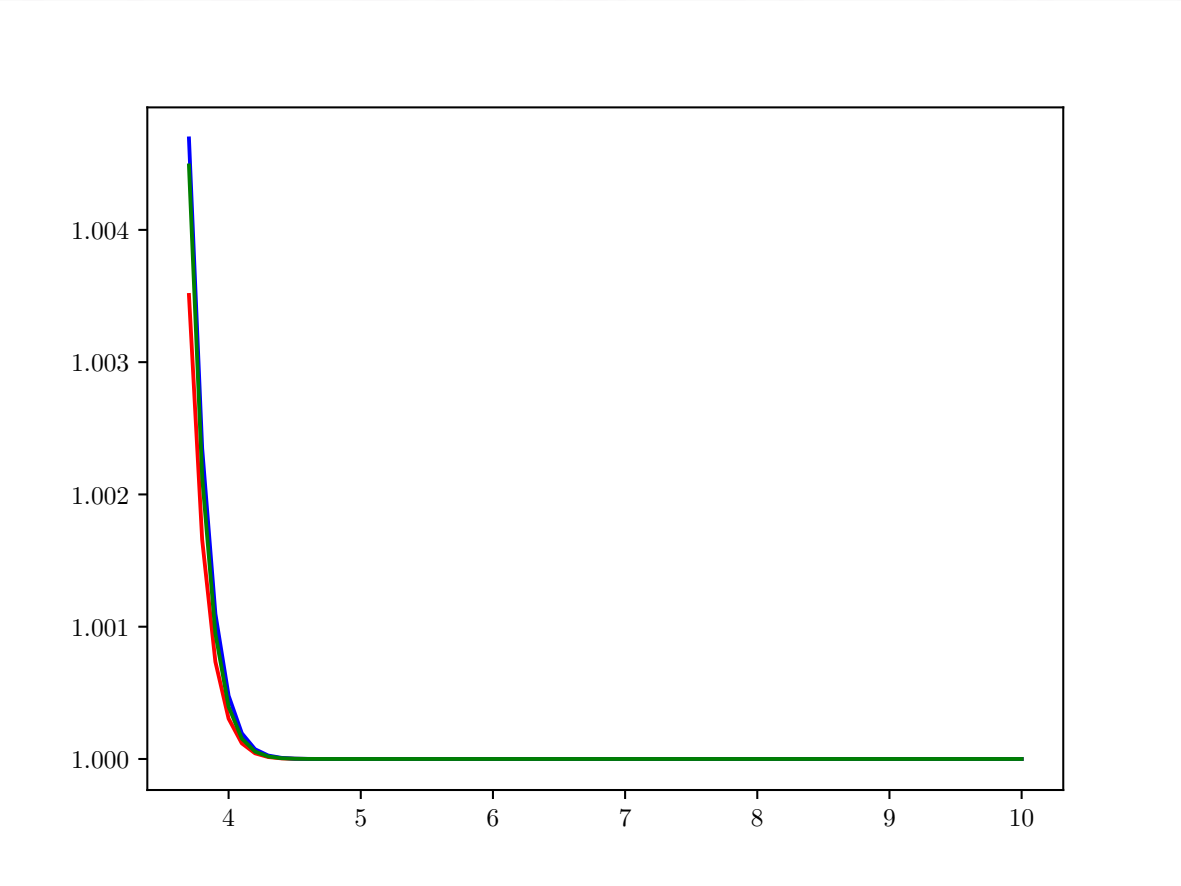


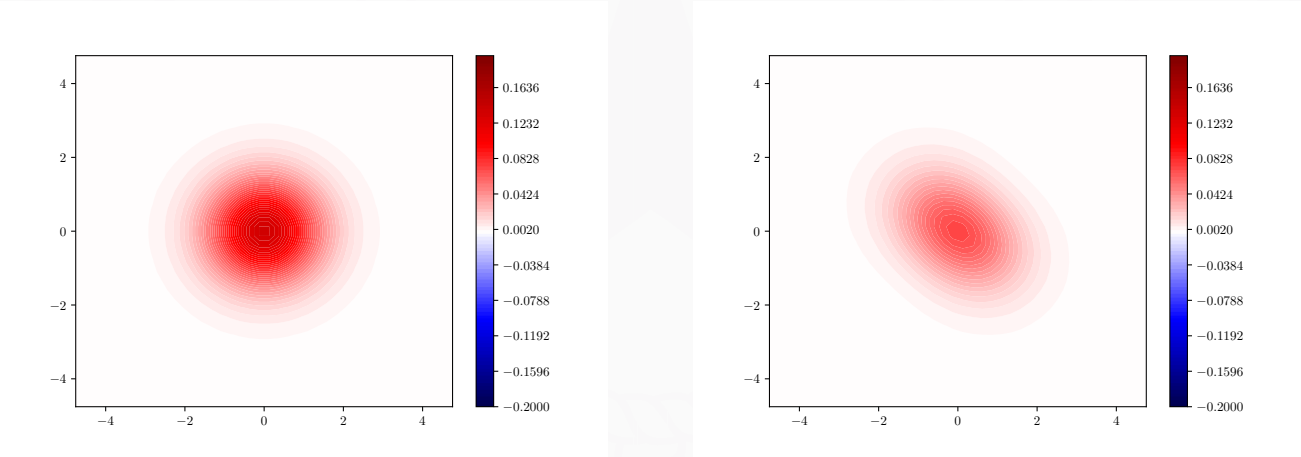
Figure 4: Relative energy to L

Red: ground state; green: 1st excited state; blue: 2nd excited state.
Relative to when $L = 10$, $n = 400$

Example: 2-D harmonic oscillator

$$V = \frac{1}{2}x^2 + \frac{1}{2}y^2 + \frac{1}{4}xy, \quad n = 40, \quad L = 10 \quad \text{(in a. u.)}$$

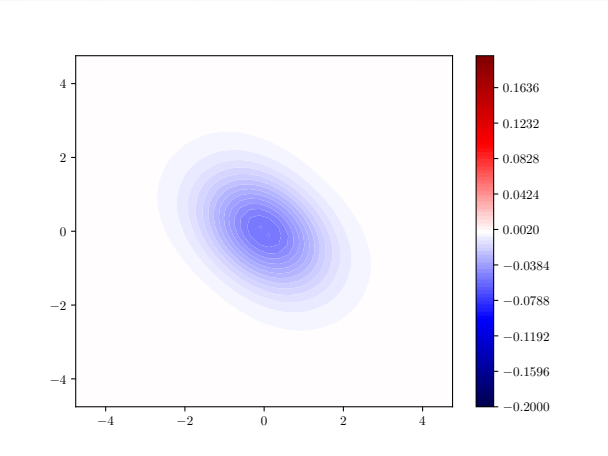
Start from the ground state when $V = \frac{1}{2}x^2 + \frac{1}{2}y^2$.



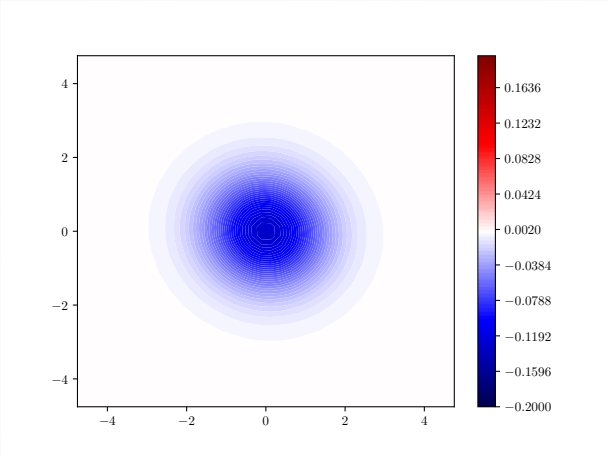
$t = 0.00$ a. u. $t = 1.00$ a. u.

Figure 5: Wavefunctions of a 2-D harmonic oscillator at t (using RK45 as ODE solver, $\Delta t = 0.01$ a. u.)

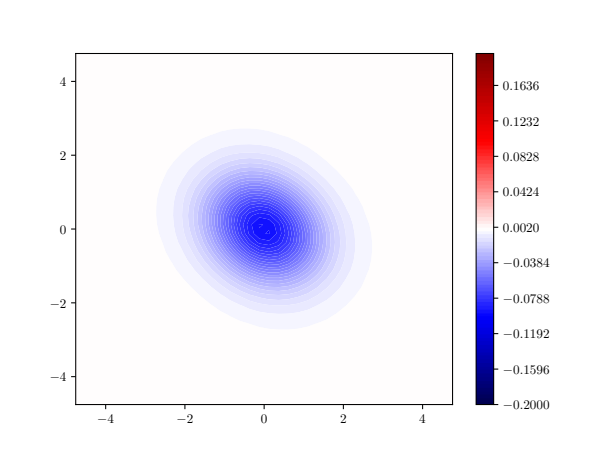
Example: 2-D harmonic oscillator (Cont'd)



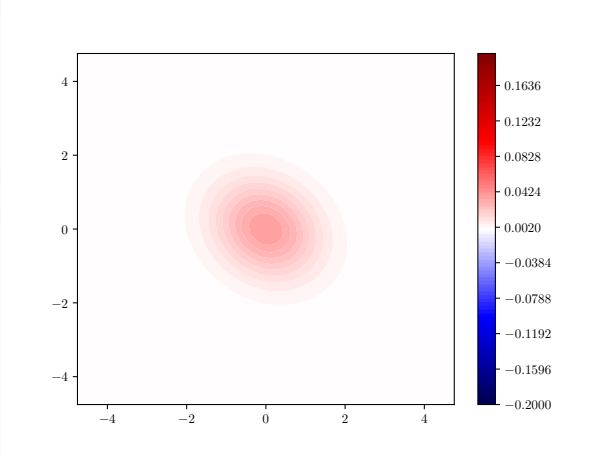
$t = 2.00$ a. u.



$t = 3.00$ a. u.



$t = 4.00$ a. u.



$t = 5.00$ a. u.

Example: 2-D harmonic oscillator

Autocorrelation function: $a(t) = \langle \Psi(0) | \Psi(t) \rangle$, and when initial state $|\Psi(0)\rangle$ is real, $a(t) = \langle \Psi^*(t/2) | \Psi(t/2) \rangle$

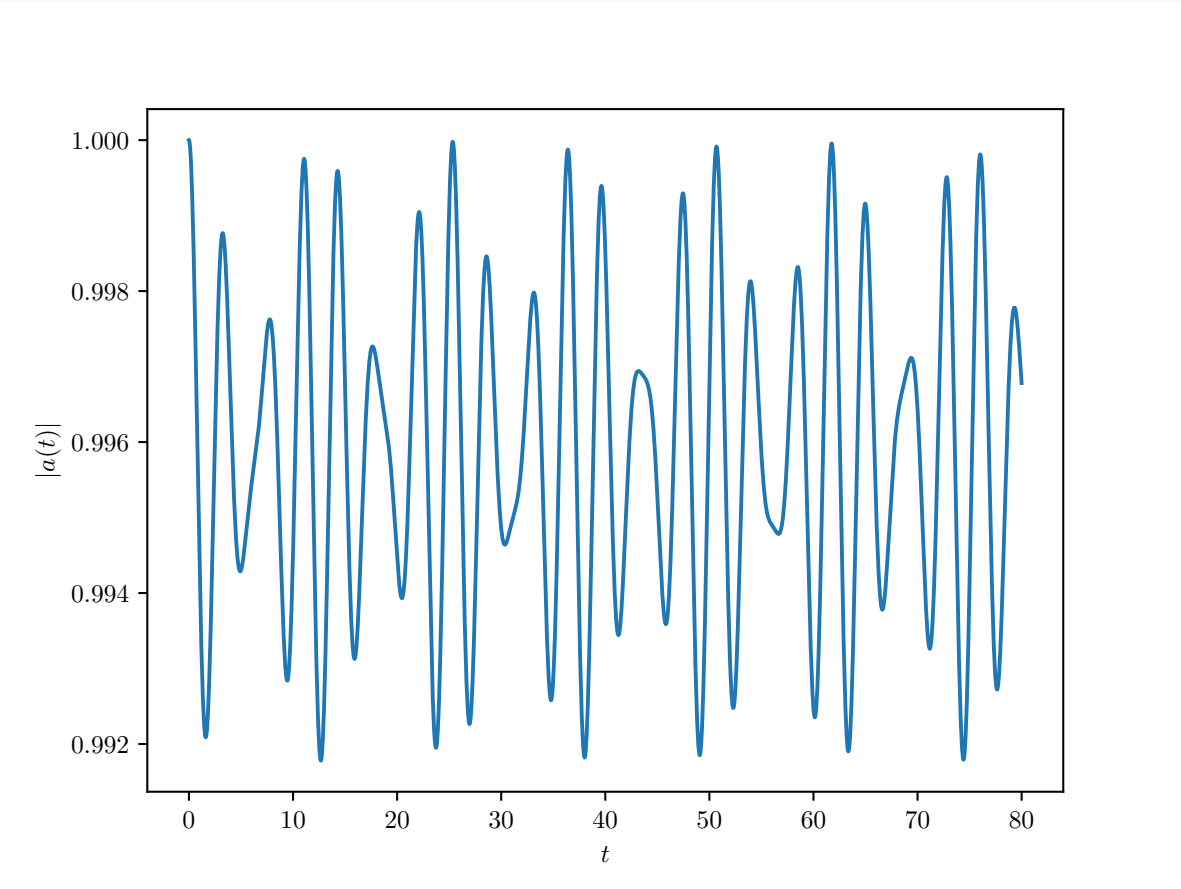
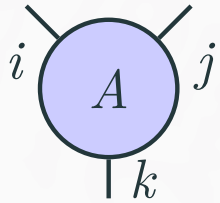


Figure 6: $|a(t)|$ – t (using RK45 as ODE solver, $\Delta t = 0.001$ a. u.)

Multi-Configuration Time Dependent Hartree

Language: Tensor Network Notation

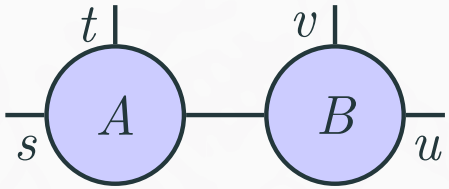
- Tensors



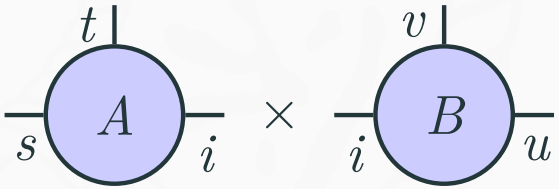
$:= \quad A_{ijk}$

$:= \quad H_{ij}$

- Contraction



$:= \sum_i$



Bridgeman, J. C. & Chubb, C. T. J. Phys. A: Math. Theor. 50 223001 (2017). (arXiv:1603.03039)

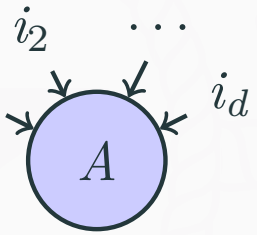
Multi-Configuration Time Dependent Hartree

Motivation

Express the Standard Procedure in TNN

- Wavefunction

$$\langle \Phi_I | \Psi \rangle \quad =$$

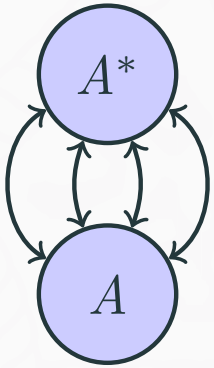


where $i_\kappa \in \{1, \ldots, n_\kappa\}, \kappa = 1, \ldots, d.$
Space for saving a wavefunction: $\prod_{\kappa=1}^{d} n_\kappa$ floats.

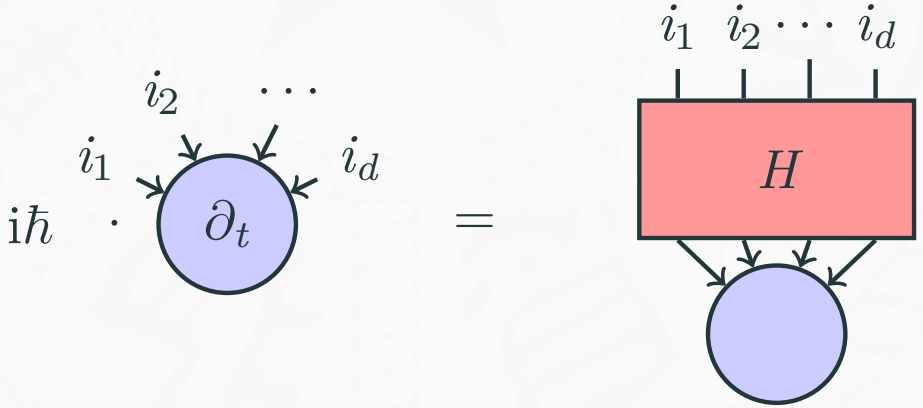
Express the Standard Procedure in TNN

- Normalization condition

$$1 = \langle \Psi | \Psi \rangle \approx \langle \Psi | P | \Psi \rangle =$$

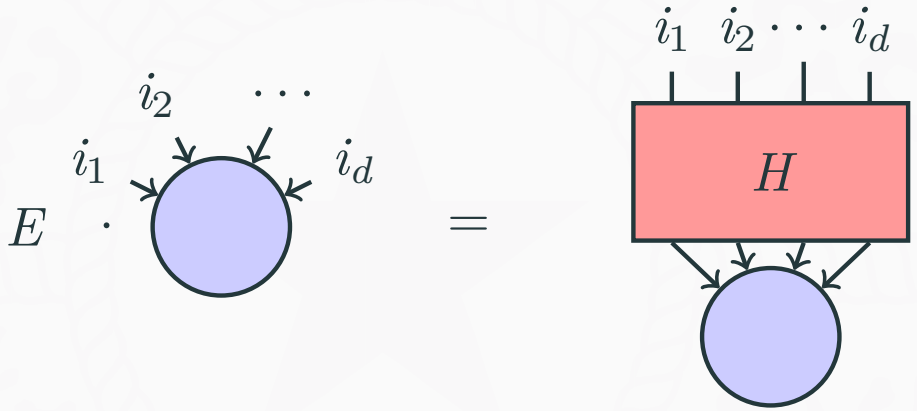


- TDSE



Express the Standard Procedure in TNN

- TISE



where $i_\kappa \in \{1, \ldots, n_\kappa\}, \kappa = 1, \ldots, d$.

Problem: $N = \prod_{\kappa=1}^{d} n_\kappa$ exponentially increase as d grows.

Motivation of MCTDH

Motivation: construct the wavefunction without form the whole space.

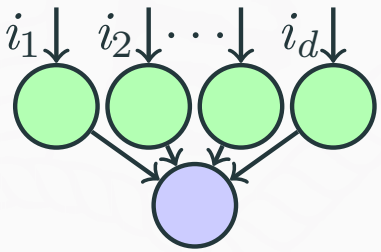
One simple way: Hartree method.

---

http://www.pci.uni-heidelberg.de/tc/usr/mctdh/lit/introMCTDH.pdf

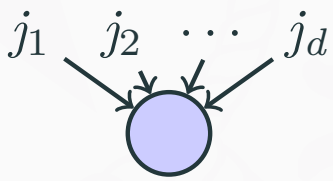
Hartree method in TNN

$$\langle \Phi_I | \Psi \rangle =$$



where

$$\left\langle \Phi_J^{(1)} \middle| \Psi \right\rangle =$$

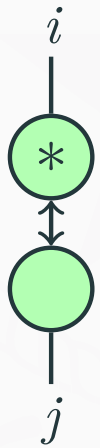


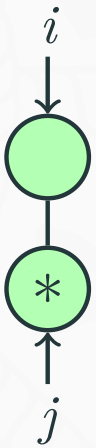
and $j_\kappa \in \{1\}, \kappa = 1, \ldots, d$.

Space for saving a wavefunction: $\sum_{\kappa=1}^{d} n_\kappa$ floats.

Hartree method in TNN

Extra normalization condition at the κ-th set of single particle functions (SPFs):

$\delta_{ij} =$ 

$P^{(\kappa)}_{ij} =$ 

Variational Principle

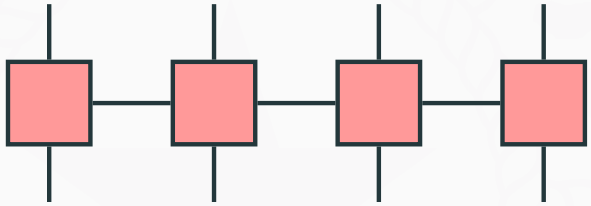
Solve TISE

$$\delta\Big(\langle \quad | H | \quad \rangle - \lambda \big(\langle \quad | \quad | \quad \rangle - 1 \big) \Big) = 0$$

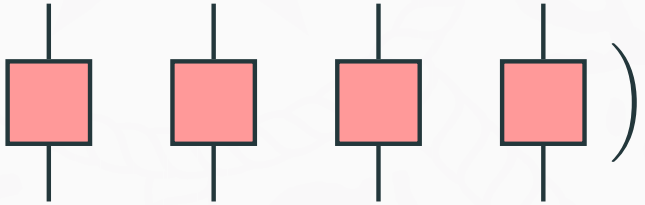
Only special “structure” of $\mathbf{H}$ can simply the equation.

Structure of $\mathbf{H}$

- Matrix product operators (MPOs)



- Summation of products of operators

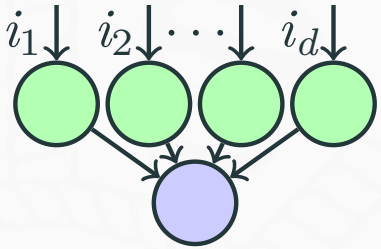
$$\sum_{i=1}^{t}$$ 

Multi-Configuration Time Dependent Hartree

Data Structure

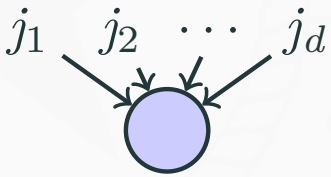
Structure of Wavefunction

$$\langle \Phi_I | \Psi \rangle \quad = \quad$$



where

$$\left\langle \Phi_J^{(1)} \middle| \Psi \right\rangle \quad = \quad$$



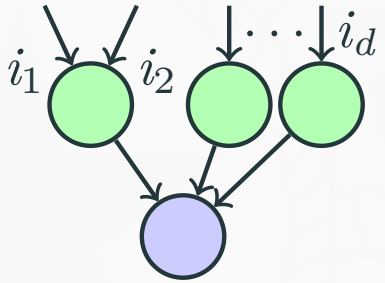
Idea: $j_\kappa \in \{1, \ldots, n_\kappa^{(1)}\}, \kappa = 1, \ldots, d$, and $n_\kappa^{(1)} < n_\kappa$.

Space for saving a wavefunction: $\prod_{\kappa=1}^{d} n_\kappa^{(1)} + \sum_{\kappa=1}^{d} n_\kappa^{(1)} n_\kappa$ floats.

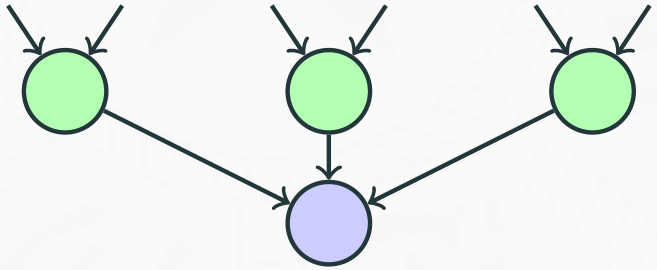
Mode Combination

Examples:

$$\langle \Phi_I | \Psi \rangle =$$

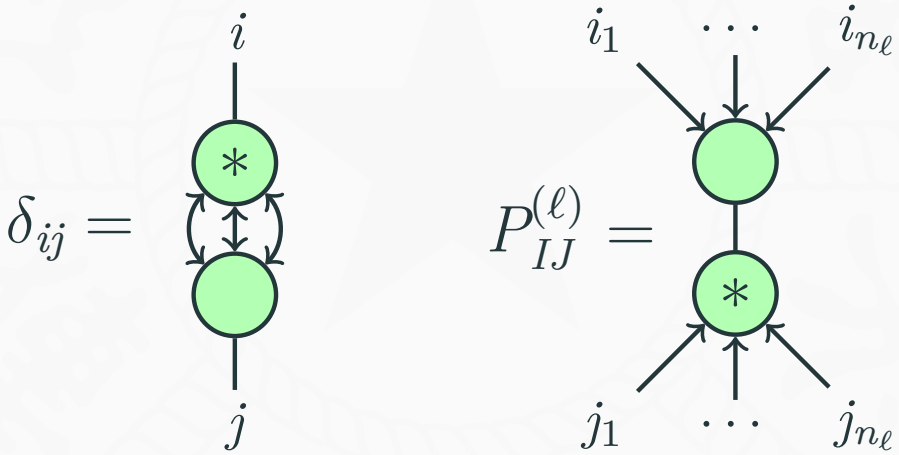


$$\mathbf{c} =$$



Normalization

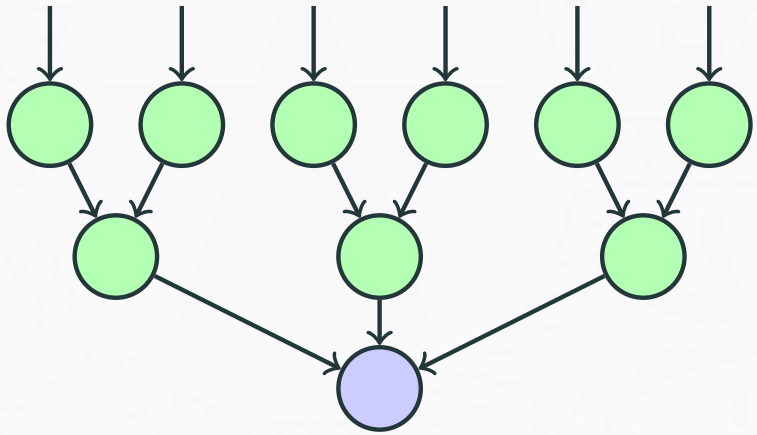
General normalization condition at the ℓ-th node:



Multi-Layer

More nodes, but smaller ranks.

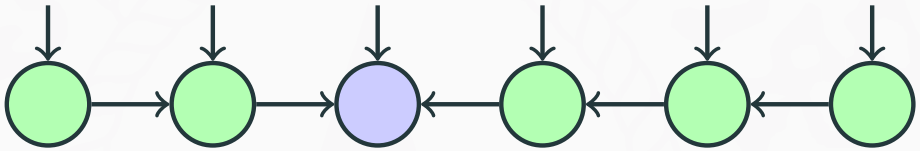
Example 1:

$\mathbf{c} =$ 

Wang, H & Thoss, M. J. Chem. Phys. 119, 1289 (2003)

Multi-Layer

Example 2: matrix product states (MPSs) in DMRG

$\mathbf{c} =$ 

For a complete binary tree, the space for saving a wavefunction is $\mathcal{O}(dn^3)$ floats, if $n_\ell = \mathcal{O}(n)$ for all ℓ.

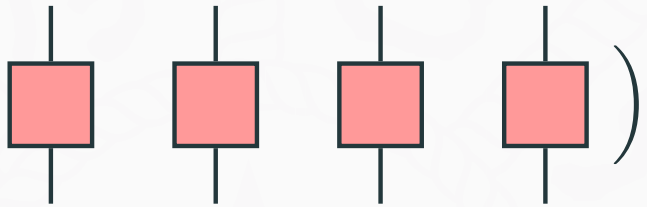
Generally, if $\mathrm{rank} \leqslant p$ for all nodes, the space for saving a wavefunction is of $\mathcal{O}(dn^p)$.

Multi-Configuration Time Dependent Hartree

Algorithm

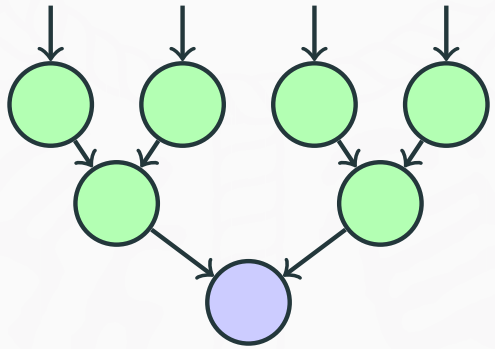
Solve TDSE

Use the same type of $\mathbf{H}$ in Hartree method:

$$\sum_{i=1}^{t}$$ 

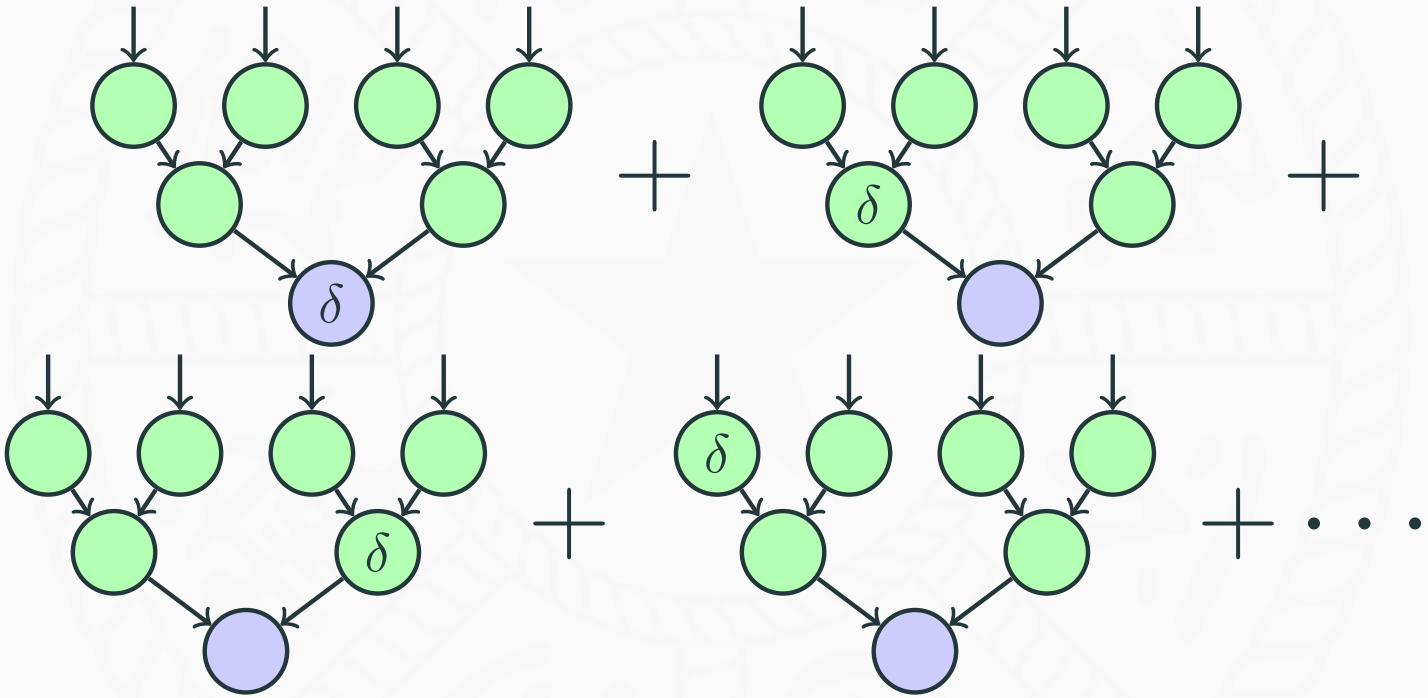
Dirac-Frenkel variational principle: $\langle \delta\Psi | \mathrm{i}\hbar\frac{\partial}{\partial t} - H|\Psi\rangle = 0.$

Without loss of generality, let $\mathbf{c} =$



Solve TDSE

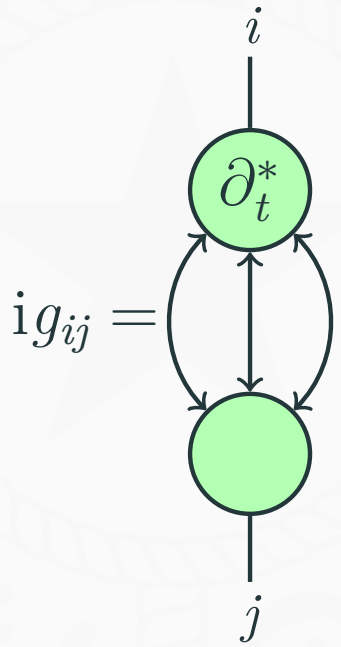
$\delta \mathbf{c} =$



Similarly, $\dot{\mathbf{c}}$.

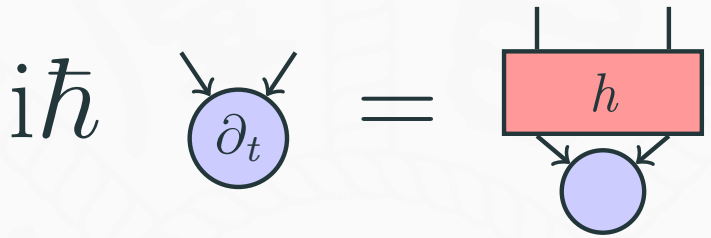
Normalization

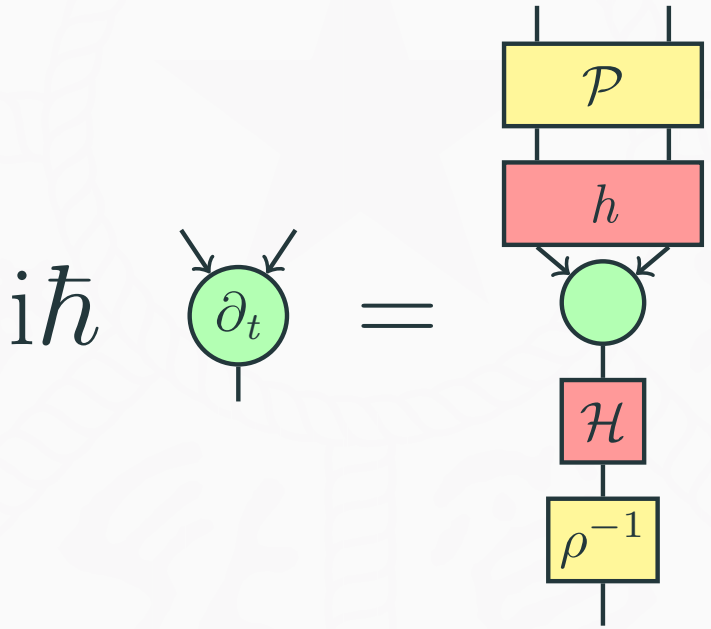
In order to hold all general normalization conditions during the propergation, one must have



where $\mathbf{g}$ is Hermitian. For simplicity, choose $\mathbf{g} = 0$.

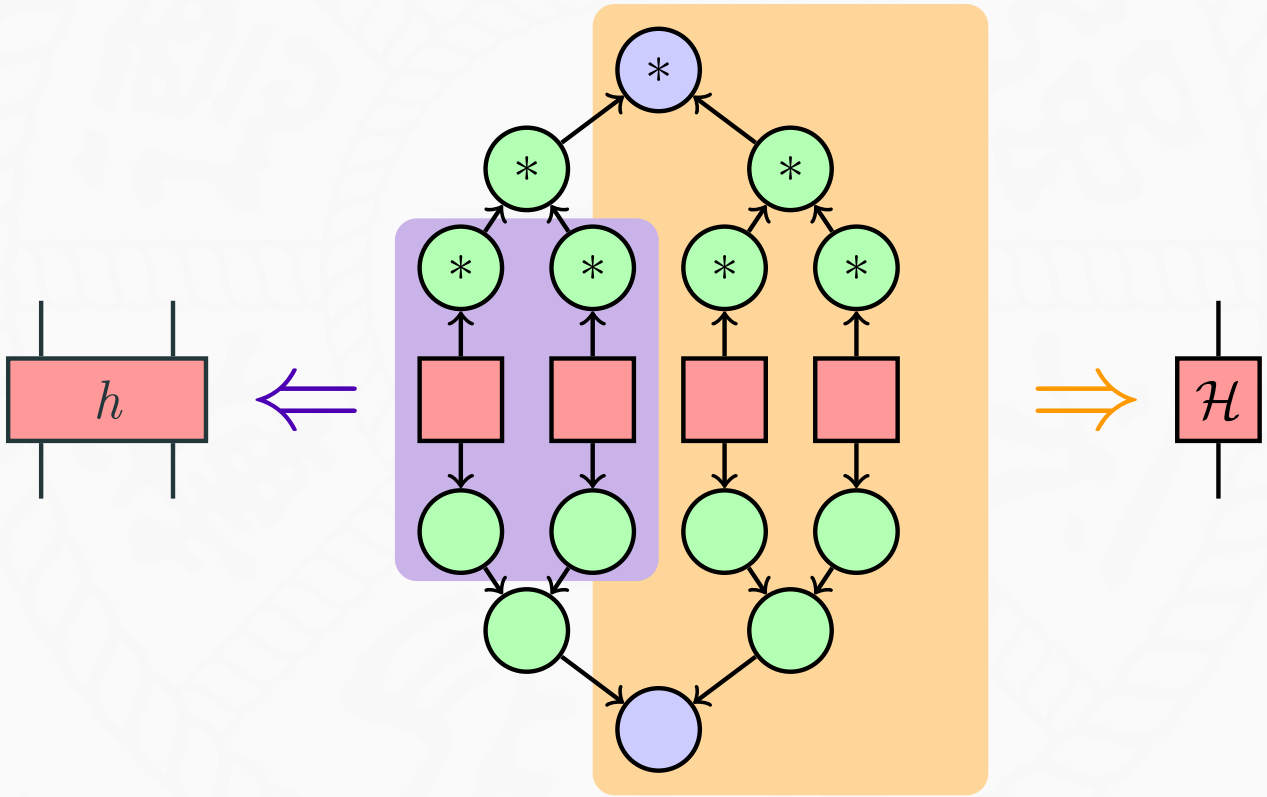
Equations of Motion





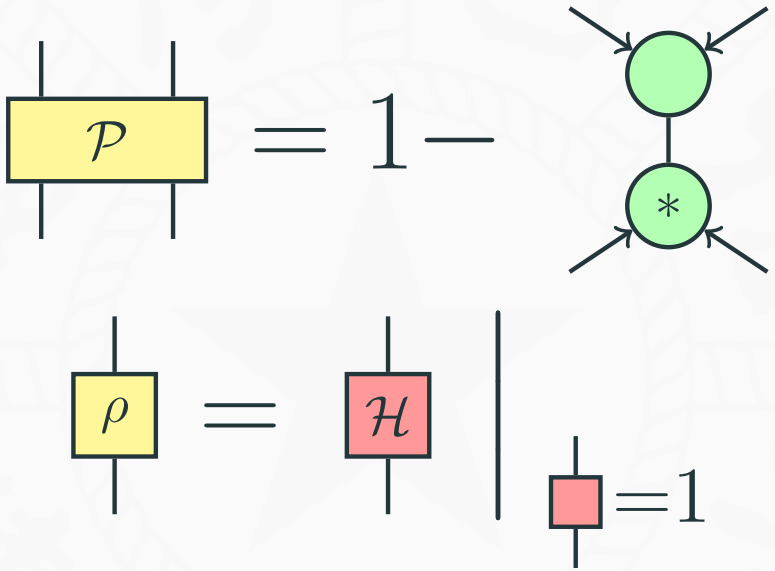
Equations of Motion (Cont'd)

where for all nodes, w. l. o. g., choose one term in $\mathbf{H}$ and one node as an example:



Equations of Motion (Cont'd)

and



Time complexity: if $\mathrm{rank} \leqslant p$ for all nodes, then a step of multiplication is of $\mathcal{O}(tpdn^{p+1})$;

Space complexity: $\mathcal{O}(tpdn^2 + dn^p)$.

Example: 2-D harmonic oscillator

$V = \frac{1}{2}x^2 + \frac{1}{2}y^2 + \frac{1}{4}xy$ (all in a. u.).

Start from the ground state when $V = \frac{1}{2}x^2 + \frac{1}{2}y^2$. Use Sine-DVR as the (primitive) basis set and $n = 40$, $L = 10$.

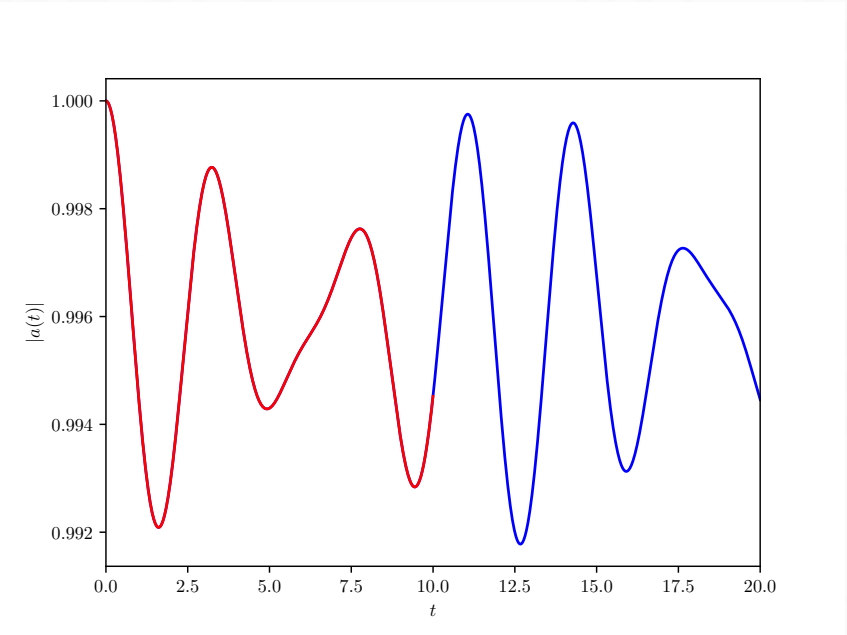


Figure 7: $|a(t)| - t$ (using RK45 as ODE solver, $\Delta t = 0.001$ a. u., renormalize all nodes during the propergation, $\Delta E < 10^{-6}$.)
Red: MCTDH; blue: Standard procedure.

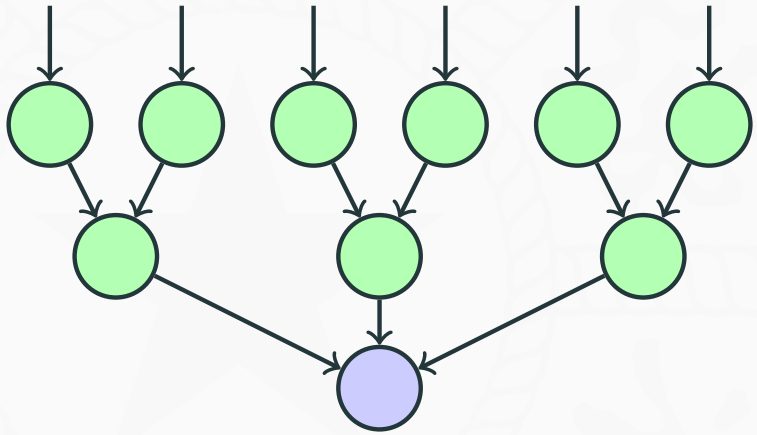
MCTDH vs. DMRG

MCTDH vs. DMRG

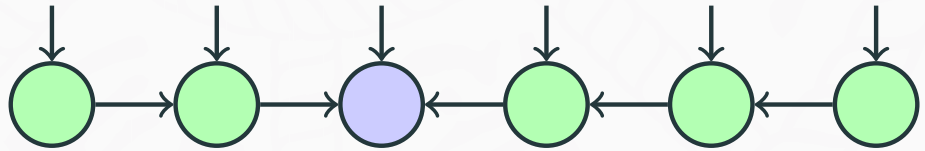
Data Structure: a TN perspective

Structure of Wavefunction

- MCTDH

$\mathbf{c} =$ 

- DMRG

$\mathbf{c} =$ 

MCTDH vs. DMRG

Algorithm: Differnet Choices

Algorithms

	TDSE	TISE
DMRG	Based on propergators	DMRG1, DMRG2
MCTDH	Based on DFVP	Self-consistent

- Other combinations?

Renormalization

The essence of sweeping over the tensor train.

Realized by (compressed) singular value decomposition (SVD).

- Use it in other TN-type wavefunctions.
- Equations often get simpler at the root node.

Nakatani, N. & Chan, G. K.-L. J. Chem. Phys. 138, 134113 (2013). (arXiv:1302.2298)

Another Problem

- How to determine the TN structure of a wavefunction of a specific Hamiltonian *a priori*?

Conclusions

- The structure of wavefunctions in MCTDH and DMRG can be unified in tensor network theory;
- The algorithms used in traditional MCTDH and DMRG are interchangeable in principle;
- The proper structure of wavefunctions in a specific problem needs further studying.

Acknowledgments

Thank “Tsinghua Undergraduate Overseas Traning Support Program” for the financial support;

Thank Professor Haobin Wang for his patient help in DVR and (ML-)MCTDH theory;

Thank Jiajun Ren for discussions about DMRG theory.

Thank you for your listening!