Asian Winter School 2015 in Quantum Chemistry

Matrix Product States & Density Matrix Renormalization Group

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Outline

Many-body wavefunction

Matrix Product States & Matrix Product Operators

DMRG from variational principle for MPS

Time-evolution

DMRG linear response theory

Useful reference

"The density-matrix renormalization group in the age of matrix product states"
Ulrich Schollwöck, *Annals of Physics* **326**, 96-192 (2011).

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Time-evolution

DMRG linear response theory

Many-body wavefunction

A solution of Schödinger equation

$$\mathcal{H}\Psi = E\Psi$$

where

$$\Psi = \Psi(x_1, x_2, \ldots, x_N)$$

is a function of **all particles**

Only 1 particle system can be solved analytically

(e.g. electron in H atom)

Many-body wavefunction cont'd

In second quantization (expanded by a set of orbitals)

$$\Psi = \sum_{n_1 n_2 \cdots n_k} \Phi(n_1, n_2, \ldots, n_k)$$

is **a superposition of electron configurations**

where

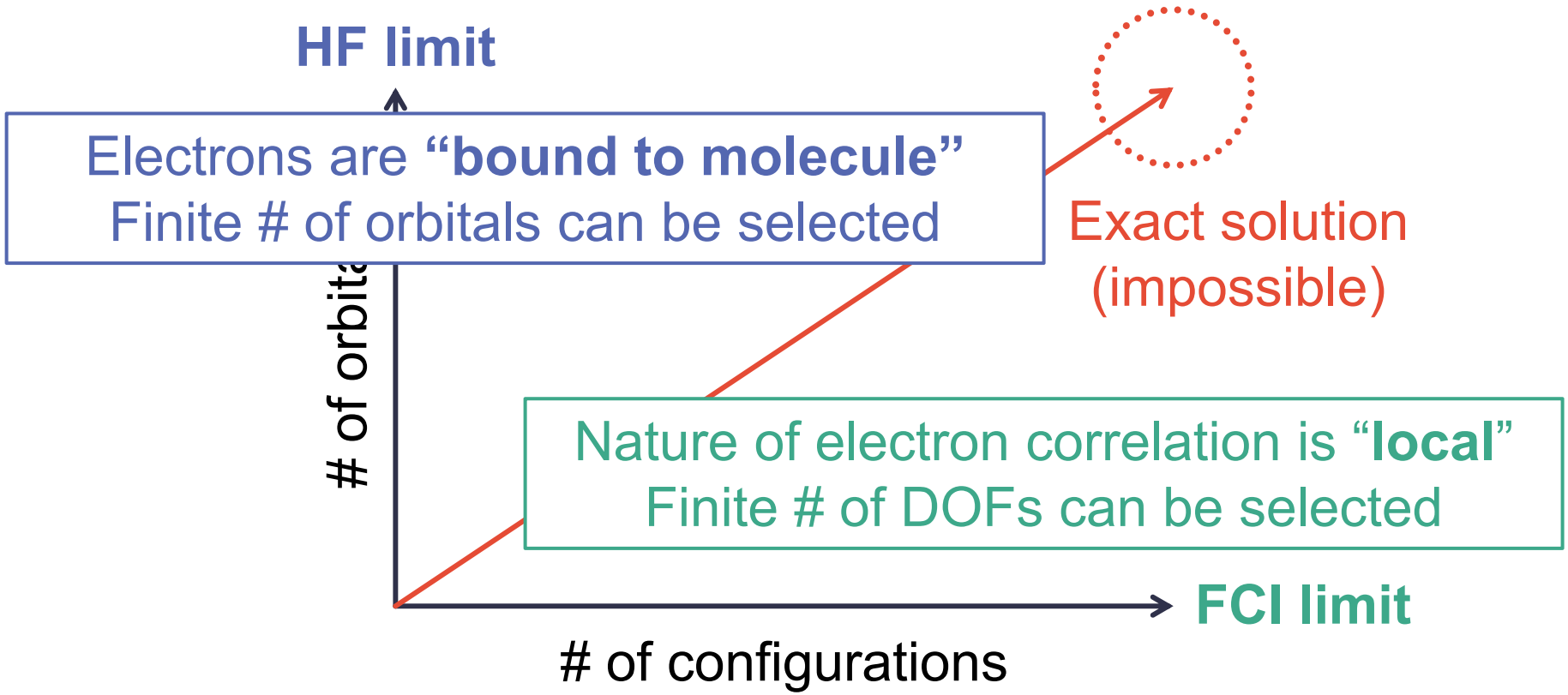
$$n_i = \left\{ \text{—} \;,\; \uparrow \;,\; \downarrow \;,\; \updownarrow \right\}$$

are occupation states of each 1-electron orbital

Degrees Of Freedom (DOF) is $\mathbf{4^k}$

(where *k* is # orbitals)

Many-body wavefunction cont'd



How to reduce DOFs for the best approximation?

Many-body wavefunction cont'd

One succeeded way is of coupled-cluster theory

$$|\Psi\rangle = \exp(\hat{T}_1 + \hat{T}_2)|\Psi_0\rangle$$

Many-particle interaction can be well approximated

as a product of 1 or 2 particle interactions

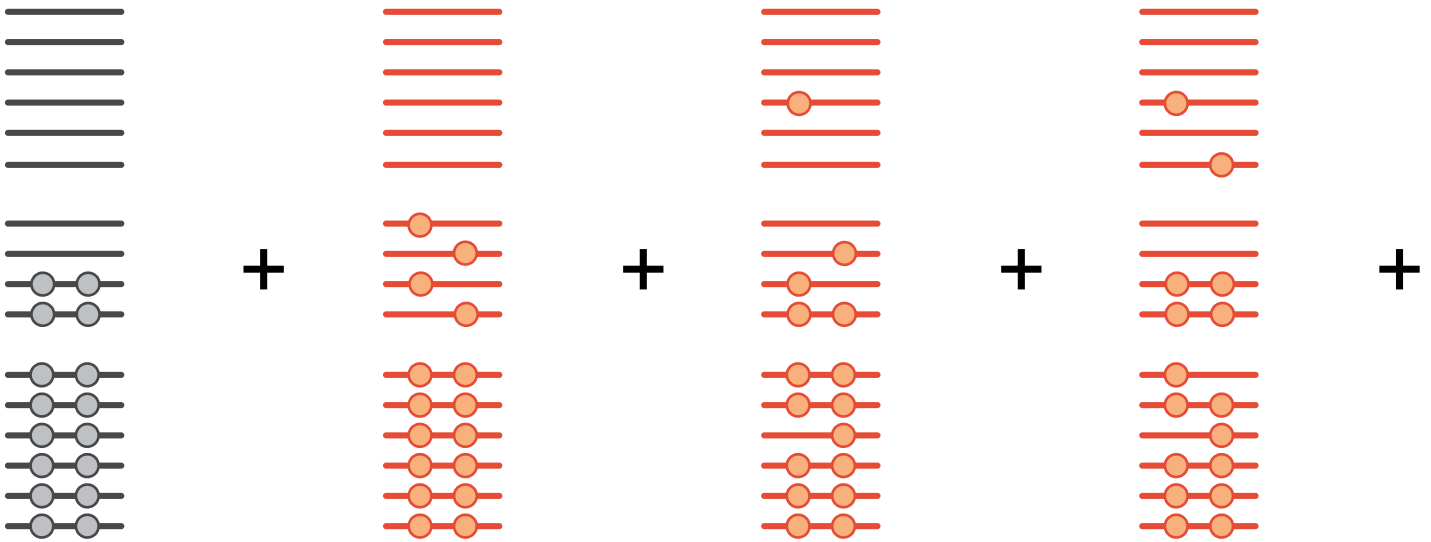
as long as the HF wavefunction is a good reference

Actually, **99%** of electronic energy
comes from HF configuration *for common molecules*

Many-body wavefunction cont'd

When is HF **"NOT"** a good reference wavefunction?

i.e. "*multi-reference*" character arises

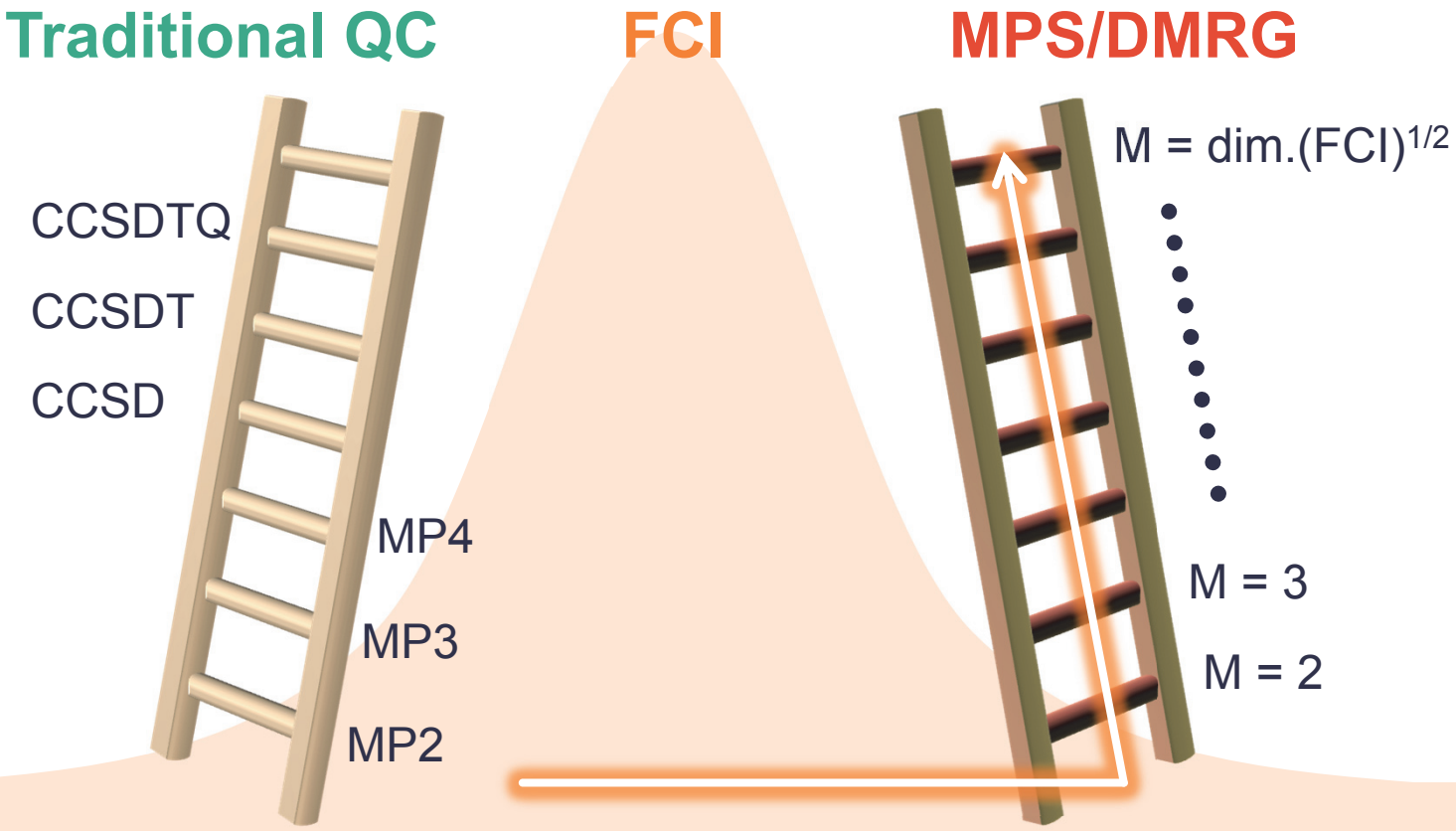


HF Excited configurations

Approximation from particle view is useless

Many-body wavefunction cont'd

Climbing up the Ladder to FCI



Hartree-Fock
(independent particle limit)

=

"Classical" state
(low-entangled limit)

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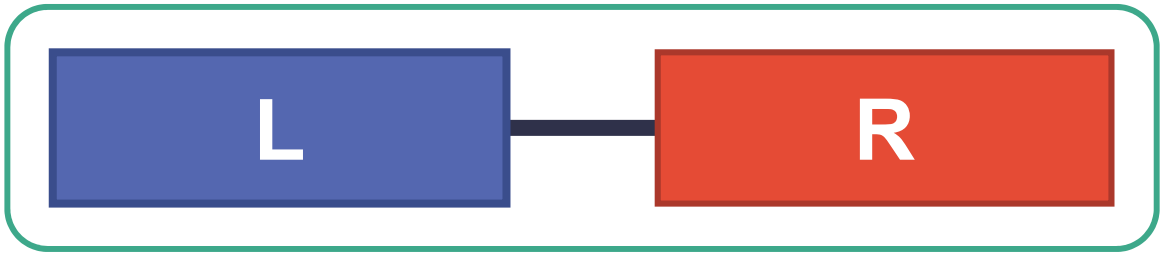
Time-evolution

DMRG linear response theory

Schmidt decomposition

Consider a system with two orthogonal subspaces **L** and **R**



$$\{|i\rangle_{\mathrm{L}}\} \qquad \{|j\rangle_{\mathrm{R}}\}$$

A wavefunction of the system is given by

$$|\Psi\rangle = \sum_{ij} \psi_{ij} |i\rangle_{\mathrm{L}} |j\rangle_{\mathrm{R}}$$

Schmidt decomposition cont'd

Doing SVD on ψ_{ij} leads

$$|\Psi\rangle = \sum_{ij}\sum_{a} L_{ia}\Lambda_{aa}R^{\dagger}_{aj}|i\rangle_{\mathrm{A}}|j\rangle_{\mathrm{B}}$$

Transforming each basis by left- or right-singular vectors

$$|a\rangle_{\mathrm{L}} = \sum_{i}|i\rangle_{\mathrm{L}}L_{ia}, \quad |a\rangle_{\mathrm{R}} = \sum_{j}R^{\dagger}_{aj}|j\rangle_{\mathrm{R}}$$

$$|\Psi\rangle = \sum_{a}\Lambda_{a}|a\rangle_{\mathrm{L}}|a\rangle_{\mathrm{R}}$$

Schmidt decomposition

Schmidt decomposition cont'd

How much **L** and **R** are "**entangled**"?

$$|\Psi\rangle = \sum_a \Lambda_a |a\rangle_{\mathrm{L}} |a\rangle_{\mathrm{R}}$$

"Classical" state

Having only **1** non-zero singular value

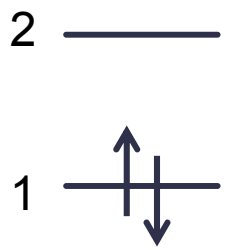
"Quantum" state

Having "***M***" non-zero singular values ($M > 1$)

Schmidt decomposition cont'd

A simple example of "classical" and "quantum" state

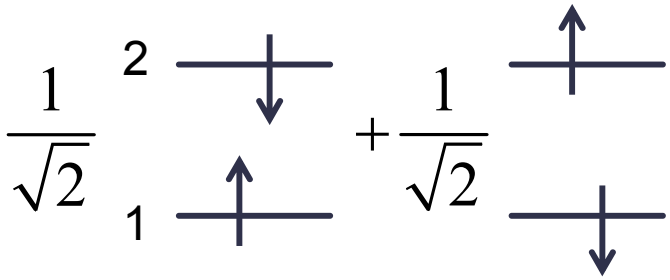
Closed-shell singlet is divided into a product of 2 states



$$|\Psi\rangle = |\uparrow\downarrow\rangle_1 \otimes |\ \ \rangle_2$$

Classical state

Open-shell singlet is never divided into a simple product

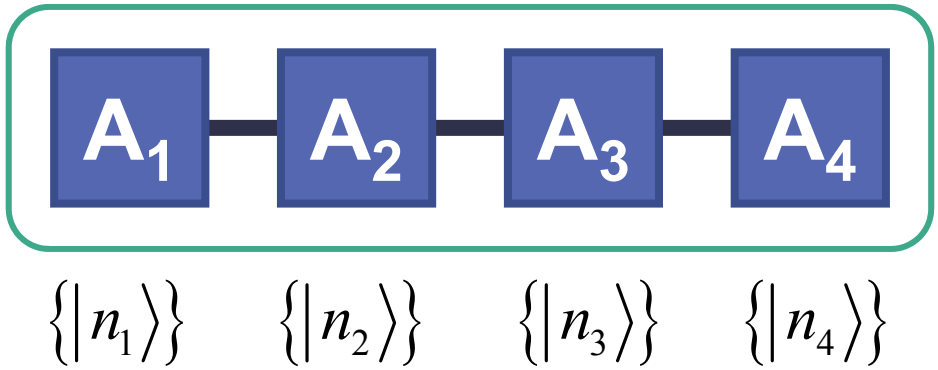


$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 + |\downarrow\rangle_1 \otimes |\uparrow\rangle_2\right)$$

Quantum state (entangled)

Matrix Product States

Consider a system with a set of orthogonal subspaces $\{|\mathbf{A}_i\rangle\}$

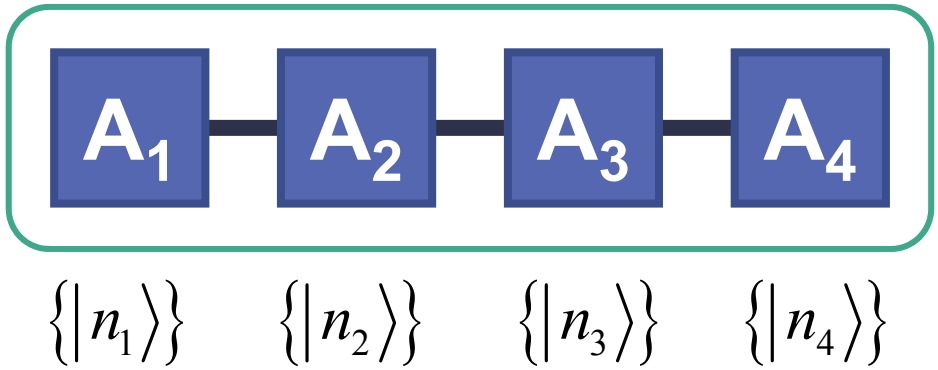


A wavefunction of the system is given by

$$|\Psi\rangle = \sum_{n_1 n_2 n_3 n_4} \psi^{n_1 n_2 n_3 n_4} |n_1 n_2 n_3 n_4\rangle$$

Matrix Product States

Consider a system with a set of orthogonal subspaces $\{|\mathbf{A}_i\rangle\}$

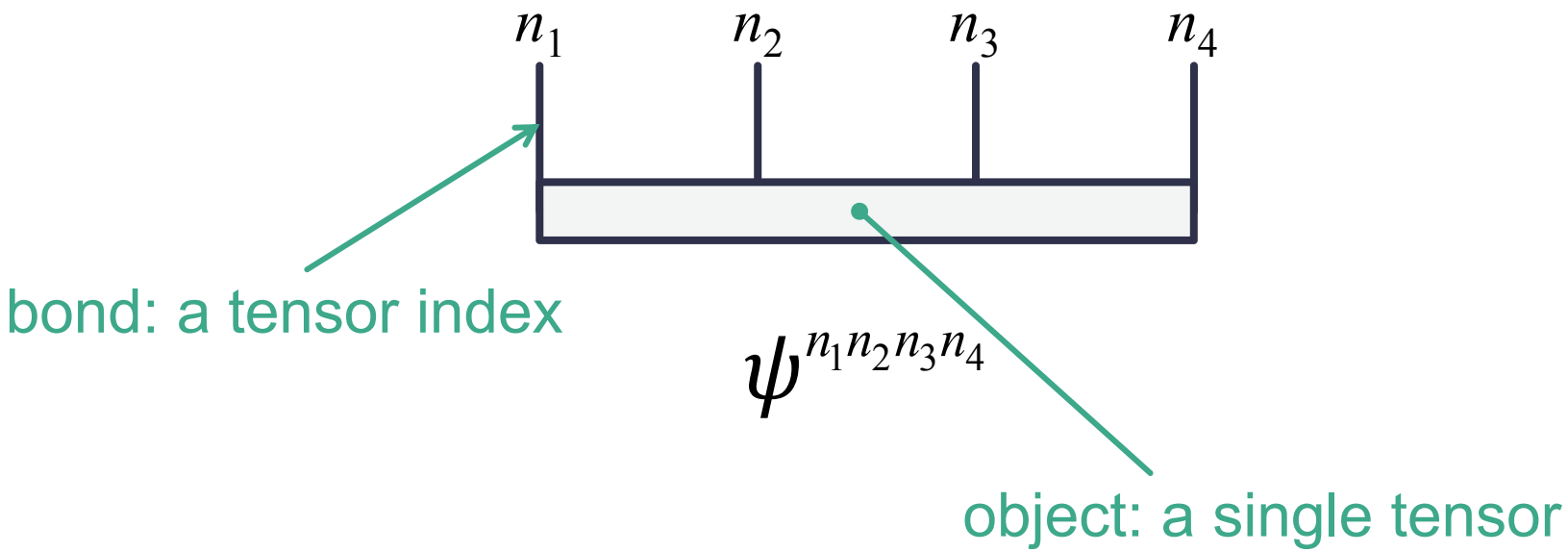


Divide $\psi^{n_1 n_2 n_3 n_4}$ into a product of block-dependent matrices

$$|\Psi\rangle = \sum_{n_1 n_2 n_3 n_4} \sum_{a_1 a_2 a_3} A^{n_1}_{a_1} A^{n_2}_{a_1 a_2} A^{n_3}_{a_2 a_3} A^{n_4}_{a_3} |n_1 n_2 n_3 n_4\rangle$$

Graphical Language

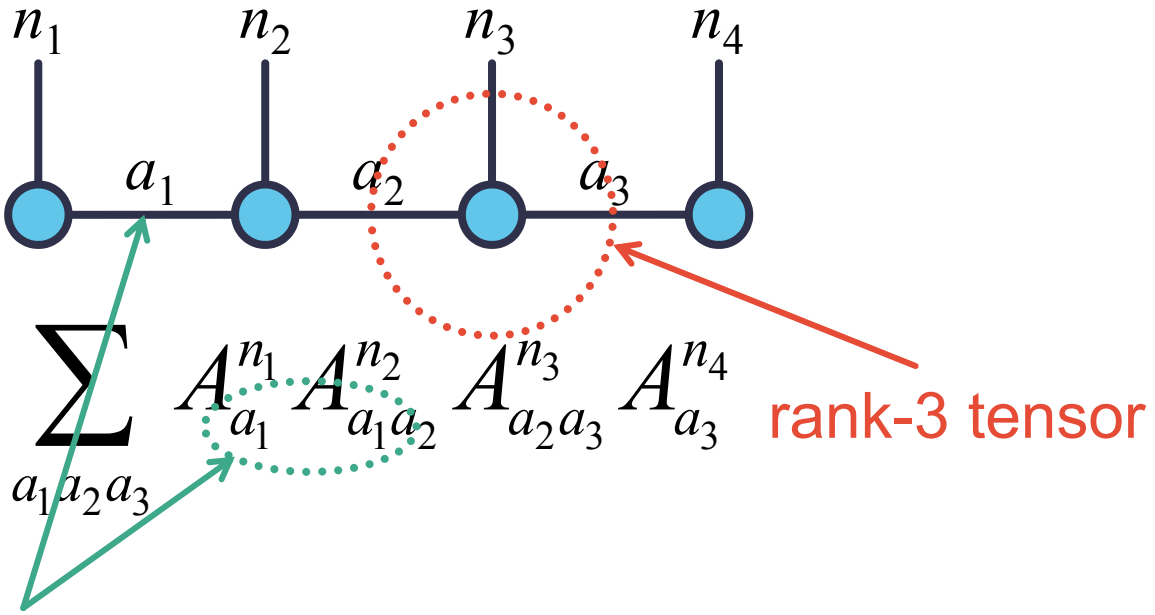
Diagrammatic representation of tensor manipulations



Wavefunction can be seen as a **rank-*k* tensor**
where *k* is a number of sites (orbitals)

Graphical Language

Diagrammatic representation of tensor manipulations

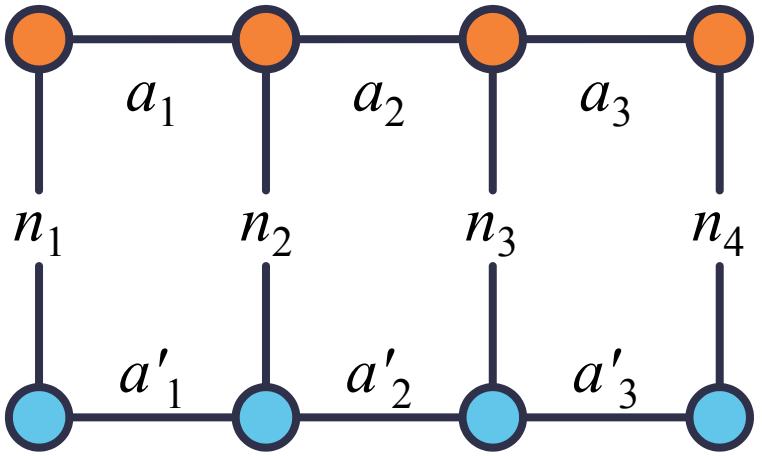


connecting bonds: index contraction

MPS consists of **a product of rank-3 tensors**

Compute overlap in terms of MPS

$$\langle \Phi | \Psi \rangle =$$

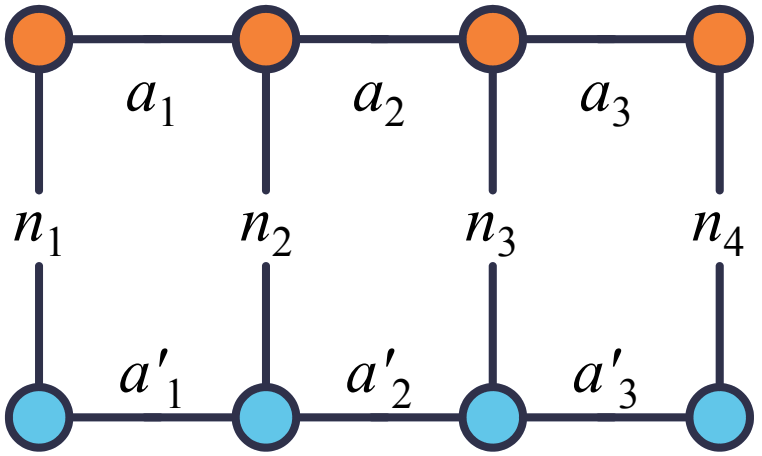


Contract all tensors...

30 mins

Compute overlap in terms of MPS

$$\langle \Phi | \Psi \rangle =$$



$\mathcal{O}(dM^3k + dM^2k)$

Contract all tensors...

If "***M***" can be a small number,

this gives a polynomial cost algorithm

MPS construction

Doing Singular Value Decomposition (SVD) recursively

$$|\Psi\rangle = \sum_{n_1 n_2 n_3 n_4} \psi^{n_1 n_2 n_3 n_4} |n_1 n_2 n_3 n_4\rangle$$

$$\text{1st SVD} = \sum_{n_1 n_2 n_3 n_4} \sum_{a_1} L^{n_1}_{a_1} \Lambda_{a_1} R^{n_2 n_3 n_4 \dagger}_{a_1} |n_1 n_2 n_3 n_4\rangle$$

$$n_1 \overbrace{\boxed{\psi^{n_1 \{n_2 n_3 n_4\}}}}^{\{n_2 n_3 n_4\}} = n_1 \overbrace{\boxed{L^{n_1}_{a_1}}}^{a_1} \cdot \overbrace{\boxed{\Lambda_{a_1}}}^{a_1} \cdot \overbrace{\boxed{R^{n_2 n_3 n_4 \dagger}_{a_1}}}^{\{n_2 n_3 n_4\}}$$

viewed as a matrix

$$\psi^{n_2 n_3 n_4}_{a_1}$$

MPS construction cont'd

Doing SVDs recursively from the **Left**

$$|\Psi\rangle = \sum_{n_1 n_2 n_3 n_4} \sum_{a_1} L^{n_1}_{a_1} \psi^{n_2 n_3 n_4}_{a_1} \left| n_1 n_2 n_3 n_4 \right\rangle$$

$$= \sum_{n_1 n_2 n_3 n_4} \sum_{a_1 a_2} L^{n_1}_{a_1} L^{n_2}_{a_1 a_2} \psi^{n_3 n_4}_{a_2} \left| n_1 n_2 n_3 n_4 \right\rangle$$

$$= \sum_{n_1 n_2 n_3 n_4} \sum_{a_1 a_2 a_3} L^{n_1}_{a_1} L^{n_2}_{a_1 a_2} L^{n_3}_{a_2 a_3} \psi^{n_4}_{a_3} \left| n_1 n_2 n_3 n_4 \right\rangle$$

Gauge Freedom of MPS

SVDs can also be carried out from the **Right**

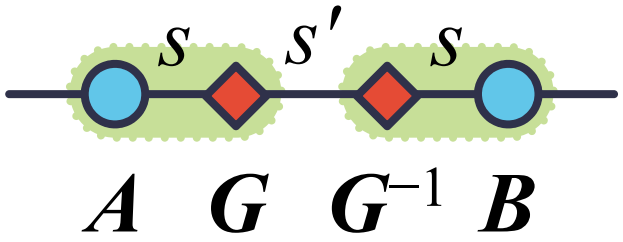
$$
\begin{aligned}
|\Psi\rangle &= \sum_{n_1 n_2 n_3 n_4} \psi^{n_1 n_2 n_3 n_4} \left| n_1 n_2 n_3 n_4 \right\rangle \\
&= \sum_{n_1 n_2 n_3 n_4} \sum_{a_3} L^{n_1 n_2 n_3}_{a_3} \Lambda_{a_3} R^{n_4 \dagger}_{a_3} \left| n_1 n_2 n_3 n_4 \right\rangle \\
&\vdots \\
&= \sum_{n_1 n_2 n_3 n_4} \sum_{a_1 a_2 a_3} \psi^{n_1}_{a_1} R^{n_2 \dagger}_{a_1 a_2} R^{n_3 \dagger}_{a_2 a_3} R^{n_4 \dagger}_{a_3} \left| n_1 n_2 n_3 n_4 \right\rangle
\end{aligned}
$$

The same wavefunction with the different representation

Gauge freedom of MPS cont'd

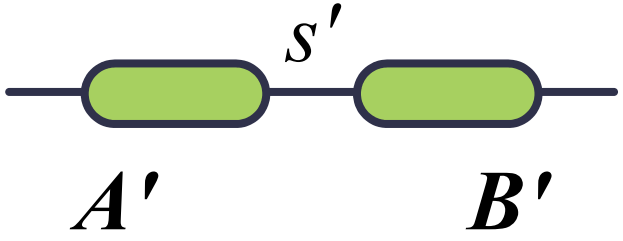
$$(AB)_{ij} = \sum_s A_{is} B_{sj}$$

inserting identity



$$AB = A\left(GG^{-1}\right)B$$

regrouping



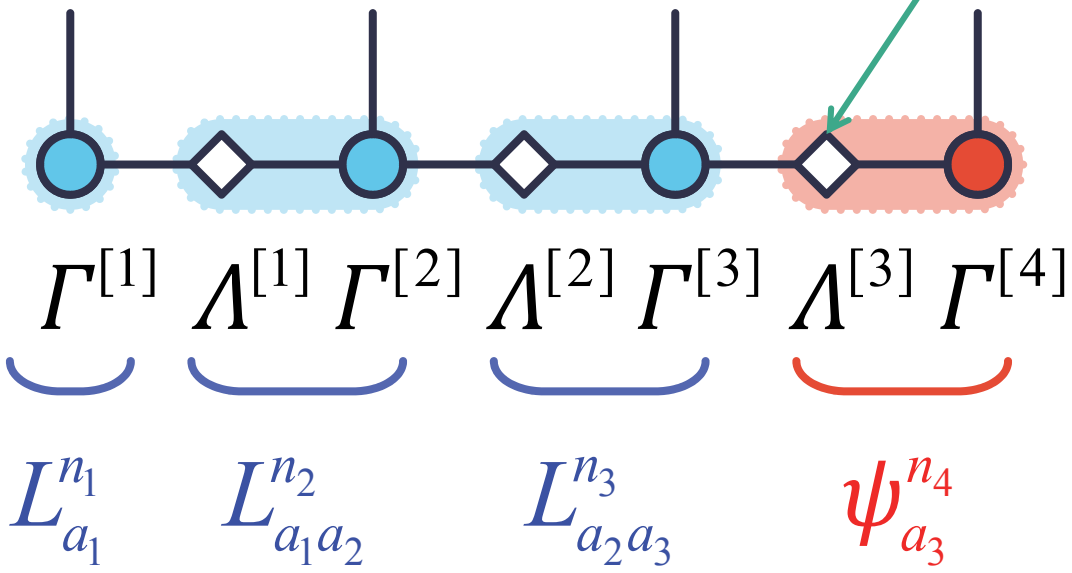
$$\left(AG\right)\left(G^{-1}B\right) = A'B'$$

matrix product with different gauge

Gauge freedom of MPS cont'd

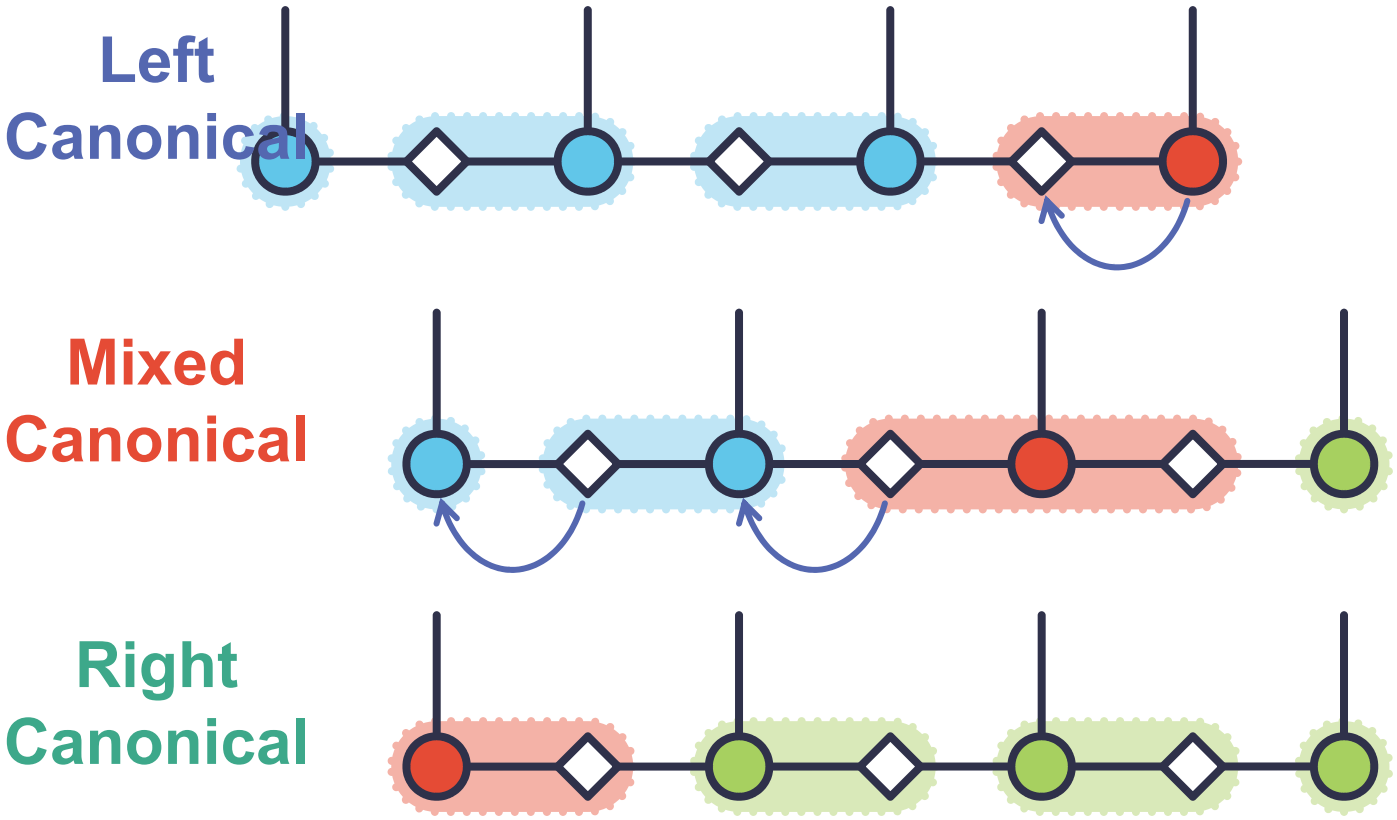
Vidal's representation

singular values



Canonical form

Of which site is a wavefunction?



Note canonical forms are interchangeable

Canonical form cont'd

Left-canonical form

$$|\Psi\rangle = \sum_{n_1 n_2 n_3 n_4} \sum_{a_1 a_2 a_3} L^{n_1}_{a_1} L^{n_2}_{a_1 a_2} L^{n_3}_{a_2 a_3} \psi^{n_4}_{a_3} \left| n_1 n_2 n_3 n_4 \right\rangle$$

Mixed-canonical form

$$= \sum_{n_1 n_2 n_3 n_4} \sum_{a_1 a_2 a_3} L^{n_1}_{a_1} L^{n_2}_{a_1 a_2} \psi^{n_3}_{a_2 a_3} R^{n_4 \dagger}_{a_3} \left| n_1 n_2 n_3 n_4 \right\rangle$$

Right-canonical form

$$= \sum_{n_1 n_2 n_3 n_4} \sum_{a_1 a_2 a_3} \psi^{n_1}_{a_1} R^{n_2 \dagger}_{a_1 a_2} R^{n_3 \dagger}_{a_2 a_3} R^{n_4 \dagger}_{a_3} \left| n_1 n_2 n_3 n_4 \right\rangle$$

Canonical form cont'd

Why "canonical" form?

$$|a_1\rangle = \sum_{n_1} L_{a_1}^{n_1} |n_1\rangle$$

$$|a_2\rangle = \sum_{n_1 n_2} \sum_{a_1} L_{a_1}^{n_1} L_{a_1 a_2}^{n_2} |n_1 n_2\rangle = \sum_{a_1 n_2} L_{a_1 a_2}^{n_2} |a_1 n_2\rangle$$

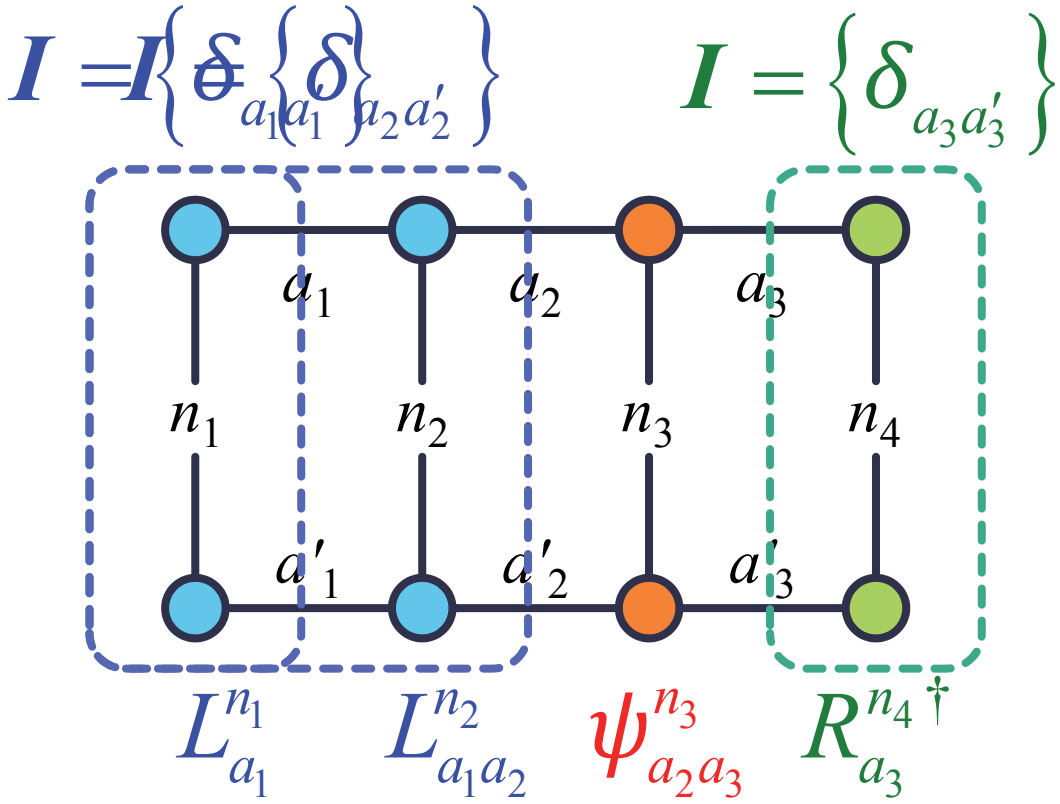
$$\vdots$$

$$|a_i\rangle = \sum_{a_{i-1} n_i} L_{a_{i-1} a_i}^{n_i} |a_{i-1} n_i\rangle$$

$$\langle a_i | a_i' \rangle = \delta_{a_i a_i'}$$

Gives orthonormal bases for *i*-th boundary

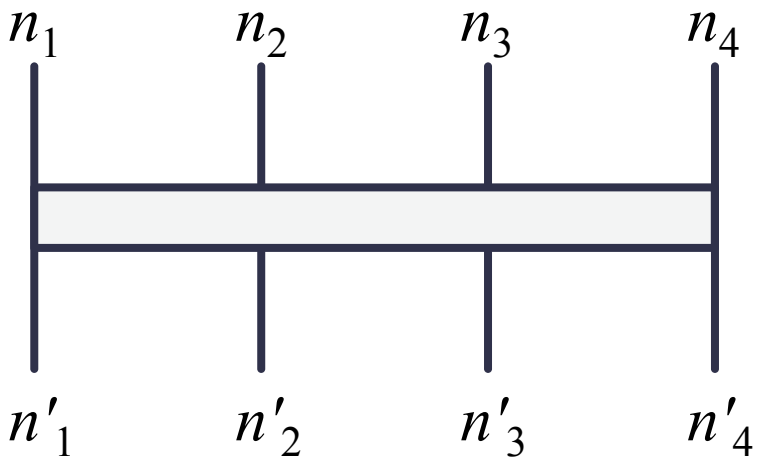
Canonical form cont'd



Consequently, $\langle \Psi | \Psi \rangle = \sum_{a_2 n_3 a_3} \psi^{n_3 \dagger}_{a_2 a_3} \psi^{n_3}_{a_2 a_3}$

Matrix Product Operators

General operator $\hat{O} = \sum_{nn'} |n_1 n_2 n_3 n_4\rangle O^{n_1 n_2 n_3 n_4}_{n'_1 n'_2 n'_3 n'_4} \langle n'_1 n'_2 n'_3 n'|$

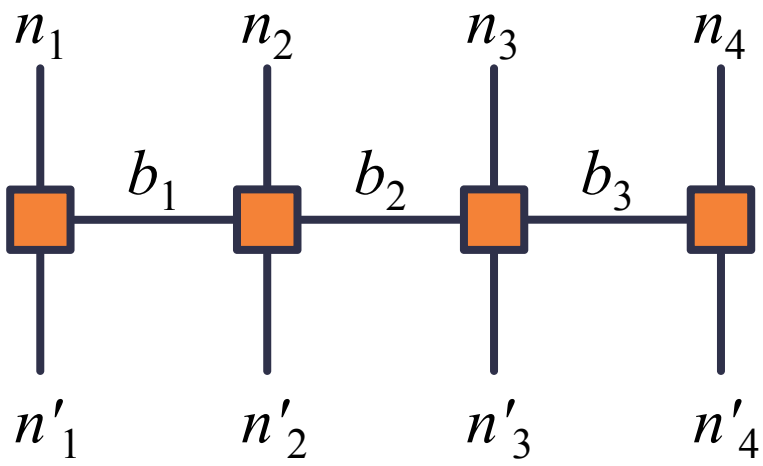


$$O^{n_1 n_2 n_3 n_4}_{n'_1 n'_2 n'_3 n'_4}$$

Rank-2*k* tensor

Matrix Product Operators

General operator $\hat{O} = \sum_{nn'} |n_1 n_2 n_3 n_4\rangle O^{n_1 n_2 n_3 n_4}_{n'_1 n'_2 n'_3 n'_4} \langle n'_1 n'_2 n'_3 n'|$

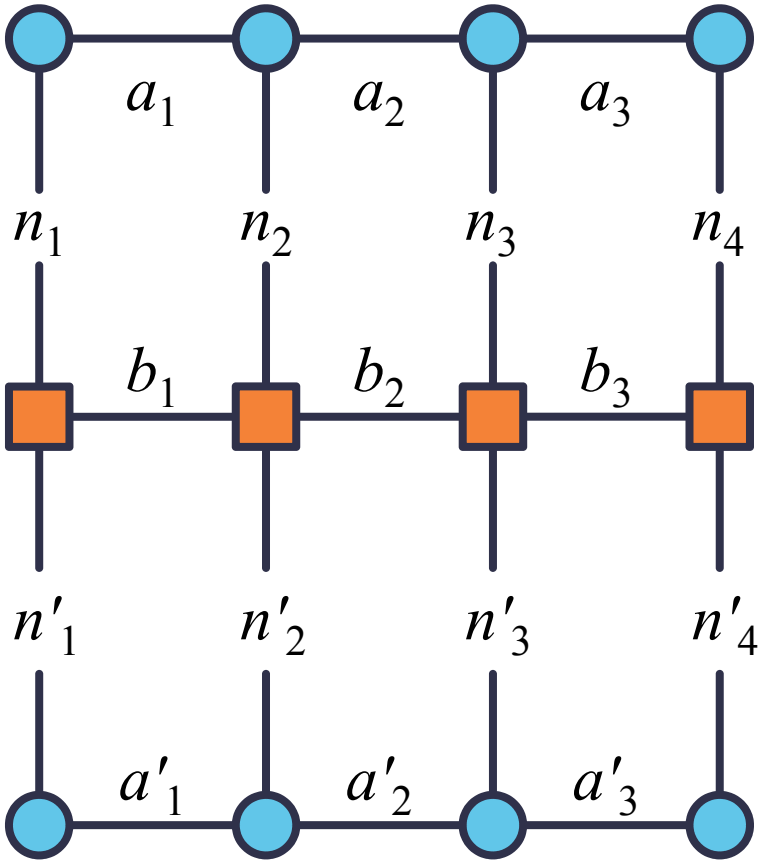


$$\sum_{b_1 b_2 b_3} W^{n_1 n'_1}_{b_1} W^{n_2 n'_2}_{b_1 b_2} W^{n_3 n'_3}_{b_2 b_3} W^{n_4 n'_4}_{b_3}$$

Product of rank-4 tensors

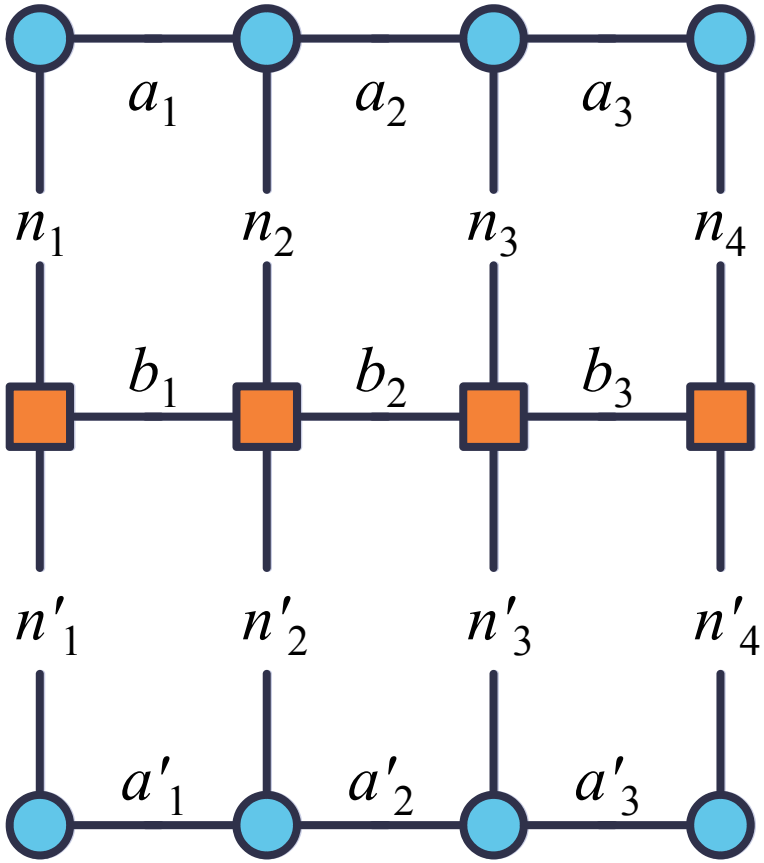
Compute expectation value

$$\langle \Psi | \hat{O} | \Psi \rangle =$$



Compute expectation value

$$\langle \Psi | \hat{O} | \Psi \rangle =$$



$$\mathcal{O}(dM^3Dk + d^2M^2D^2k)$$

If "***D***" and "***M***" can be a small number,

again, this gives a polynomial cost algorithm

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Variational principle

Lagrange multiplier

Minimization with constraints (normalization condition)

$$\mathcal{L} = \langle \Psi | \mathcal{H} | \Psi \rangle - \lambda \left(\langle \Psi | \Psi \rangle - 1 \right)$$

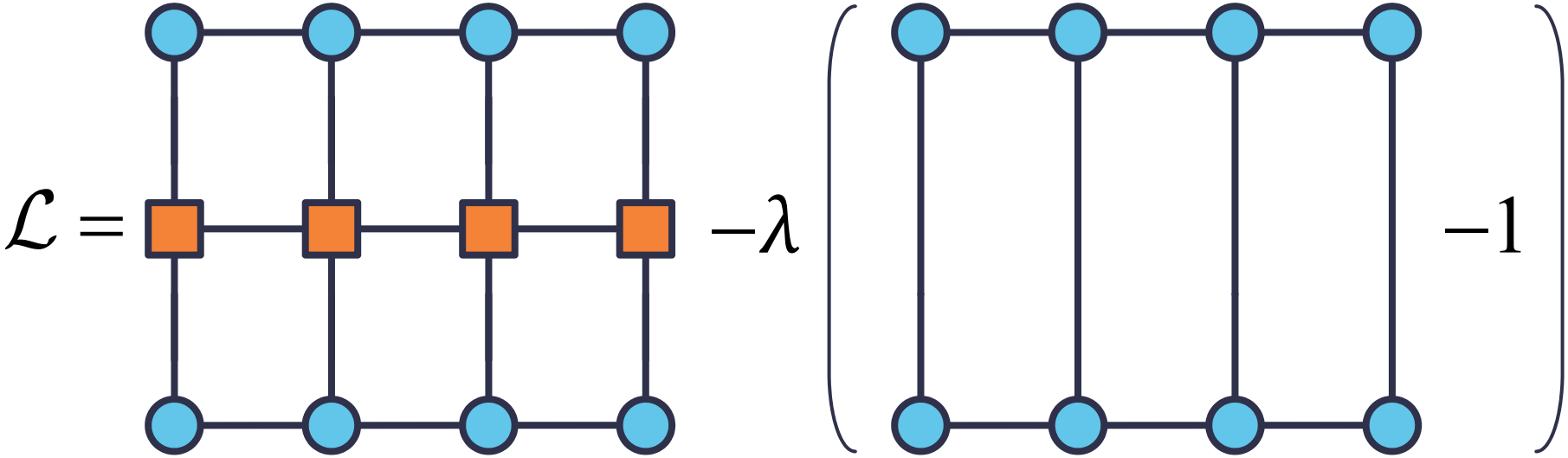
Constraint to $\langle \Psi | \Psi \rangle = 1$

Find $|\Psi\rangle$ which satisfies the variational condition

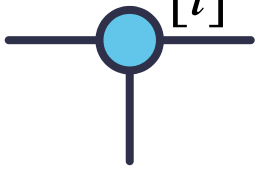
$$\delta\mathcal{L} = \langle \delta\Psi | \mathcal{H} | \Psi \rangle - \lambda \langle \delta\Psi | \Psi \rangle = 0$$

Variational Principle cont'd

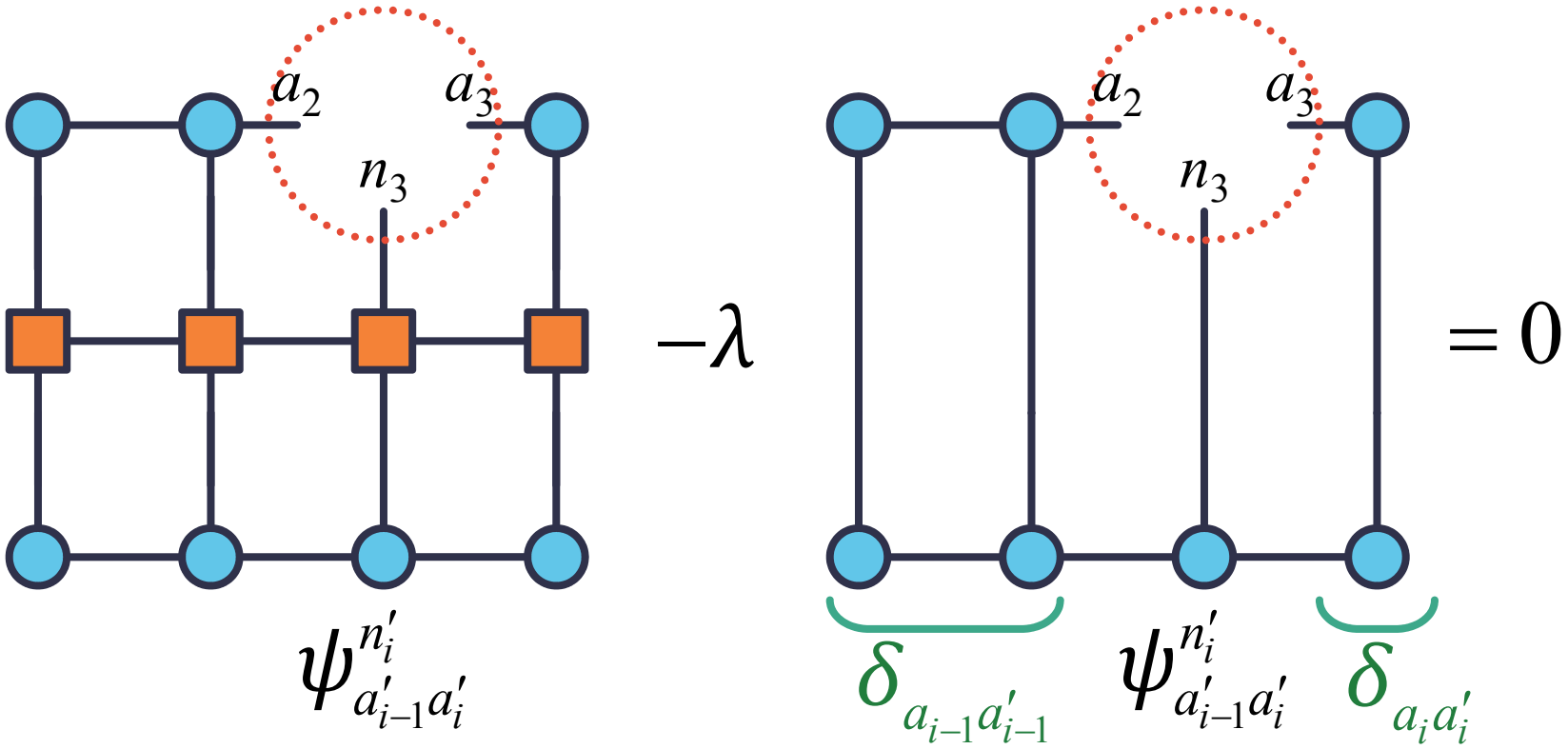
Lagrange multiplier



$$\delta\mathcal{L} = \sum_i \frac{\partial\mathcal{L}}{\partial}$$



Variational principle cont'd

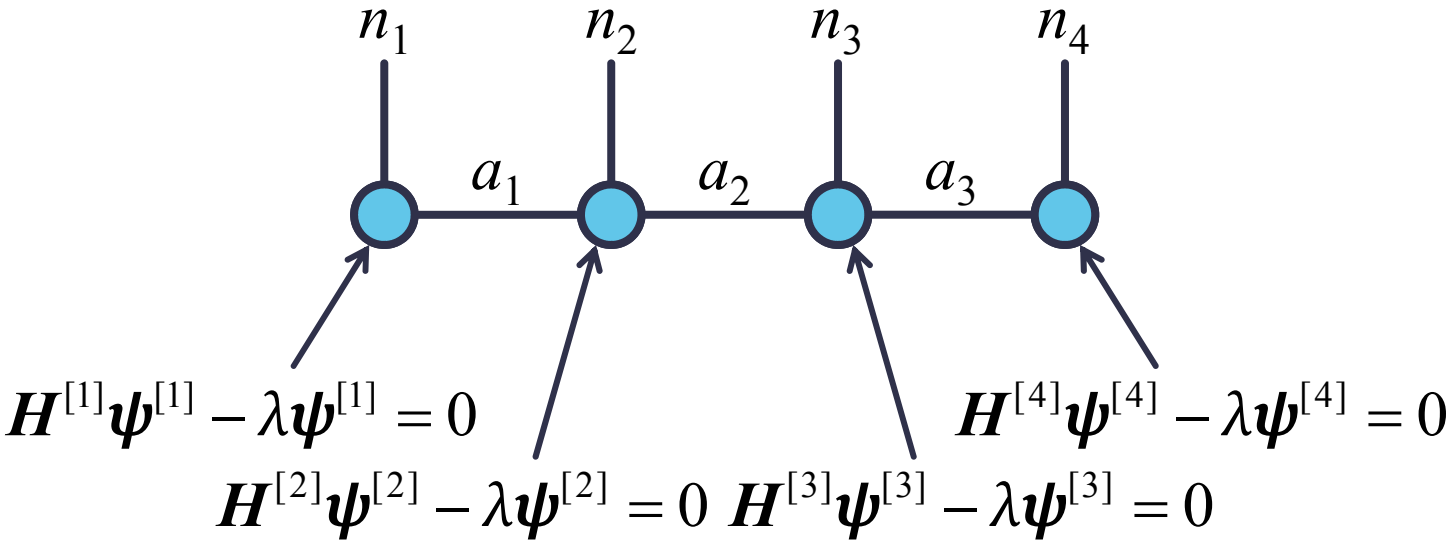


$$\sum_{n' a_{i-1}' a_i'} H^{n_i n_i'}_{a_{i-1} a_i a_{i-1}' a_i'} \psi^{n_i'}_{a_{i-1}' a_i'} - \lambda \psi^{n_i}_{a_{i-1} a_i} = 0$$

Sweep algorithm

Optimizing for each site iteratively until converged

Sweep **from Left to Right** (Forward sweep)

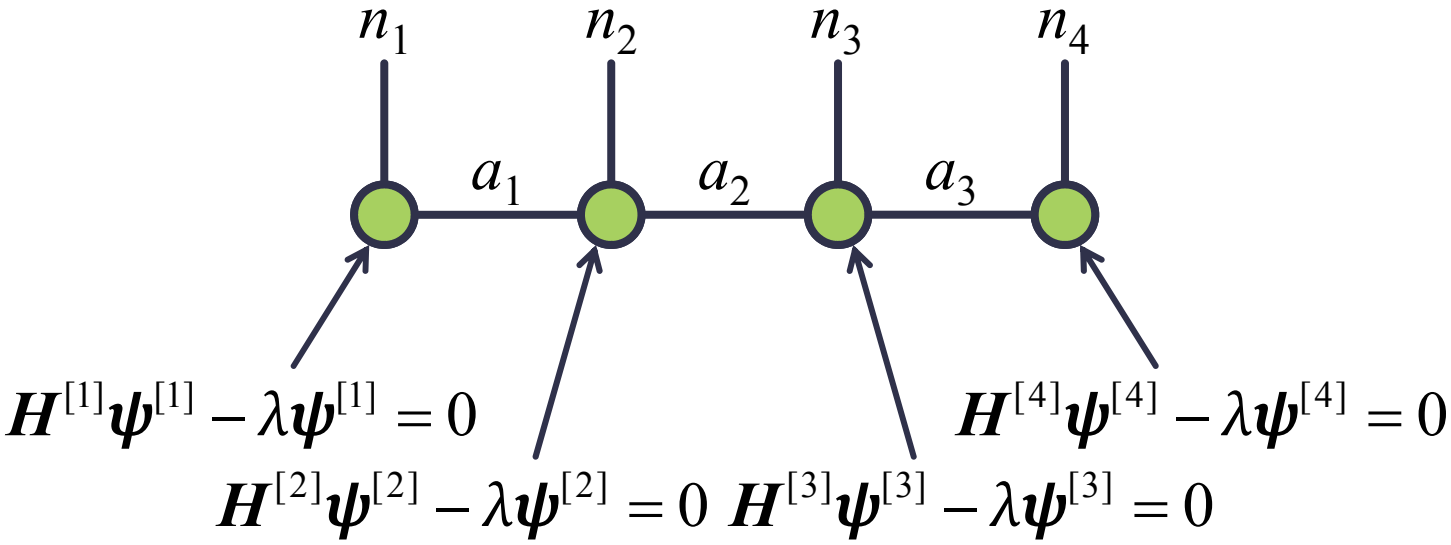


Note: $\boldsymbol{H}^{[i]} \equiv \left\{ H^{n_i n_i'}_{a_{i-1} a_i a_{i-1}' a_i'} \right\}, \quad \boldsymbol{\psi}^{[i]} \equiv \left\{ \psi^{n_i}_{a_{i-1} a_i} \right\}$

Sweep algorithm

Optimizing for each site iteratively until converged

Sweep **from Right to Left** (Backward sweep)

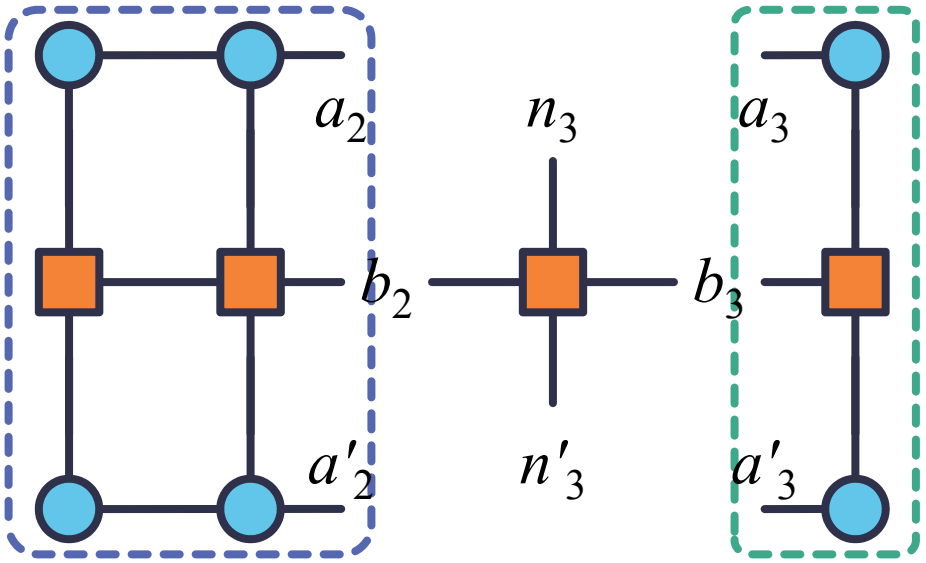


Note: $\boldsymbol{H}^{[i]} \equiv \left\{ H^{n_i n_i'}_{a_{i-1} a_i a_{i-1}' a_i'} \right\}, \quad \boldsymbol{\psi}^{[i]} \equiv \left\{ \psi^{n_i}_{a_{i-1} a_i} \right\}$

Sweep algorithm cont'd

How to efficiently compute effective Hamiltonian?

$$H^{n_3 n_3'}_{a_2 a_3 a_2' a_3'} =$$



Operators renormalized from the left

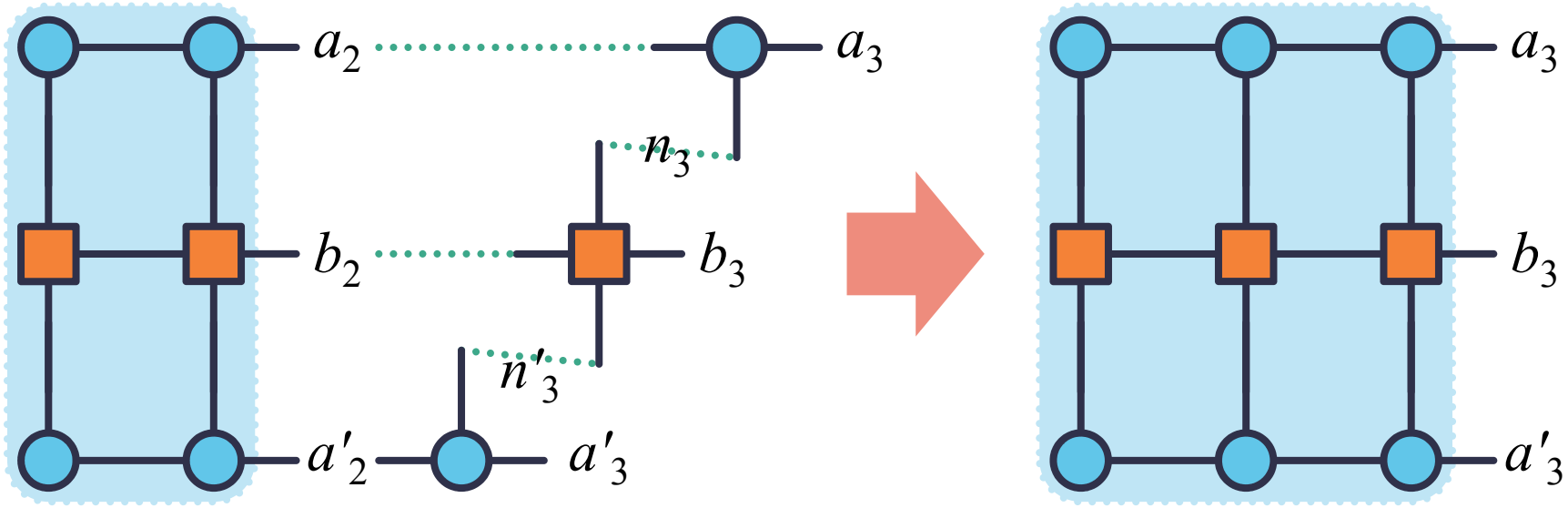
Operators renormalized from the right

$$F^{[\mathrm{L}]}_{a_2 b_2 a_2'} \qquad W^{n_3 n_3'}_{b_2 b_3} \qquad F^{[\mathrm{R}]}_{a_3 b_3 a_3'}$$

$$H^{n_3 n_3'}_{a_2 a_3 a_2' a_3'} = \sum_{b_2 b_3} F^{[\mathrm{L}]}_{a_2 b_2 a_2'} W^{n_3 n_3'}_{b_2 b_3} F^{[\mathrm{R}]}_{a_3 b_3 a_3'}$$

Sweep algorithm cont'd

Renormalizing operators to the next



Rank-3 tensor **Rank-3 tensor**

enables to reuse the intermediate tensors

60 mins

QC-DMRG

In quantum chemistry,
Hamiltonian consists of one- and two-electron interactions

$$\hat{\mathcal{H}}_{\text{elec}} = \sum_{ij} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{ijkl} v_{ijlk} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l$$

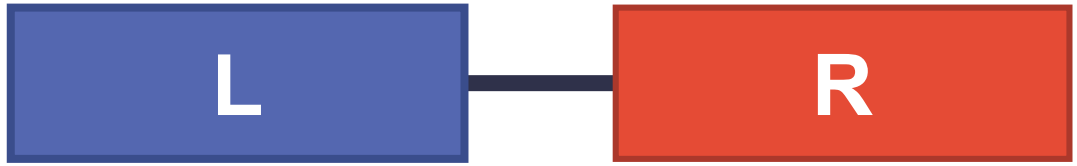
while MPO formalism involves "*any-particle*" operators

implies that QC-MPO is highly sparse!

QC-DMRG cont'd

Instead using MPO formalism,
block structure of Hamiltonian is considered

$$\mathcal{H} = \mathcal{H}^{\mathrm{L}} + \mathcal{H}^{\mathrm{R}} + \sum_I \mathcal{I}_I^{\mathrm{L}} \mathcal{I}_I^{\mathrm{R}}$$



$$\mathcal{H}^{\mathrm{L}} \quad \left\{\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l\right\}_{ijkl\in \mathrm{L}} \quad \cdots\cdots \quad \hat{1}$$

$$\mathcal{I}_I^{\mathrm{L}} \mathcal{I}_I^{\mathrm{R}} \quad \left\{\hat{a}_i^\dagger \hat{a}_j\right\}_{ij\in \mathrm{L}} \quad \cdots\cdots \quad \left\{\hat{a}_k^\dagger \hat{a}_l\right\}_{kl\in \mathrm{R}}$$

$$\mathcal{H}^{\mathrm{R}} \quad \hat{1} \quad \cdots\cdots \quad \left\{\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l\right\}_{ijkl\in \mathrm{R}}$$

QC-DMRG cont'd

Then taking a partial sum, such as

$$\sum_{\substack{ij\in \mathrm{L}\\ kl\in \mathrm{R}}} v_{ikjl}\hat{a}_i^\dagger \hat{a}_j \otimes \hat{a}_k^\dagger \hat{a}_l = \sum_{ij\in \mathrm{L}} \hat{a}_i^\dagger \hat{a}_j \otimes \underbrace{\left(\sum_{kl\in \mathrm{R}} v_{ikjl}\hat{a}_k^\dagger \hat{a}_l \right)}_{\hat{Q}_{ij}^{\mathrm{R}}}$$

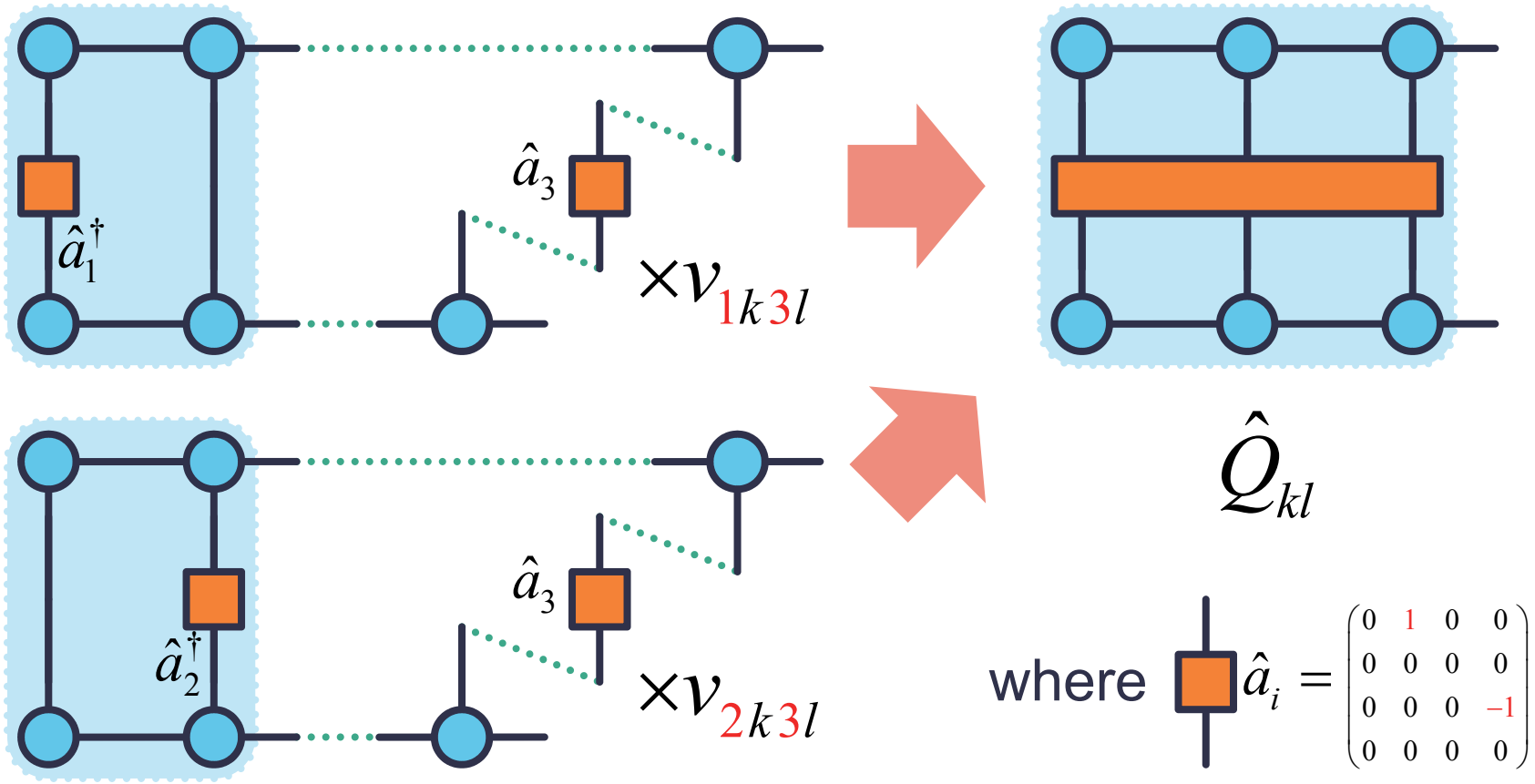
complementary operator

$\mathcal{O}(k^4)$ summation is divided into two $\mathcal{O}(k^2)$ summations

$$\sum_I \mathcal{I}_I^{\mathrm{L}} \mathcal{I}_I^{\mathrm{R}} = \sum_{i\in \mathrm{L}} \hat{a}_i^\dagger \hat{S}_i^{\mathrm{R}} + \sum_{i\in R} \hat{S}_i^{\mathrm{L}\dagger} \hat{a}_i + \sum_{ij\in \mathrm{L}} \left(\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{P}_{ij}^{\mathrm{R}} + \hat{a}_i^\dagger \hat{a}_j \hat{Q}_{ij}^{\mathrm{R}} \right) + \text{adjoints}$$

QC-DMRG cont'd

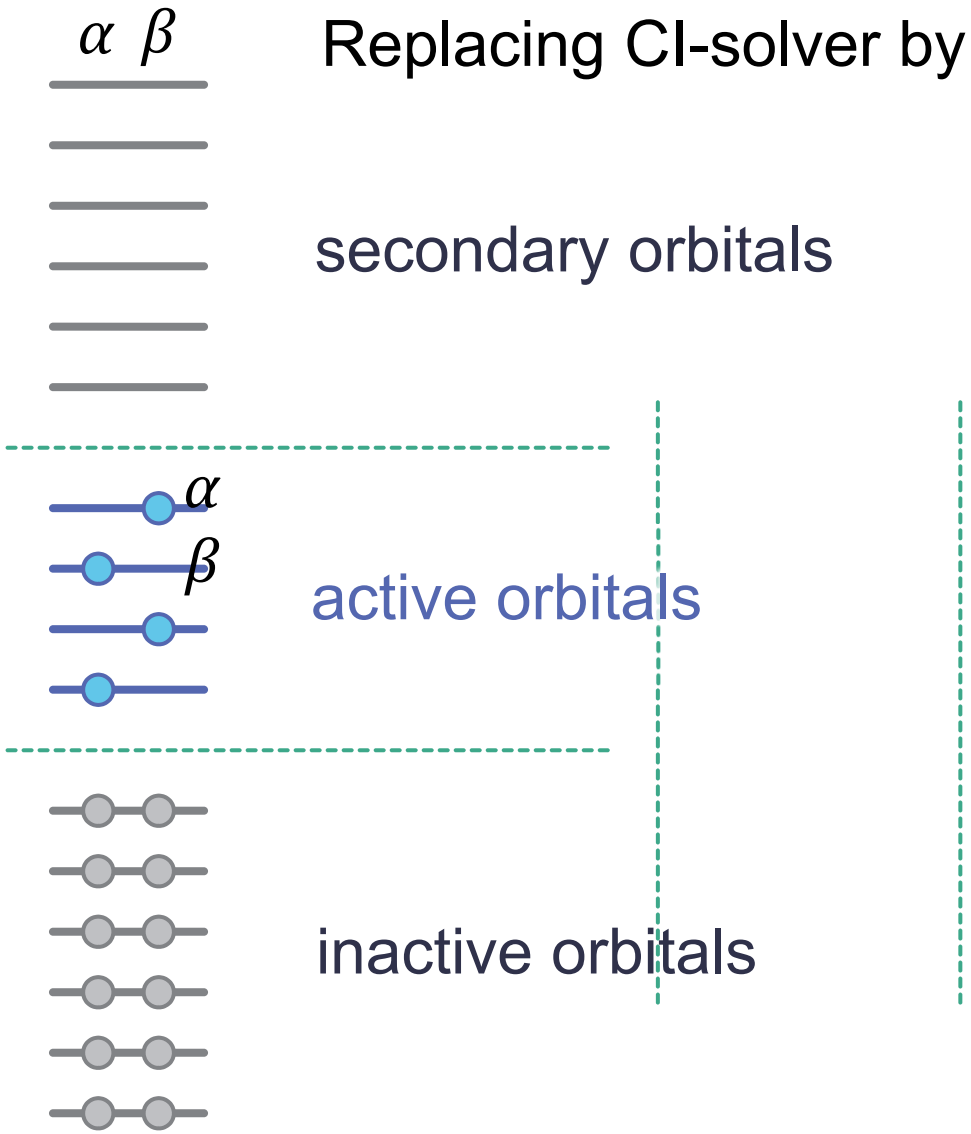
Renormalizing operators to the next



Consequently, QC-DMRG scales $\mathcal{O}(dM^3k^3 + d^2M^2k^4)$

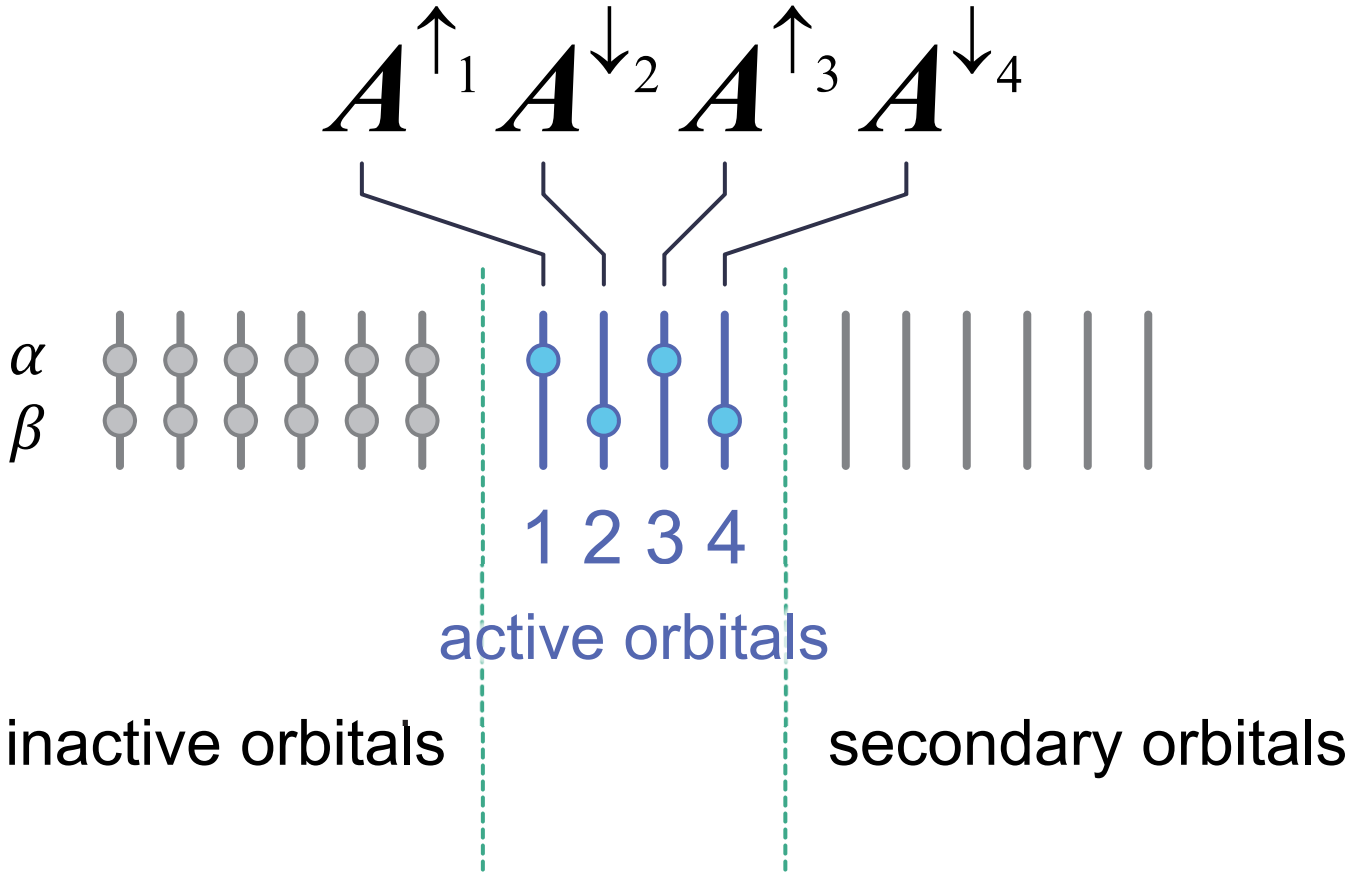
CAS approach

Replacing CI-solver by QC-DMRG



CAS approach

Replacing CI-solver by QC-DMRG



Orbital ordering

1*D* feature of MPS wavefunction arises because

$$AB \neq BA$$

e.g.

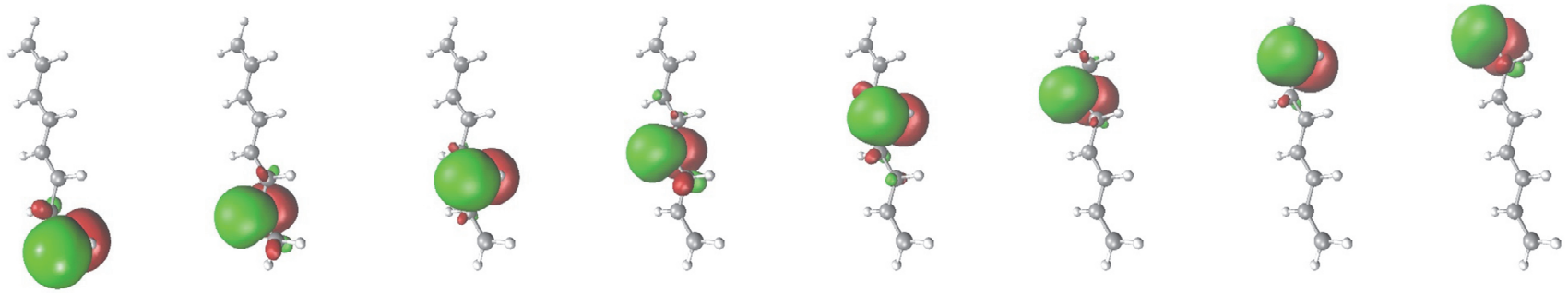
$$A^{n_1} A^{n_2} A^{n_3} A^{n_4} \neq A^{n_1} A^{n_3} A^{n_2} A^{n_4}$$

MPS wavefunction is "unitary variant"

Find the orbital set and the ordering which give the lowest energy

Orbital ordering cont'd

Trivial case

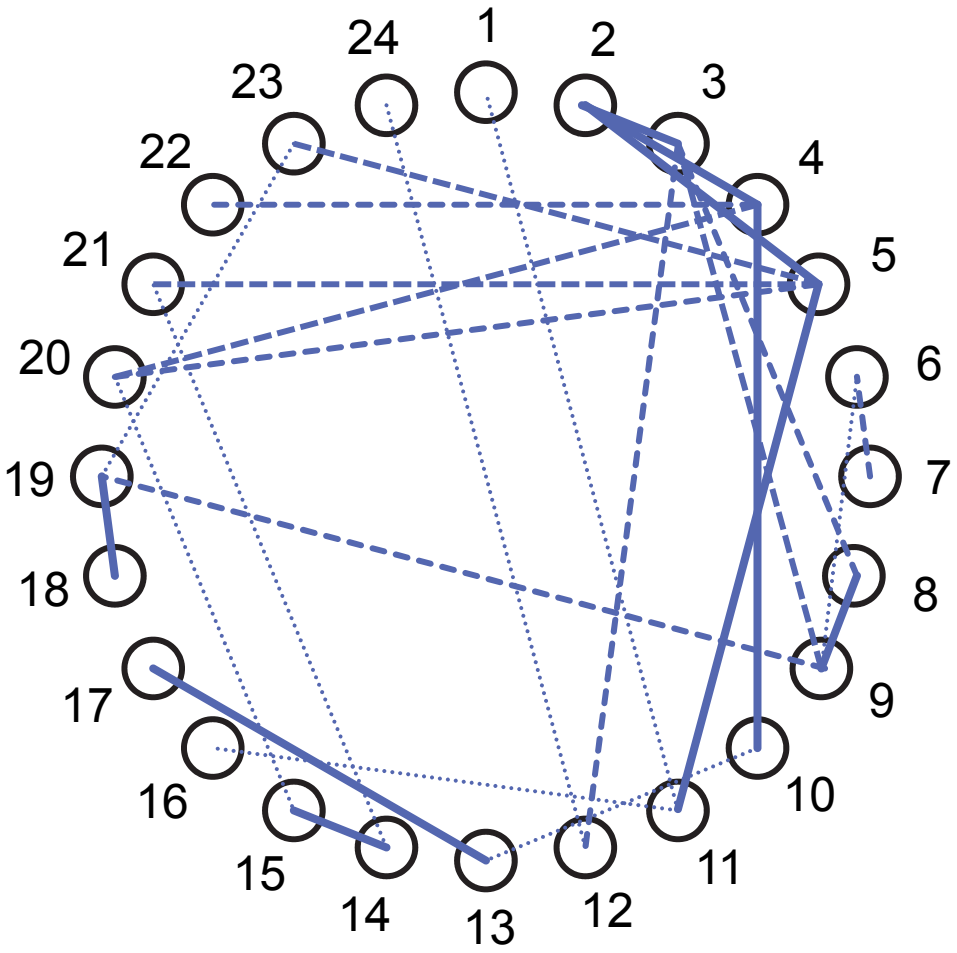


First, orbitals are localized

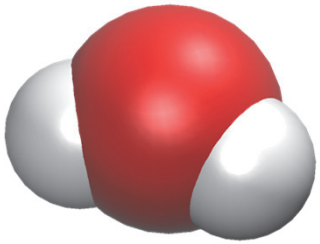
Then, sorted manually to form 1*D* geometry

Orbital ordering cont'd

Non-trivial case



H_2O / cc-pVDZ
(10e in 24o)



Stronger interaction
to be closer position

Block DMRG code

Developed by G. Chan group

https://github.com/gkc1000/Block

Now, Block is integrated into...

Free softwares

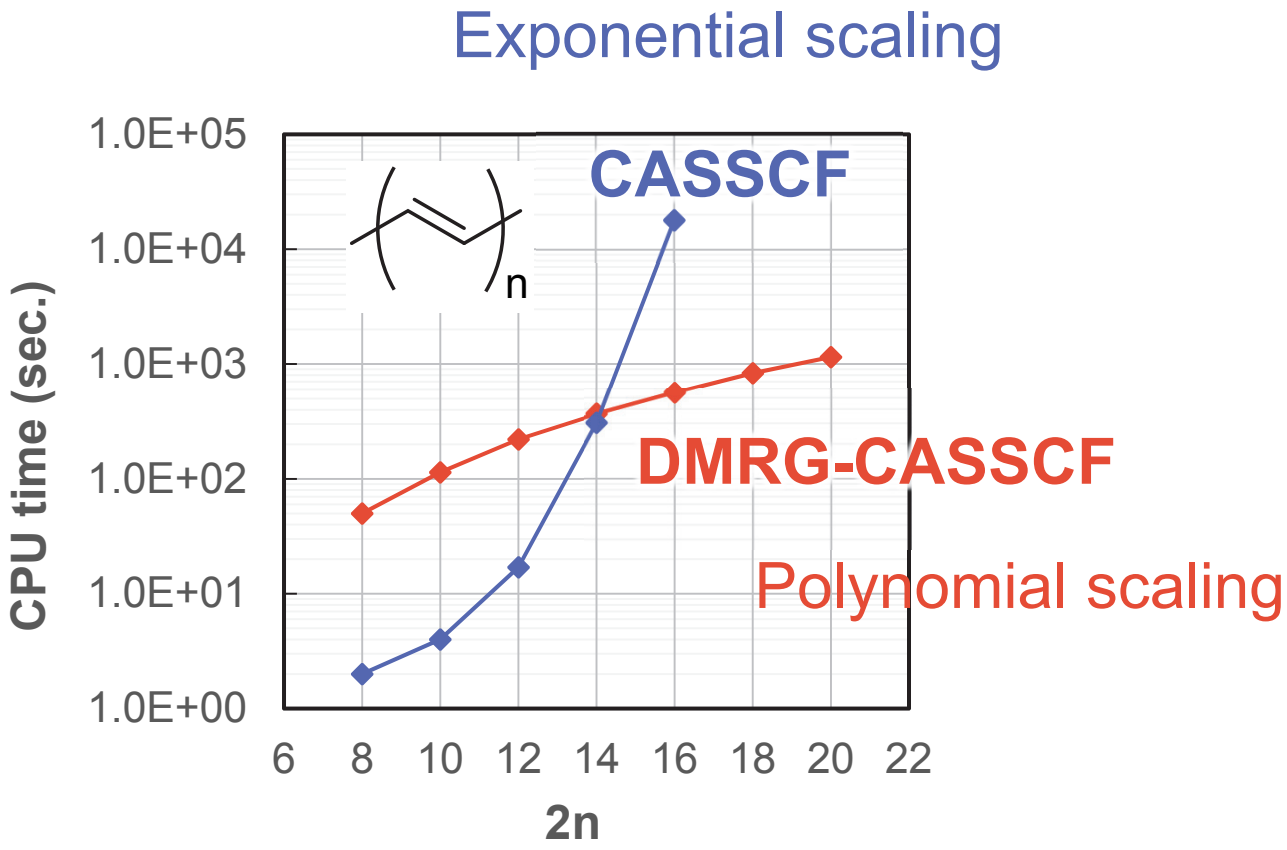
- pyscf
- ORCA

Just to run, doesn't need to know details about DMRG!!!

Commercial packages

- Molpro
- Molcas (coming soon)

Benchmarks


Exponential scaling
CASSCF
DMRG-CASSCF
Polynomial scaling
CPU time (sec.)
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
6
8
10
12
14
16
18
20
22
2n
n

Coffee break

MPS/MPO are general language to compress information

M	1024	700	500	300	200	100	50	20
storage	67%	48%	36%	21%	11%	4%	1%	0.2%

Outline

Many-body wavefunction

Matrix Product States & Matrix Product Operators

DMRG from variational principle for MPS

Time-evolution

DMRG linear response theory

Outline

Many-body wavefunction

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General concepts

Time-dependent wavefunction

$$\Psi(t) = e^{-i\hat{\mathcal{H}}t/\hbar}\Psi(0)$$

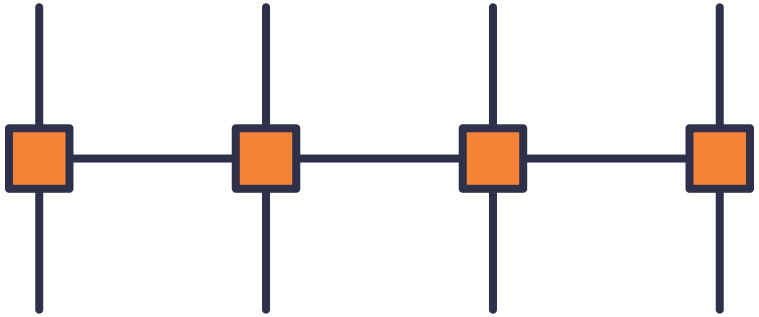
is a formal solution of time-dependent Schrödinger eq.

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = \hat{\mathcal{H}}\Psi(t)$$

General concepts cont'd

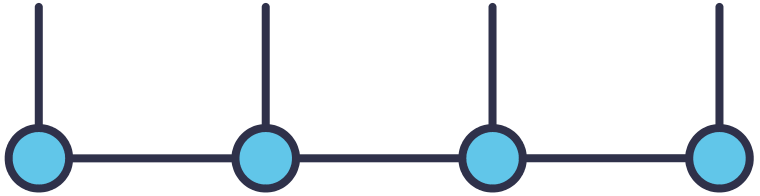
MPO formalism of propagator ($t \rightarrow t + \Delta t$)

$e^{-i\hat{\mathcal{H}}\Delta t/\hbar} =$



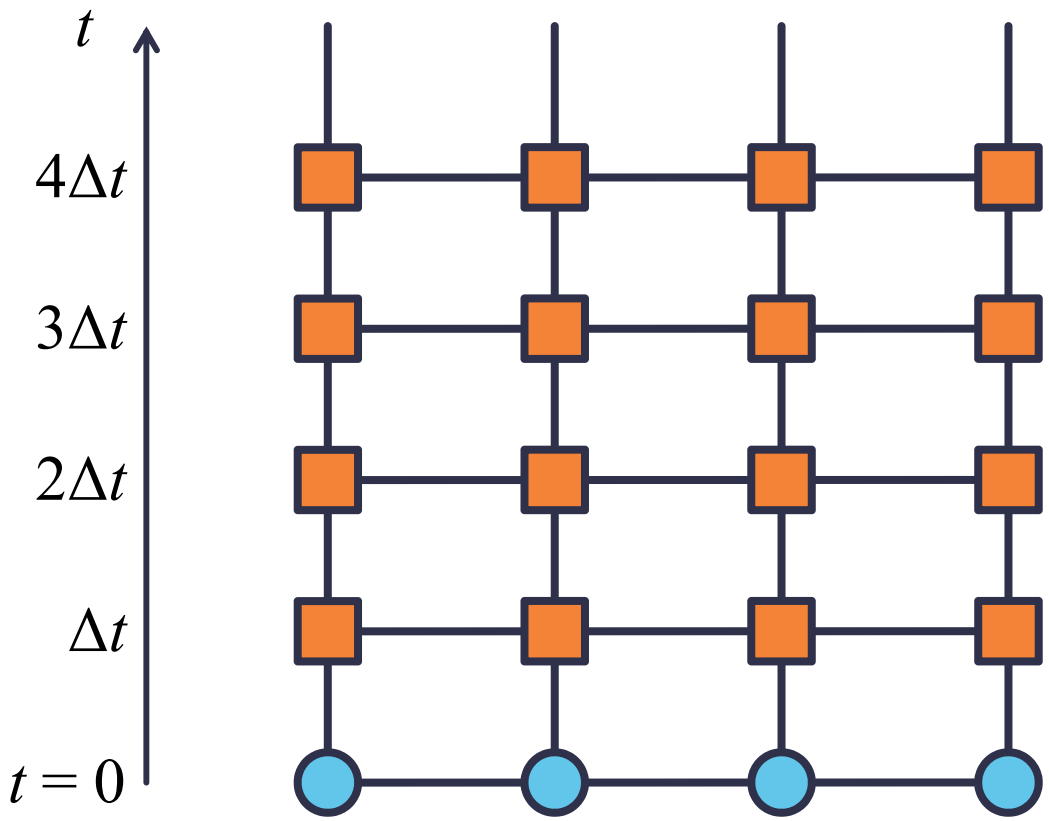
MPS formalism of wavefunction ($t = 0$)

$\Psi(0) =$



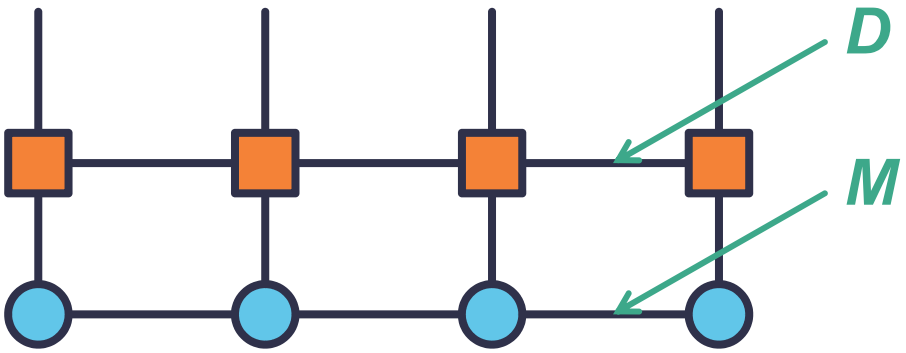
General concepts cont'd

Now, carry out time-evolution of the wavefunction



General concepts cont'd

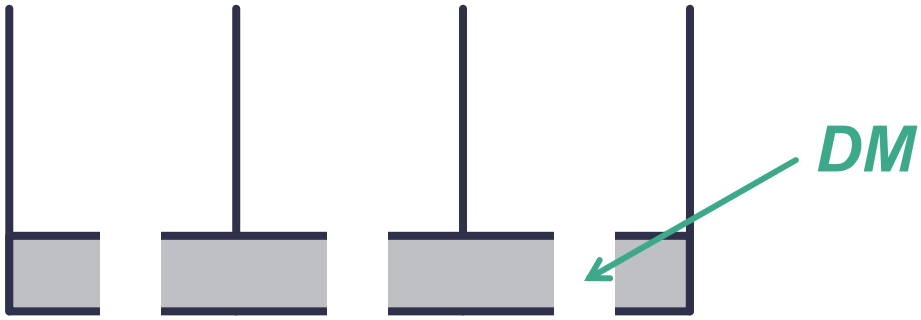
For each time step,



Propagate...

General concepts cont'd

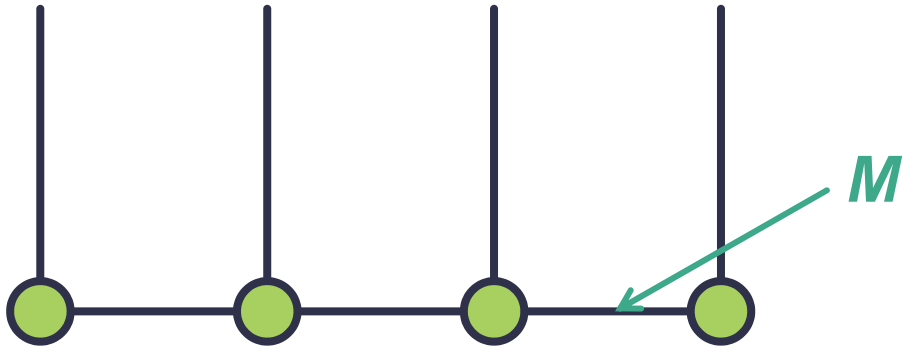
For each time step,



Contract...
Doing SVD...

General concepts cont'd

For each time step,

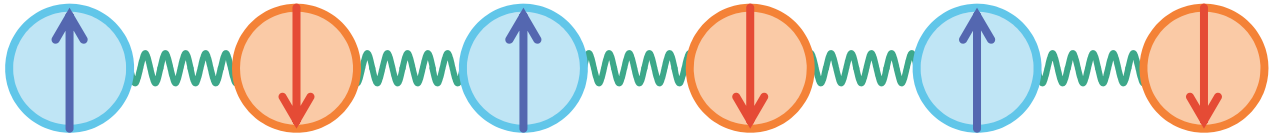


Decimate...

Time-evolution I., TEBD

(Time-Evolving Block Decimation)

Consider 1*D* lattice system
with nearest neighbor interactions



$J\hat{S}(i)\hat{S}(i+1)$

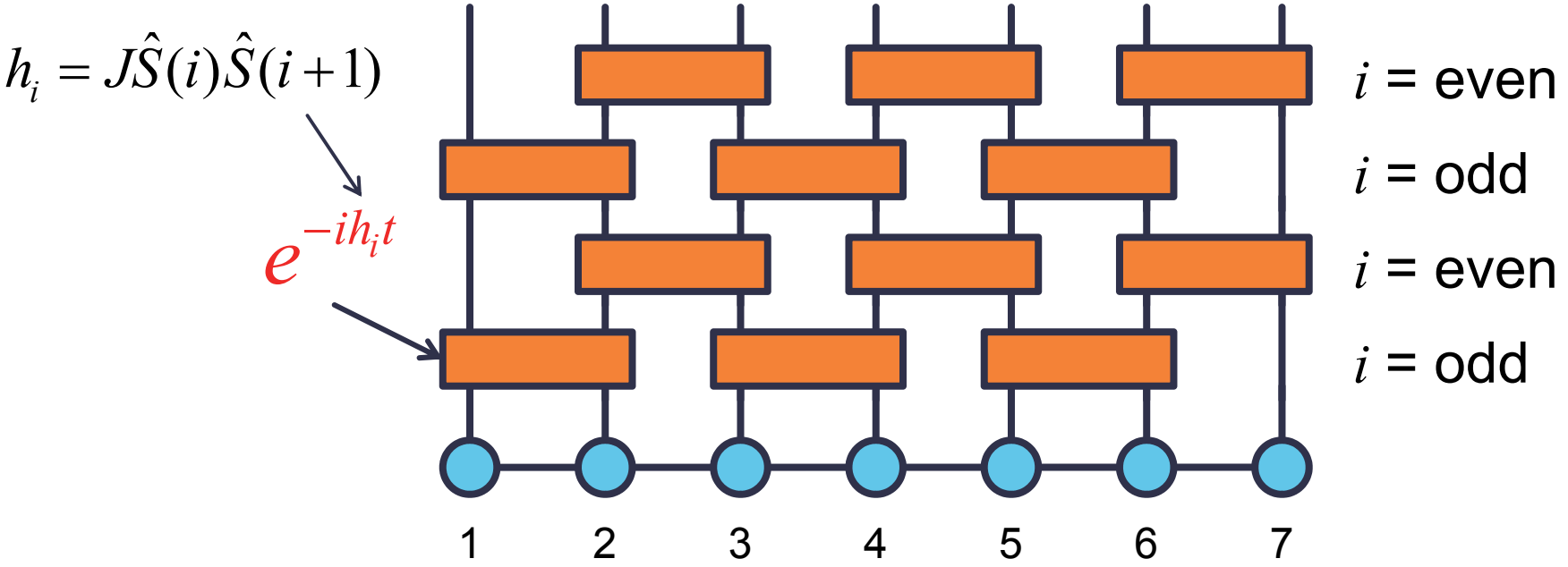
Heisenberg Hamiltonian

$$\mathcal{H} = \sum_i J\hat{S}(i)\hat{S}(i+1)$$

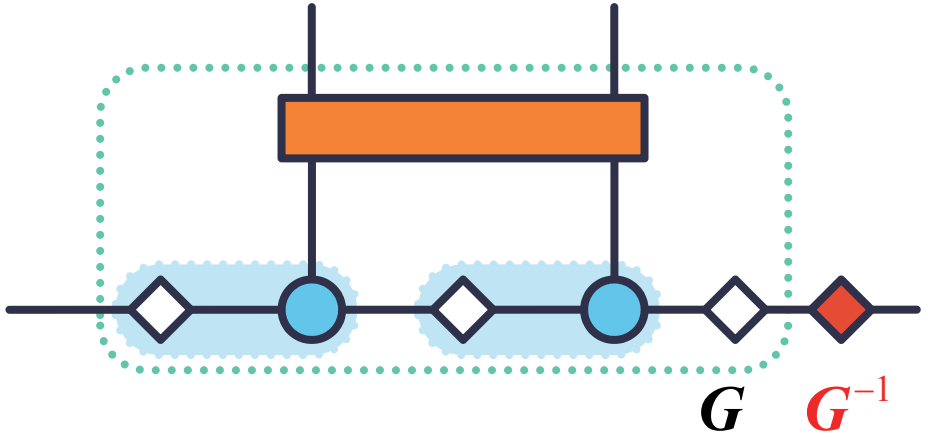
Time-evolution I., TEBD cont'd

Trotter form of propagator

$$e^{-i\mathcal{H}t} = e^{-ih_1 t} \cdots e^{-ih_i t} \cdots e^{-ih_L t} + \mathcal{O}(t^2)$$

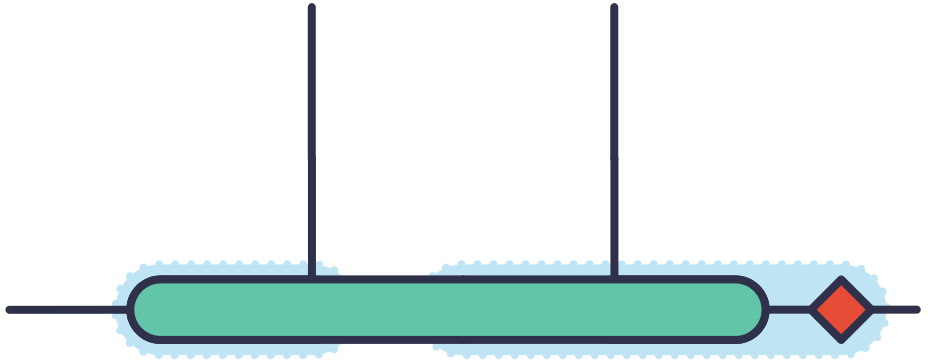


Time-evolution I., TEBD cont'd



propagate...

Time-evolution I., TEBD cont'd

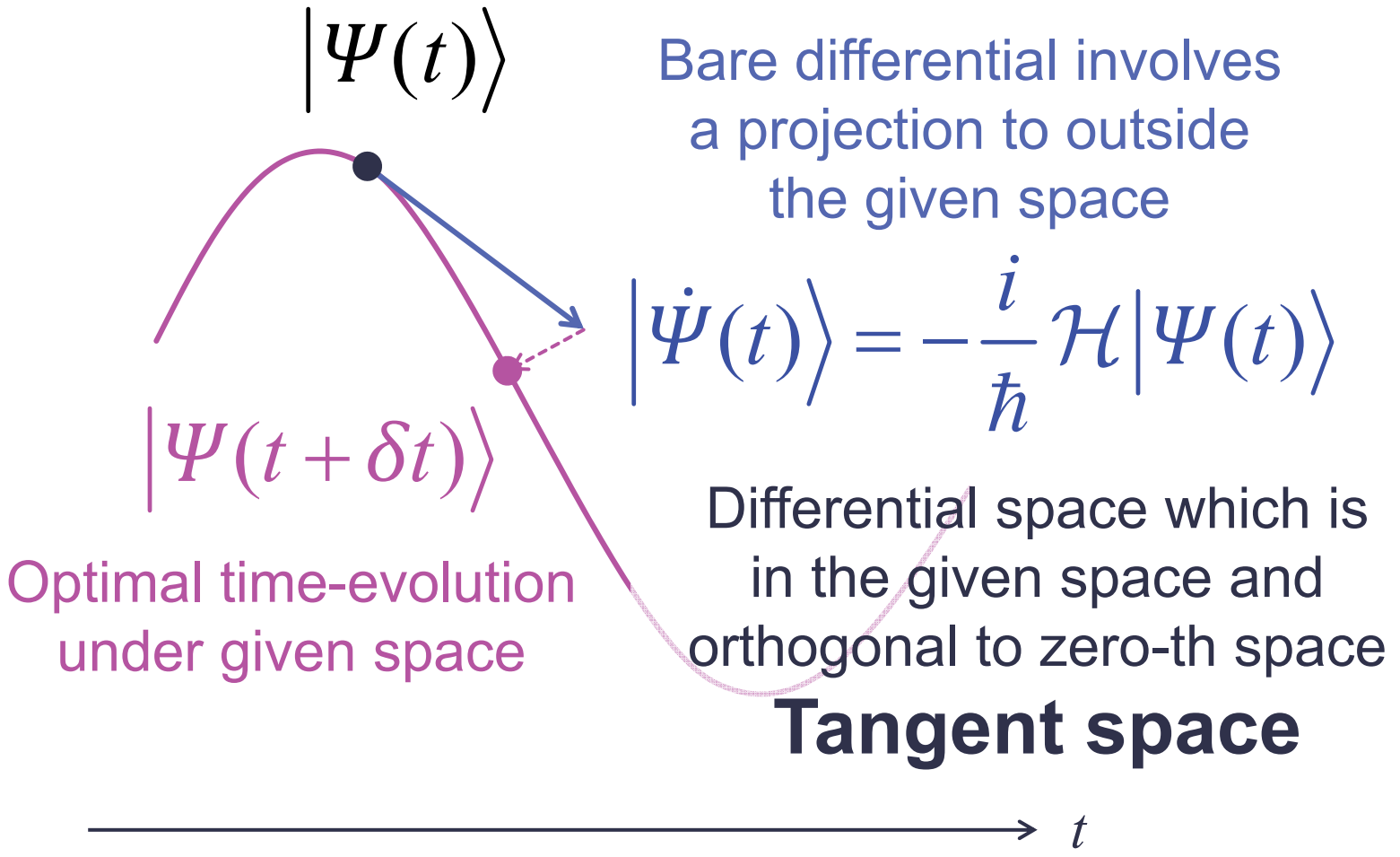


fix the gauge...

SVD

Time-evolution II., TDVP

(Time-Dependent Variational Principle)



Outline

Many-body wavefunction

Matrix Product States & Matrix Product Operators

DMRG from variational principle for MPS

Time-evolution

DMRG linear response theory

Similarity to Hartree-Fock theory

Product structure of wavefunction

HF: Product of **1-particle** orbitals

$$\Psi_{\mathrm{HF}}(x_1,\ldots,x_i,\ldots,x_N) = \hat{\mathcal{A}}\left(\chi_1(x_1)\cdots\chi_i(x_i)\cdots\chi_N(x_N)\right)$$

Particle-independent mean-field

DMRG: Product of **1-site** matrices

$$\Psi_{\mathrm{DMRG}}(n_1,\ldots,n_i,\ldots,n_k) = \sum_{n_1\ldots n_k} A^{[1]}\cdots A^{[i]}\cdots A^{[k]}\left|n_1\cdots n_i\cdots n_k\right\rangle$$

Site-independent mean-field

Similarity to Hartree-Fock theory cont'd

Variational principle

HF: Schrödinger eq. for **each orbital**

$$\hat{f}(x_i)\chi_i(x_i) - \varepsilon_i \chi_i(x_i) = 0$$

Effective Hamiltonian at *i*-th orbital

DMRG: Schrödinger eq. for **each matrix**

$$\boldsymbol{H}^{[i]}\boldsymbol{A}^{[i]} = E_0 \boldsymbol{A}^{[i]}$$

Effective Hamiltonian at *i*-th site

Similarity to Hartree-Fock theory cont'd

Time-dependent variational principle

HF: EOM for **each orbital**

$$i\hbar \frac{\partial}{\partial t} \chi_i(x_i,t) = \hat{f}(x_i,t)\chi_i(x_i,t)$$

DMRG: EOM for **each matrix**

$$i\hbar \boldsymbol{S}^{[i]}(t) \frac{\partial}{\partial t} \boldsymbol{A}^{[i]}(t) = \boldsymbol{H}^{[i]}(t)\boldsymbol{A}^{[i]}(t)$$

Any post-DMRG methods can be derived?

Linear Response Theory

Investigate the first order response for a time-dependent perturbation, such as

$$\hat{V}(t) = Ve^{-i\omega t} + V^* e^{i\omega t}$$

Investigate the first order response for a time-dependent perturbation, such as

$$i\hbar \frac{\partial}{\partial t}\Psi(\boldsymbol{x},t) = \left(\hat{H}_0 + \lambda \hat{V}(t)\right)\Psi(\boldsymbol{x},t)$$

time-independent term
(zero-th order)

time-dependent term
(perturbation)

Linear Response Theory cont'd

Consider a perturbation expansion of the wavefunction

$$\Psi(\boldsymbol{x},t)=\left(\Psi^{(0)}(\boldsymbol{x})+\lambda\Psi^{(1)}(\boldsymbol{x},t)+\lambda^2\Psi^{(2)}(\boldsymbol{x},t)+\cdots\right)e^{-i\omega_0 t}$$

phase factor

First order equation is therefore,

E_0

$$\left(\hat{H}_0-\hbar\omega_0-i\hbar\frac{\partial}{\partial t}\right)\Psi^{(1)}(\boldsymbol{x},t)=-\hat{Q}\hat{V}(t)\Psi^{(0)}(\boldsymbol{x})$$

Fourier transform,

$$\left(\hat{H}_0-E_0+\hbar\omega\right)\Psi^{(1)}(\boldsymbol{x},\omega)=-\hat{Q}\hat{V}(\omega)\Psi^{(0)}(\boldsymbol{x})$$

Linear Response Equation

Linear Response Theory cont'd

What's the first order **HF** wavefunction?

Consider perturbation expansion for "***i-th orbital***"

$$\chi_i(x_i,t) = \chi_i^{(0)}(x_i) + \lambda\chi_i^{(1)}(x_i,t) + \lambda^2\chi_i^{(2)}(x_i,t) +$$

The first order HF wavefunction is of

$$\begin{aligned}\Psi_{\mathrm{HF}}^{(1)}(\boldsymbol{x},t) = \hat{\mathcal{A}}\left(\chi_1^{(1)}(x_1,t)\cdots\chi_i^{(0)}(x_i)\cdots\chi_N^{(0)}(x_N)\right)+\cdots \\ +\hat{\mathcal{A}}\left(\chi_1^{(0)}(x_1)\cdots\chi_i^{(1)}(x_i,t)\cdots\chi_N^{(0)}(x_N)\right)+\cdots \\ +\hat{\mathcal{A}}\left(\chi_1^{(0)}(x_1)\cdots\chi_i^{(0)}(x_i)\cdots\chi_N^{(1)}(x_N,t)\right)\end{aligned}$$

Linear Response Theory cont'd

Response equation is therefore,

$$\left(\hat{f}_i - \varepsilon_i + \hbar\omega\right)\chi_i^{(1)}(x_i,\omega) = -\hat{Q}\hat{V}(\omega)\chi_i^{(0)}(x_i)$$

What's the first order change in orbital?

$$\hat{\mathcal{A}}\left(\chi_1^{(0)}(x_1)\cdots\chi_i^{(1)}(x_i,t)\cdots\chi_N^{(0)}(x_N)\right)$$

reads *i*-th orbital is changed to the other which is orthogonal to zero-th orbitals

$$\chi_i^{(1)}(x,t) = \sum_a c_i^a(t)\chi_a(x)$$

sum. over virtual orbitals

Linear Response Theory cont'd

What's the first order **MPS** wavefunction?

Consider perturbation expansion for "***i-th matrix***"

$$A^{[i]}(t) = A^{[i](0)} + \lambda A^{[i](1)}(t) + \lambda^2 A^{[i](2)}(t) +$$

The first order MPS wavefunction is of

$$\begin{aligned}\Psi^{(1)}_{\mathrm{MPS}}(\mathbb{A},t) = {} & A^{[1](1)}(t)\cdots A^{[i](0)}\cdots A^{[k](0)} + \cdots \\ & + A^{[1](0)}\cdots A^{[i](1)}(t)\cdots A^{[k](0)} + \cdots \\ & + A^{[1](0)}\cdots A^{[i](0)}\cdots A^{[k](1)}(t)\end{aligned}$$

45 mins

Linear Response Theory cont'd

Response equation for MPS is of the form

$$\left(\boldsymbol{H}^{[i](0)} - E_0 + \hbar\omega\right) A^{[i](1)}(\omega) = -\hat{Q}\left(\boldsymbol{V}^{[i]}(\omega) + \Delta\boldsymbol{H}^{[i](1)}\right) A^{[i](0)}$$

1. What's the first order change in matrix?
2. What's the first order change in Hamiltonian?

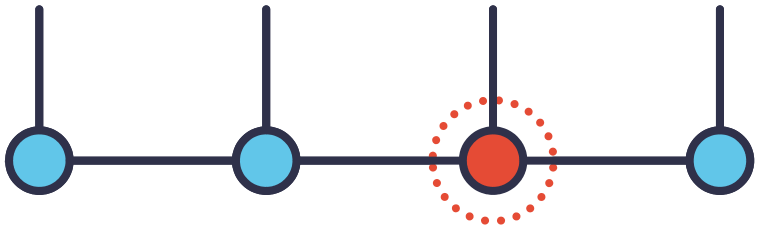
Gauge degrees of freedom in MPS wavefunction introduce some complications...

MPS tangent space

First order change of MPS wavefunction is expanded as

$$\left|\Psi^{(1)}_{\mathrm{MPS}}(\mathbb{A})\right\rangle = \sum_i A^{[i](1)} \left|\partial_i \Psi^{(0)}_{\mathrm{MPS}}(\mathbb{A})\right\rangle$$

$$A^{[3](1)} \left|\partial_3 \Psi^{(0)}_{\mathrm{MPS}}(\mathbb{A})\right\rangle =$$



MPS tangent space cont'd

Naïve differential w.r.t. a site component

$$\left|\partial_i \Psi_0(\mathbb{A})\right\rangle = \frac{\partial}{\partial \boldsymbol{A}^{[i]}}\left|\Psi_0(\mathbb{A})\right\rangle$$

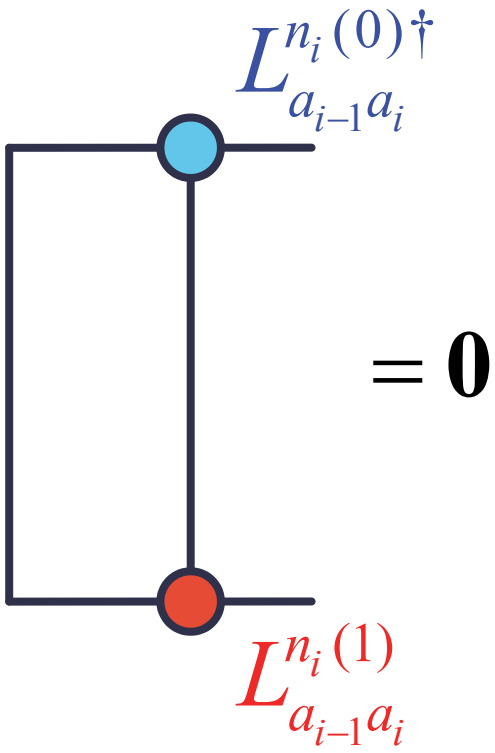
is **redundant** to a differential of another site component

$$\left\langle \partial_i \Psi_0(\mathbb{A}) \middle| \partial_j \Psi_0(\mathbb{A}) \right\rangle \neq 0 \qquad (i \neq j)$$

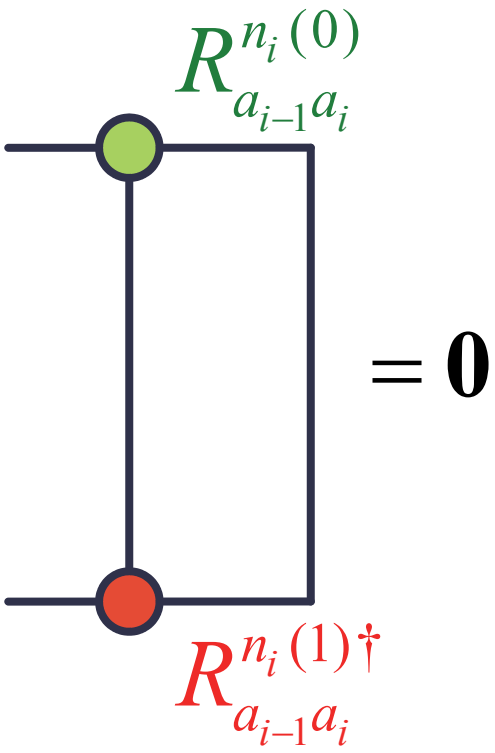
MPS tangent space cont'd

Non-redundant parameterization will satisfy

From the left



From the right



MPS tangent space cont'd

MPS tangent space with left gauge fixed

$$\left|\partial_i \Psi_0(\mathbb{A})\right\rangle_L = \left(\boldsymbol{I} - \boldsymbol{L}^{[i]}\boldsymbol{L}^{[i]\dagger}\right)\frac{\partial}{\partial \boldsymbol{L}^{[i]}}\left|\Psi_0(\mathbb{A})\right\rangle$$

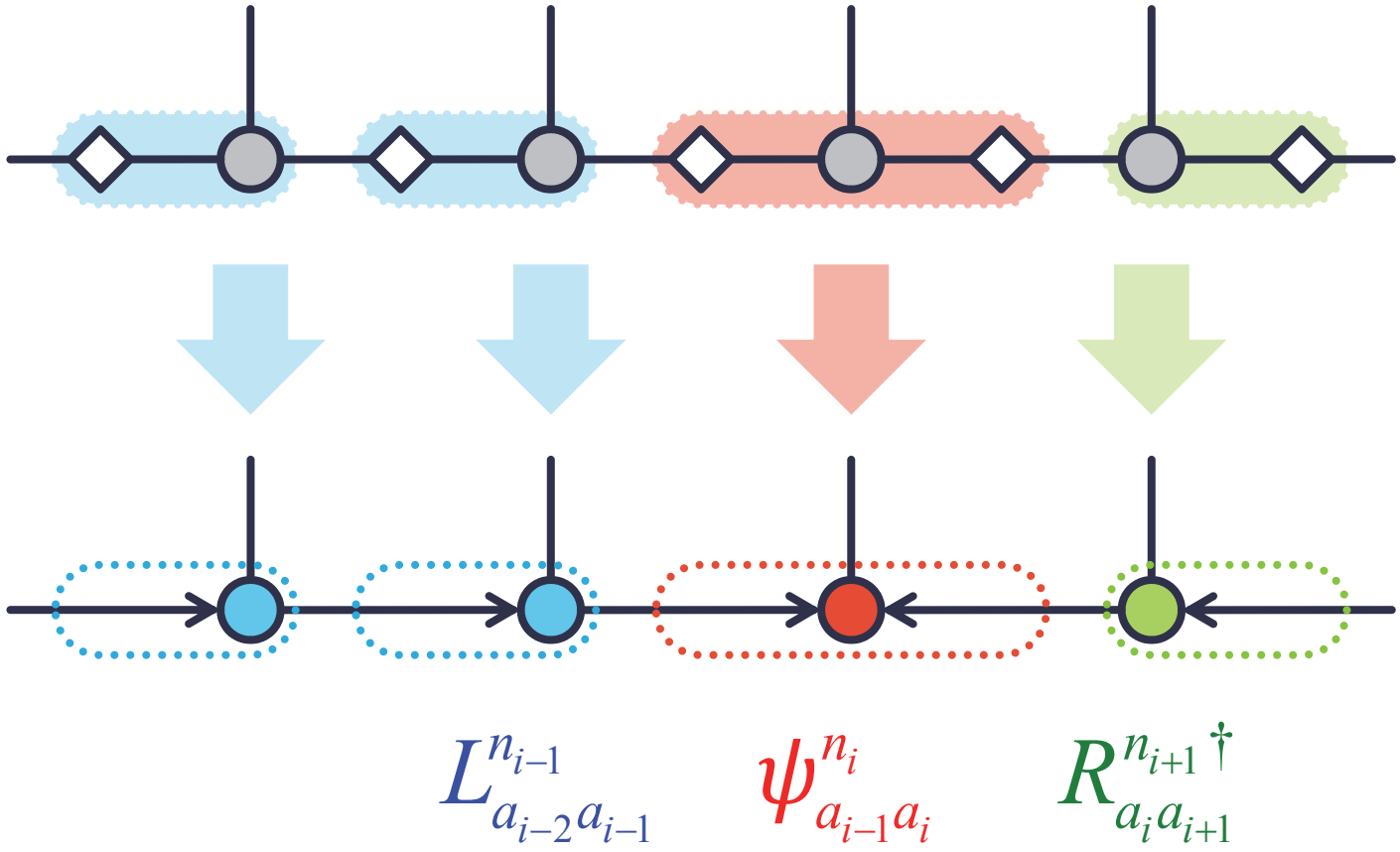
MPS tangent space with right gauge fixed

$$\left|\partial_i \Psi_0(\mathbb{A})\right\rangle_R = \left(\boldsymbol{I} - \boldsymbol{R}^{[i]\dagger}\boldsymbol{R}^{[i]}\right)\frac{\partial}{\partial \boldsymbol{R}^{[i]\dagger}}\left|\Psi_0(\mathbb{A})\right\rangle$$

Depends on choice of gauge (i.e. canonical form)

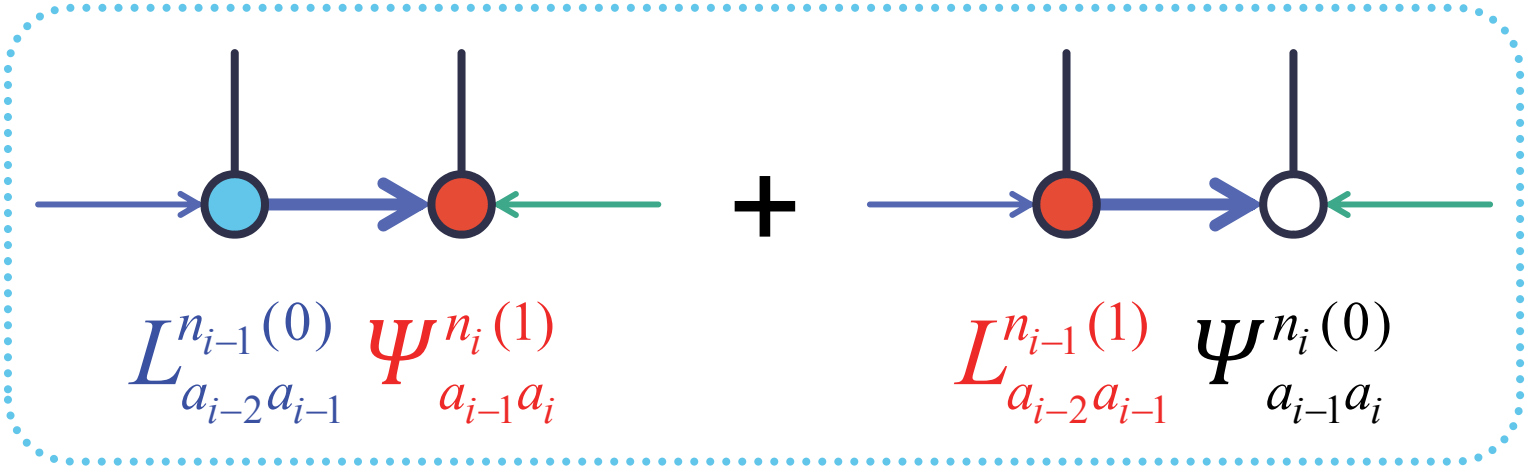
Graphical Language with Gauge

Arrows to distinguish canonical forms,



Gauge transfer

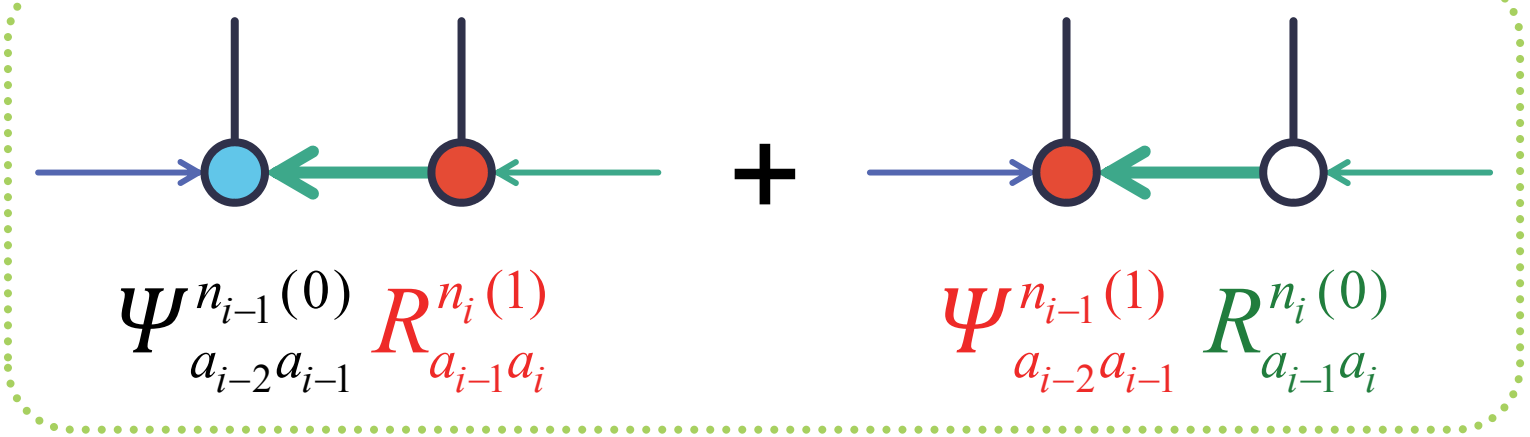
How to keep non-redundancy in the first order MPS?



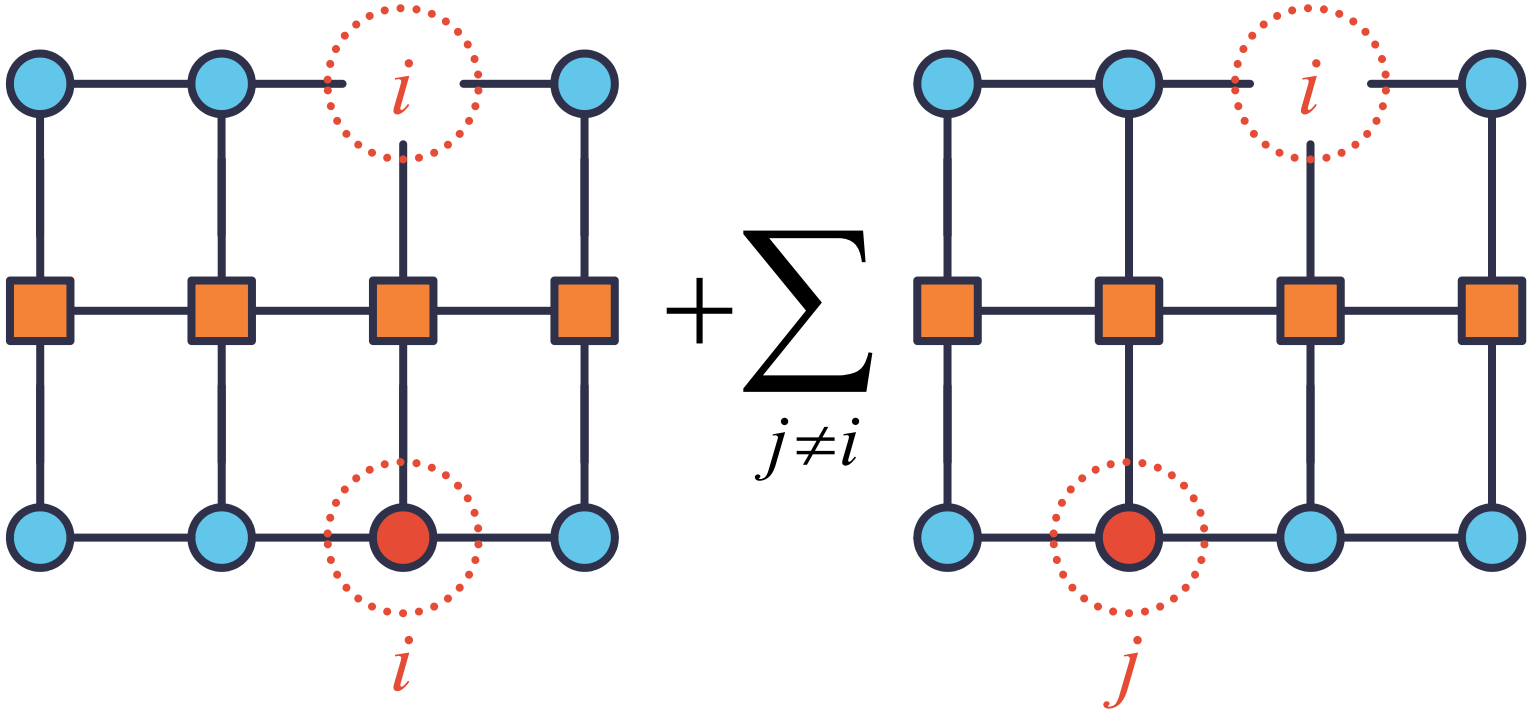
i-th mixed-canonical

=

(*i*−1)-th mixed-canonical



Effective Hamiltonian



$$\boldsymbol{H}^{[i](0)}\,\boldsymbol{A}^{[i](1)}(\omega)$$

First order contribution
from *i*-th site

$$\Delta\boldsymbol{H}^{[i](1)}\,\boldsymbol{A}^{[i](0)}$$

First order contribution
from other sites

Random Phase Approximation

First order wavefunction is approximated as
Harmonic oscillator around the ground state

$$\boldsymbol{A}^{[i](1)}(t) = \boldsymbol{X}^{[i]} e^{-i\omega t} + \boldsymbol{Y}^{[i]*} e^{i\omega t}$$

A couple of response equations
for **real** and **imaginary** parts of wavefunction

$$\left(\boldsymbol{H}^{[i](0)} - E_0 + \hbar\omega\right)\boldsymbol{X}^{[i](1)}(\omega) = -\hat{Q}\left(\Delta\boldsymbol{H}_{\mathrm{X}}^{[i](1)} + \Delta\boldsymbol{W}_{\mathrm{Y}}^{[i](1)}\right)\boldsymbol{A}^{[i](0)}$$

$$\left(\boldsymbol{H}^{[i](0)} - E_0 - \hbar\omega\right)\boldsymbol{Y}^{[i](1)}(\omega) = -\hat{Q}\left(\Delta\boldsymbol{H}_{\mathrm{Y}}^{[i](1)} + \Delta\boldsymbol{W}_{\mathrm{X}}^{[i](1)}\right)\boldsymbol{A}^{[i](0)}$$

Random Phase Approximation cont'd

DMRG-RPA equation is of the form

$$\begin{pmatrix} \boldsymbol{H} & \boldsymbol{W} \\ \boldsymbol{W}^* & \boldsymbol{H}^* \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \hbar\omega \begin{pmatrix} \boldsymbol{S} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{S}^* \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}$$

This is an eigenvalue problem of a huge matrix

$$\boldsymbol{HX} = \begin{pmatrix} \boldsymbol{H}_{11} & \boldsymbol{H}_{12} & \boldsymbol{H}_{13} & \cdots \\ \boldsymbol{H}_{21} & \boldsymbol{H}_{22} & \boldsymbol{H}_{23} & \\ \boldsymbol{H}_{31} & \boldsymbol{H}_{32} & \boldsymbol{H}_{33} & \\ & \vdots & & \end{pmatrix} \begin{pmatrix} \boldsymbol{X}_1 \\ \boldsymbol{X}_2 \\ \boldsymbol{X}_3 \\ \vdots \end{pmatrix}$$

$\mathcal{O}(kdM^2 \times kdM^2)$

$\mathcal{O}(dM^2)$

$$\boldsymbol{X}_i = \left\{ X^{n_i}_{a_{i-1}a_i} \right\}$$

is evaluated via sweep algorithm

Tamm-Dancoff approximation

The DMRG ground state is a good reference,

$$\begin{pmatrix} \boldsymbol{H} & \boldsymbol{W} \\ \boldsymbol{W}^* & \boldsymbol{H}^* \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \hbar\omega \begin{pmatrix} \boldsymbol{S} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{S}^* \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}$$

Matrix $\boldsymbol{W}$ must be almost $\boldsymbol{0}$

$$\boldsymbol{HX} = \hbar\omega \boldsymbol{SX}$$

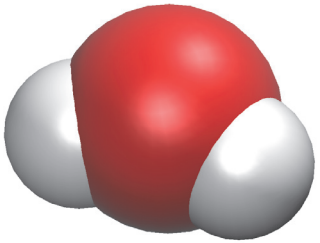
gives Tamm-Dancoff approximation (i.e. CI-Single)

DMRG-LRT: Illustrative applications

state	$E_{conv.}$ / E_h	(E – $E_{conv.}$) / mE_h		
	SA / M = 2000	SA / M = 500	**TDA / M = 500**	EOM-CCSD
X^1A_1	-76.241697	0.11	**0.01**	3.68
1^1B_1	-75.939176	0.20	**0.02**	1.50
1^1A_2	-75.864445	0.20	**0.02**	2.07
2^1A_1	-75.842487	0.18	**0.12**	2.08
1^1B_2	-75.765964	0.21	**0.02**	2.55
2^1B_2	-75.696018	0.20	**0.45**	4.14
3^1A_1	-75.584080	0.16	**0.10**	5.13
4^1A_1	-75.462977	0.26	**2.69**	N/A
2^1A_2	-75.448180	0.23	**0.04**	4.53
3^1A_2	-75.403286	0.33	**0.27**	N/A
2^1B_1	-75.401515	0.28	**0.25**	24.20
3^1B_1	-75.381977	0.26	**0.07**	N/A
3^1B_2	-75.322655	0.26	**0.07**	5.75

H_2O / cc-pVDZ

DMRG (10e in 24o)



First order space involves multi-particle excitations

MPS & DMRG

- Many-body wavefunction from low-entangled limit
- DMRG algorithm is derived from variational principle for MPS wavefunction
- Time-evolution can be done easily in terms of MPS/MPO multiplications
- The similarity b/w HF and DMRG leads “post-DMRG” methods to beyond the DMRG

Thank you for your kind attention