Title: Applying DMRG to Non-relativistic Continuous Systems in 1D and 3D

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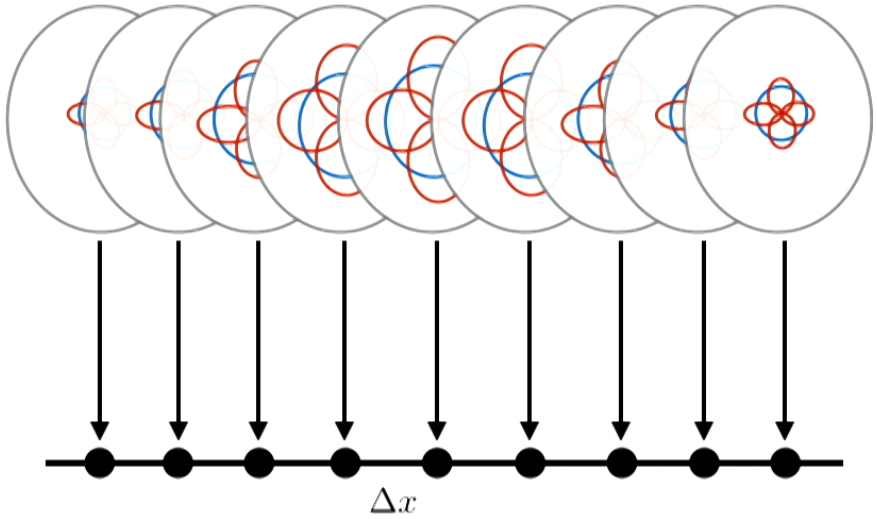
Abstract: The density matrix renormalization group works very well for one-dimensional (1D) lattice systems, and can naively be adapted for non-relativistic continuum systems in 1D by discretizing real space using a grid. I will discuss challenges inherent in this approach and successful applications. Recently, the success of the grid approach for 1D motivated us to extend the approach to 3D by treating the transverse directions with a basis set. This hybrid grid/basis-set approach allows DMRG to scale much better for long molecules and we obtain state-of-the-art results with modest computing resources. A key component of the approach is a powerful algorithm for compressing long-range interactions into a matrix product operator which I will present in some detail.

Applying DMRG to Continuous Systems in 1D and 3D



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SIMONS FOUNDATION

Why study continuum systems?

"Theory of everything" of chemistry and cond. mat.

$$H = -\frac{1}{2m}\sum_{j}^{N_e}\nabla_j^2 - \frac{1}{2M}\sum_{a}^{N_A}\nabla_a^2$$

$$-\sum_{j}^{N_e}\sum_{a}^{N_A}\frac{Z_a}{|\mathbf{r}_j - \mathbf{R}_a|} + \frac{1}{2}\sum_{j}^{N_e}\sum_{j'}^{N_e}\frac{1}{|\mathbf{r}_j - \mathbf{r}_{j'}|} + \frac{1}{2}\sum_{a}^{N_A}\sum_{a'}^{N_A}\frac{Z_a Z_{a'}}{|\mathbf{R}_a - \mathbf{R}_{a'}|}$$

Describes much of everyday world

Laughlin, Pines, PNAS **97**, 28 (2000)

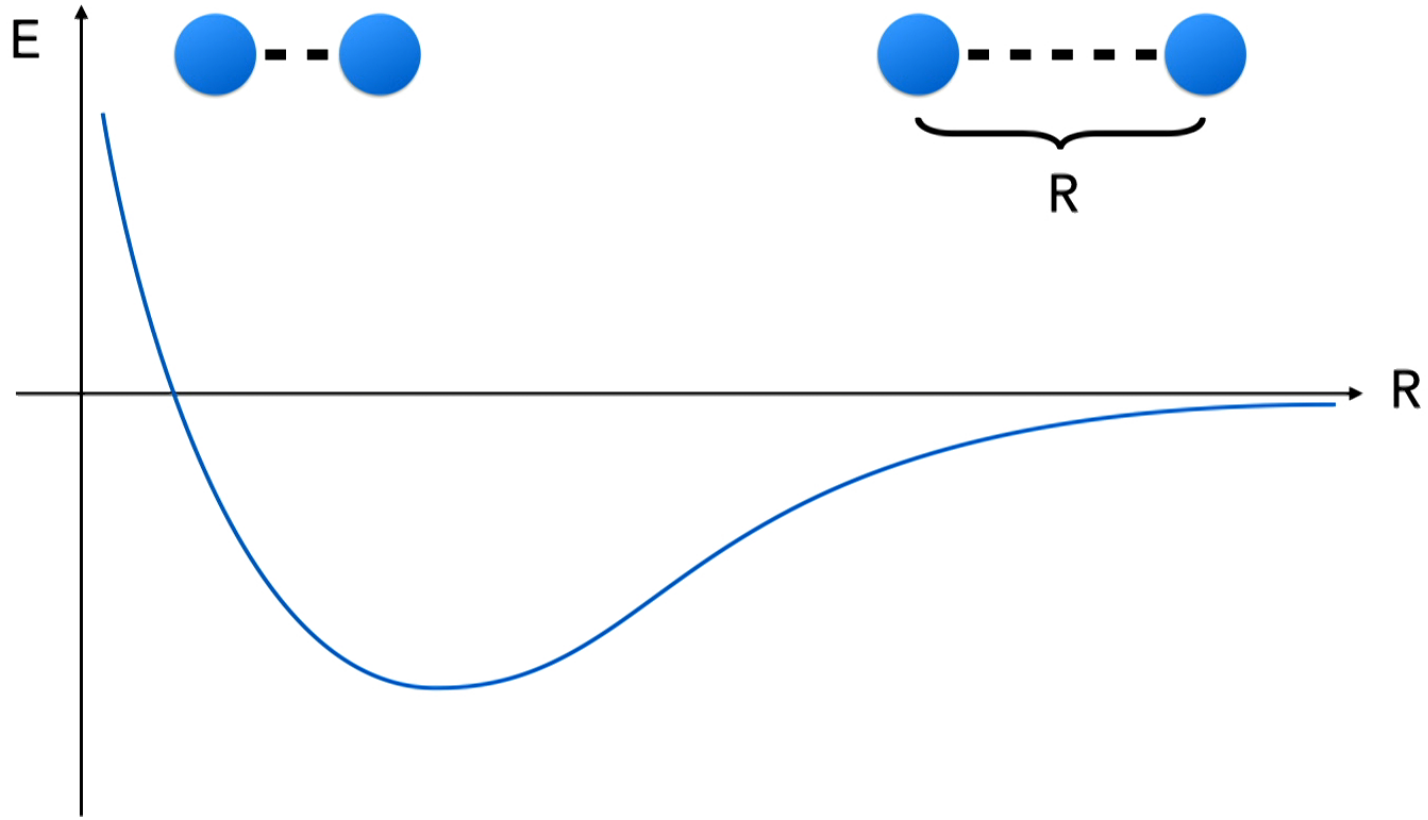
Often use Born-Oppenheimer approximation

Electronic structure problem of interacting electrons in fixed nuclear potential

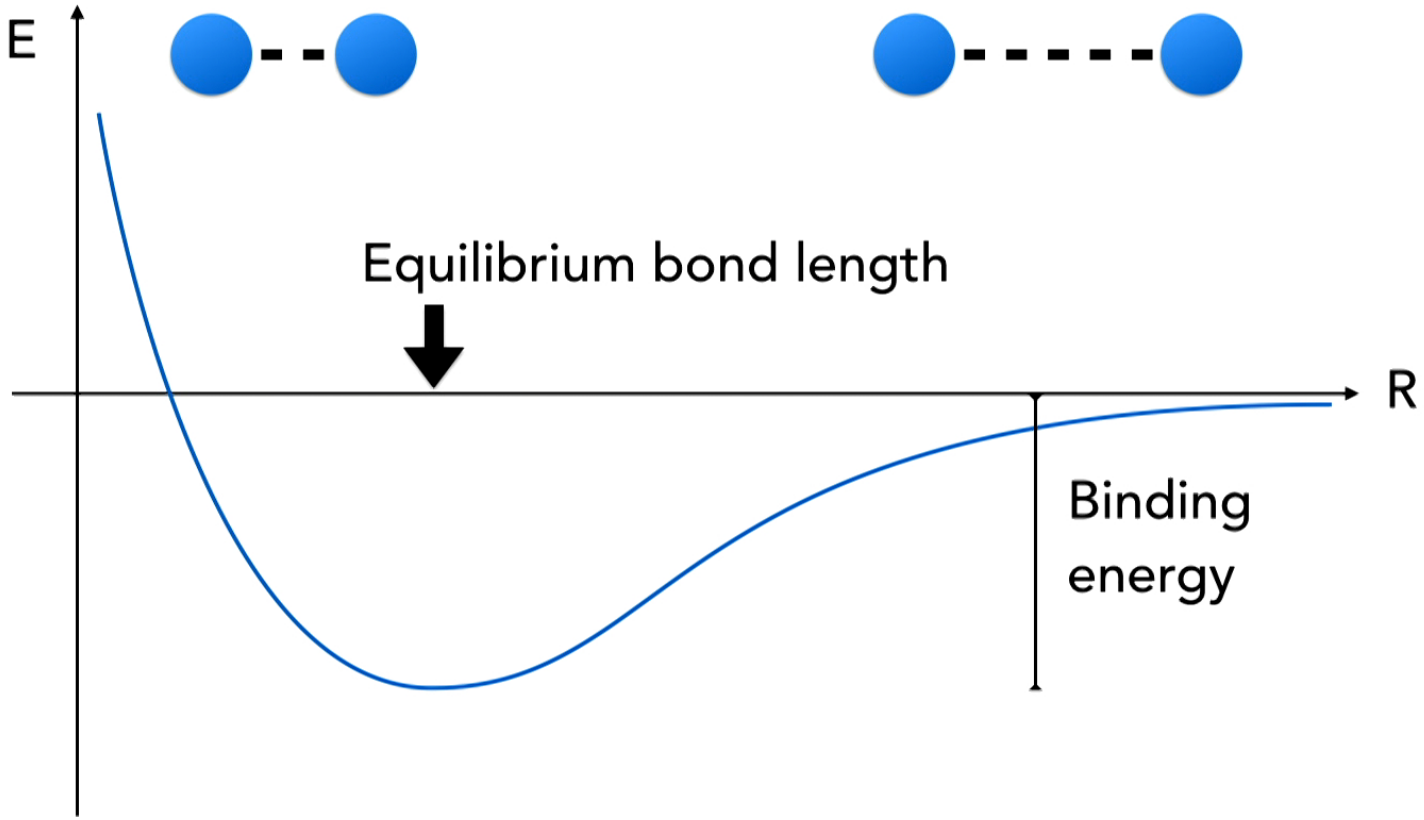
$$H = \sum_{j}^{N_e} \left(-\frac{1}{2m} \nabla_j^2 + v_{\text{nuc}}(\mathbf{r}_j) \right) + \frac{1}{2} \sum_{j}^{N_e} \sum_{j'}^{N_e} \frac{1}{|\mathbf{r}_j - \mathbf{r}_{j'}|}$$

where $$v_{\text{nuc}}(\mathbf{r}_j) = -\sum_{j}^{N_e} \sum_{a}^{N_A} \frac{Z_a}{|\mathbf{r}_j - \mathbf{R}_a|}$$

Example electronic structure problem:
energy of diatomic molecule, separation R



Contains wealth of information



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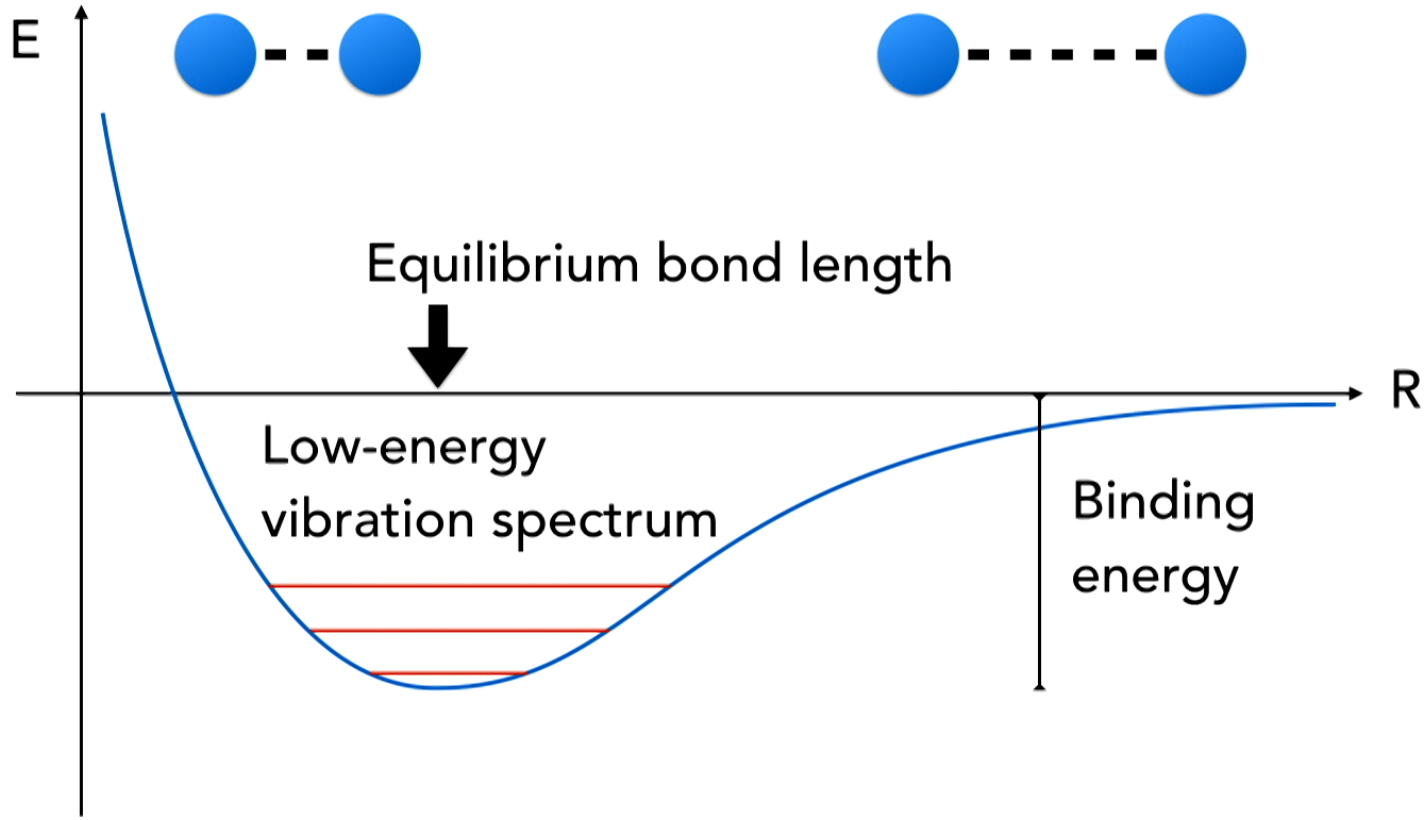


Goal: apply DMRG* to continuum systems

DMRG advantages:

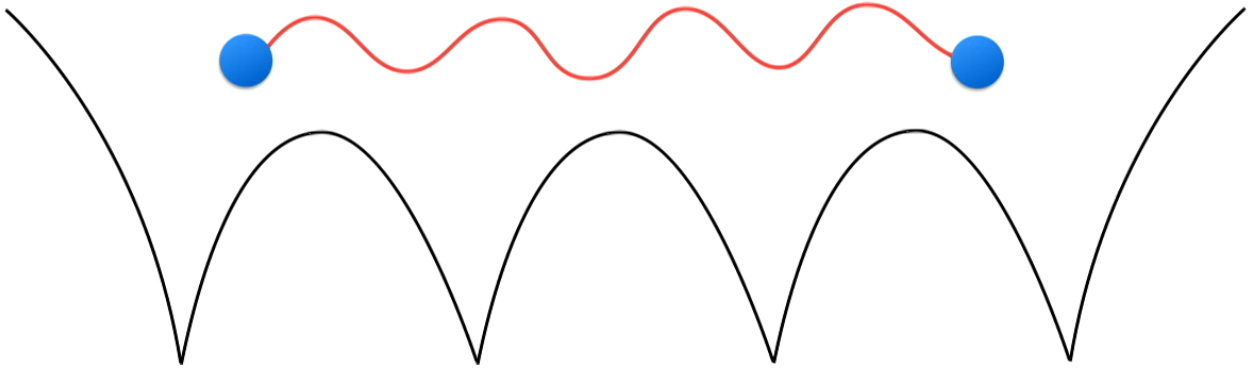
- high accuracy (and no statistical error)
- access many observables (via wavefunction)
- handle strong correlation
- excited states, finite T, dynamics

* density matrix renormalization group

Simplest starting point: 1D continuum

DMRG is a 1D method

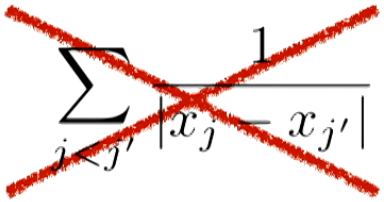
Toy "universe" for developing electronic structure methods



Coulomb interaction very pathological in 1D

$$\sum_{j<j'} \frac{1}{|x_j - x_{j'}|}$$

Coulomb interaction very pathological in 1D



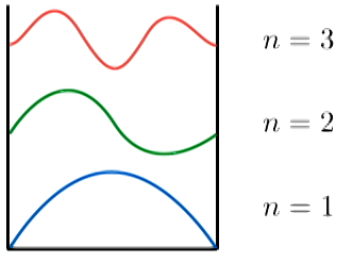
Toy system anyhow, so use one of

- exponential interaction
- "soft-Coulomb" interaction

$$v_{\mathrm{sc}}(x_j - x_{j'}) = \frac{1}{\sqrt{1 + (x_j - x_{j'})^2}}$$

Two Continuum Approaches

Approach 1: basis set $c_n = \int_x \phi_n(x)\hat{\psi}(x)$



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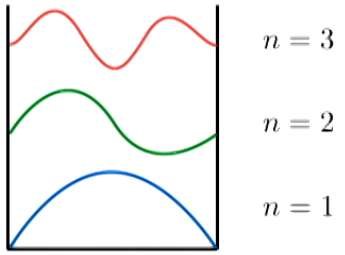

$$T = -\frac{1}{2}\int_x \hat{\psi}^\dagger(x)\partial_x^2\hat{\psi}(x) \quad \rightarrow \quad \sum_{nm} t_{nm}c_n^\dagger c_m$$

$$V = \int_{x<x'} v(x-x')n(x)n(x') \quad \rightarrow \quad \sum_{nmpq} v_{nmpq}c_n^\dagger c_m^\dagger c_p c_q$$

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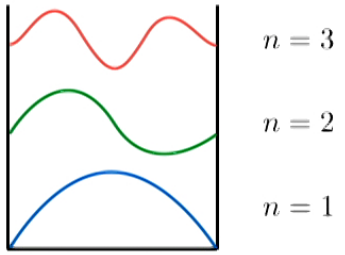

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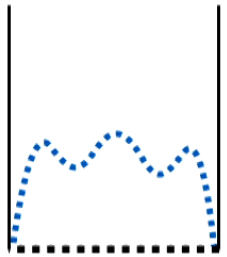
- Loss of locality
- Must compute integrals
+ Variational

Two Continuum Approaches

Approach 2: grid approximation $c_j = \sqrt{a}\ \hat{\psi}(x_j)$



$$T = -\frac{1}{2}\int_x \hat{\psi}^\dagger(x)\partial_x^2\hat{\psi}(x) \quad \rightarrow \quad -\frac{1}{2a^2}\sum_j (c_j^\dagger c_{j+1} - 2n_j + c_{j+1}^\dagger c_j) + \mathcal{O}(a^2)$$

Two Continuum Approaches

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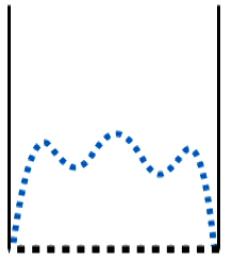

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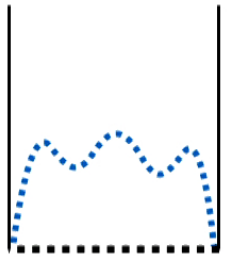

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+ Local / short range
+ No integrals to compute
- May not be variational

For DMRG, grid is a good choice

+ DMRG scales nearly linearly with 1D system size for local Hamiltonians

+ Use higher-order grid approx's to kinetic energy to reduce grid error

+ Long-range interactions retain two-body form

$$\int_{x<x'} v(x-x')n(x)n(x') \longrightarrow \sum_{j<j'} v(x_j - x_{j'})n_j n_{j'}$$

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$$\int_{x<x'} v(x-x')n(x)n(x') \longrightarrow \sum_{j<j'} v(x_j - x_{j'})n_j n_{j'}$$

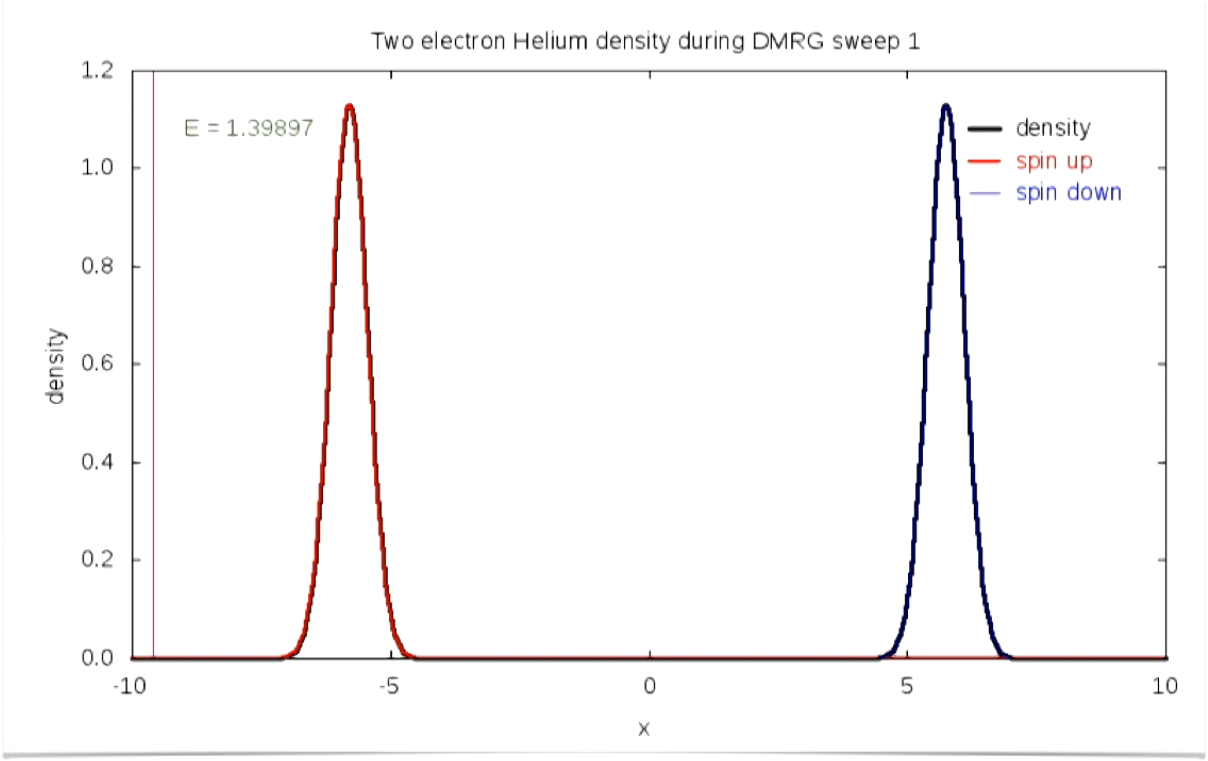
- High energy scale (grid KE) and huge Hilbert space can slow down convergence

$$H \approx -\frac{1}{2a^2}\sum_j (c_j^\dagger c_{j+1} - 2n_j + c_{j+1}^\dagger c_j) + \ldots$$

Ways to handle:

- prepare high-quality initial state using multigrid DMRG* (works well)
- just do lots of DMRG sweeps at low initial accuracy

*Dolfi, Bauer, Troyer, Ristivojevic, PRL **109**, 020604 (2012)

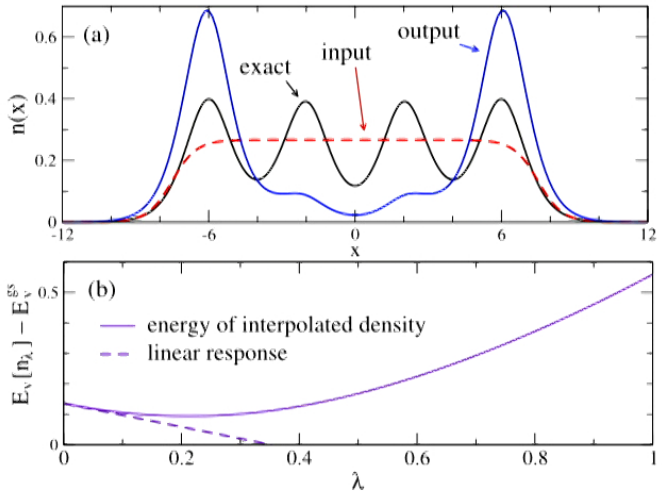

Two electron Helium density during DMRG sweep 1
E = 1.39897
density
spin up
spin down
density
x
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-10
-5
0
5
10

$v(x)$

1D Continuum Applications (Briefly)

#1: Convergence of Kohn-Sham Equations

Explore convergence of Kohn-Sham density functional theory (DFT) with exact functional



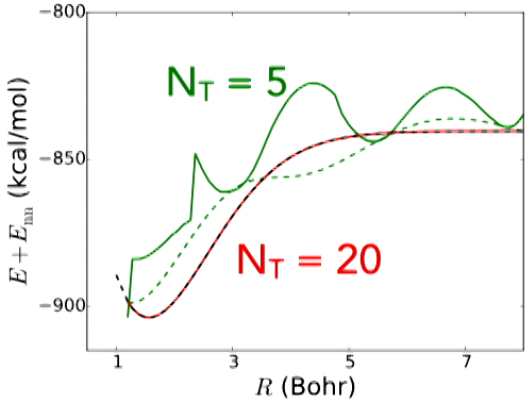
- Proof that KS eqs. always converge for small steps
- Step size needed becomes small for strong correlation

Wagner, Stoudenmire, Burke, White, PRL **111**, 093003 (2013)

Wagner, Baker, Stoudenmire, Burke, White, PRB **90**, 045109 (2014)

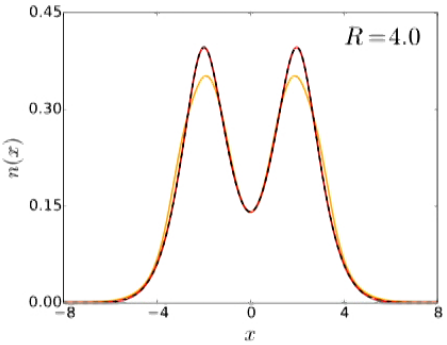
#2: Machine Learning the Density Functional

Interacting densities used to train machine-learning model of the exact DFT functional (of 1D)



Machine-learned binding energy curve

Self-consistent densities calculated using learned functional



Li, Baker, White, Burke, PRB **94**, 245129 (2016)

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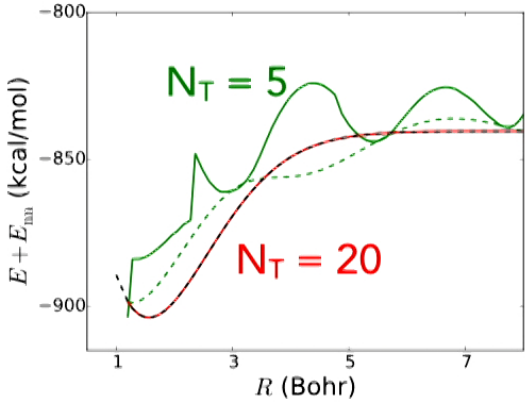

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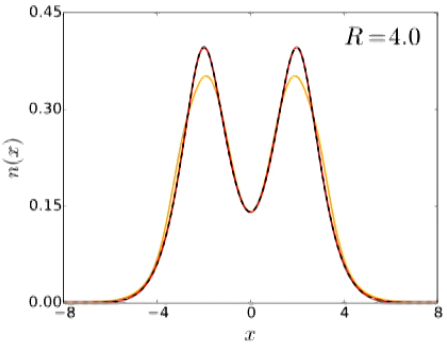
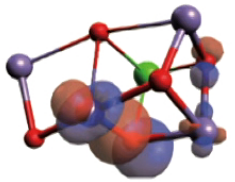


Li, Baker, White, Burke, PRB **94**, 245129 (2016)

Sliced-Basis DMRG for 3D Continuum

Motivation

DMRG powerful for quantum chemistry
Can deal well with strong correlation



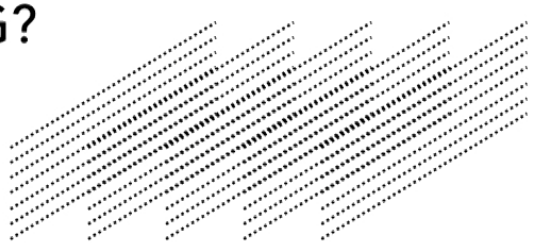
Mainly have used basis sets...
Two big problems:

1. usual limitation of DMRG to quasi-1D chains of atoms
2. limitation to 100-200 basis functions maximum

Can we use 1D continuum experience to help with #2?

Kurashige, Chan, Yanai, Nat. Chem. **5**, 660 (2013)
Chan, Sharma, Ann. Rev. Phys. Chem. **62**, 465 (2011)
White, Martin, J Chem Phys **110**, 4127 (1999)

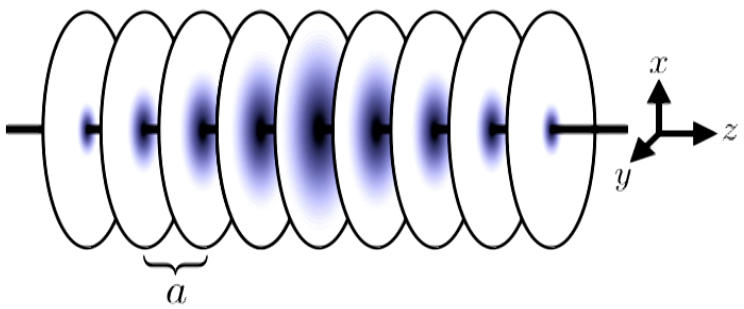
3D Grid DMRG?



Too many sites!

Hybrid grid + basis set DMRG...

High-level idea:



"Slice" 3D continuum into planes (**grid** along z direction)

Use **basis set** for remaining directions (x,y)

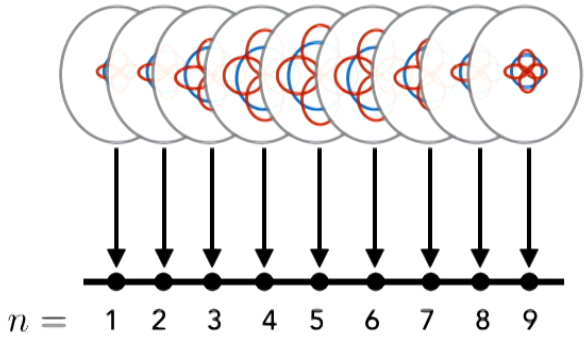
Stoudenmire, White, arxiv: 1702.03650

Sliced Basis Set

Slices roughly equivalent to using basis set of "functions":

$$\phi_{nj}(\mathbf{r}) = \delta^{\frac{1}{2}}(x - x_n)\varphi_{nj}(y, z)$$

$$x_n = n\,a$$



Functions on different slices $n' \neq n$ automatically ortho.

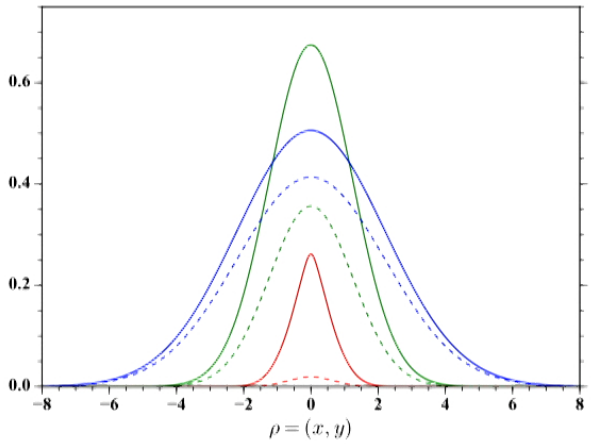
In transverse direction, orthogonalize the basis set
[$\varphi_{nj}(y, z)$ orthogonal for same n and $j' \neq j$]

Stoudenmire, White, arxiv: 1702.03650

To make basis of a slice:

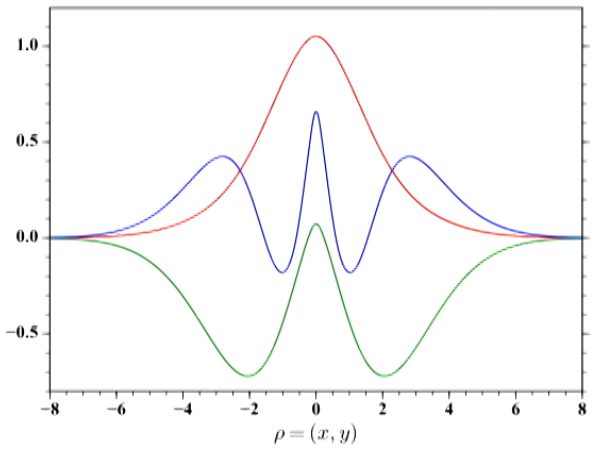
1. restrict standard basis set to each slice

2. orthogonalize functions



1

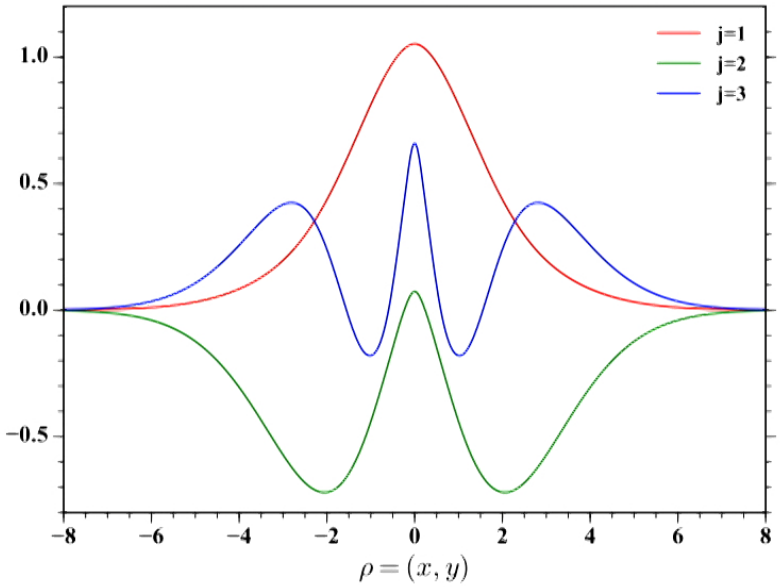
2

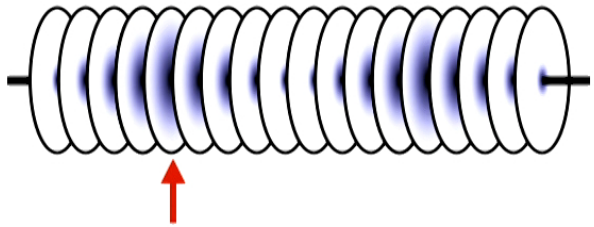


Stoudenmire, White, arxiv: 1702.03650

Constructing a Sliced Basis

H_2 molecule, slice through nucleus

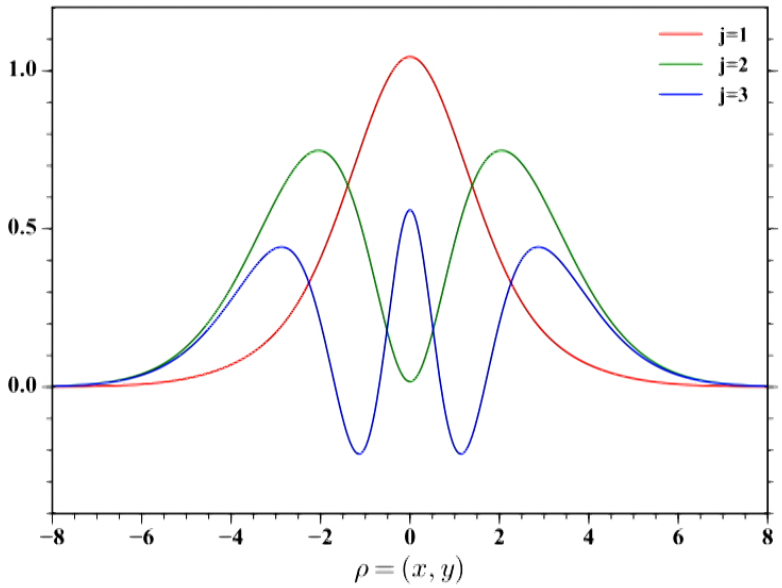


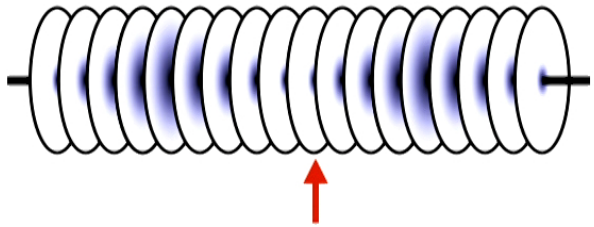


Orbitals taken from cc-pvTZ,
S orbitals only

Constructing a Sliced Basis

H_2 molecule, slice through bond

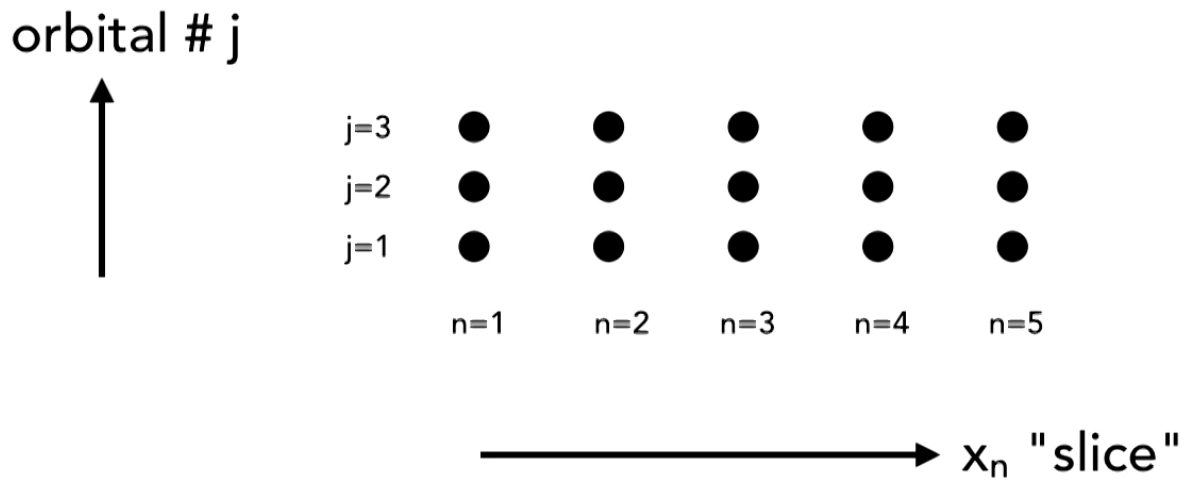




Orbitals taken from cc-pvTZ,
S orbitals only

Form of Hamiltonian

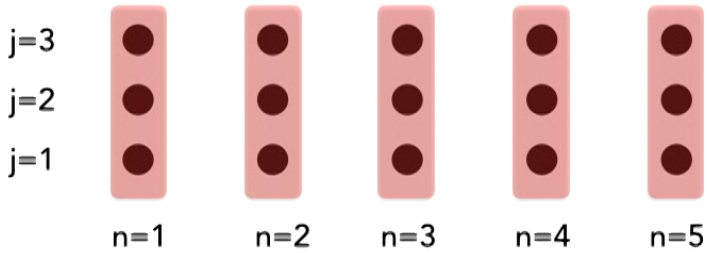
Discrete (n,j) labels can be viewed as a "ladder" lattice



Form of Hamiltonian

Hamiltonian turns into three pieces

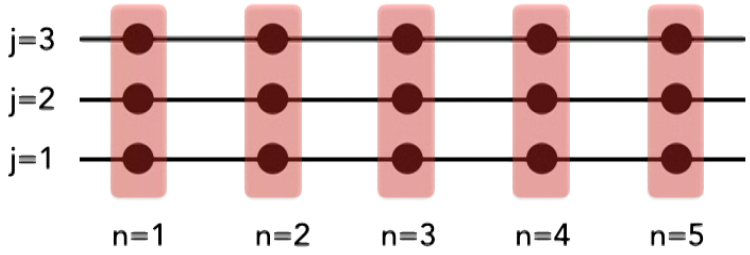
$$H = \sum_n H_n^{(\text{slice})}$$



Form of Hamiltonian

Hamiltonian turns into three pieces

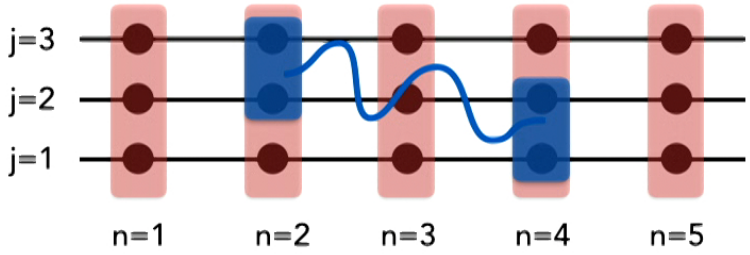
$$H = \sum_n H_n^{(\text{slice})} + T^{(\text{grid})}$$



Form of Hamiltonian

Hamiltonian turns into three pieces

$$H = \sum_n H_n^{(\text{slice})} + T^{(\text{grid})} + V$$



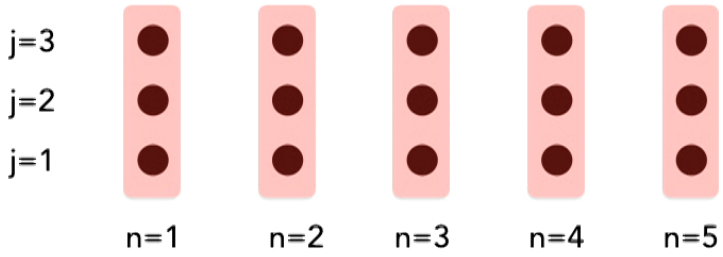
Form of Hamiltonian

$$H = \sum_n H_n^{(\text{slice})} + T^{(\text{grid})} + V$$

$$H_n^{(\text{slice})} = \sum_{ij} t_n^{ij} c_{ni}^\dagger c_{nj} + \sum_{ijkl} V_n^{ijkl} c_{ni}^\dagger c_{nj}^\dagger c_{nk} c_{nl}$$

Full complexity of orbital basis, but confined to each slice

$(N_{\text{orb}})^4$ terms but N_{orb} is small



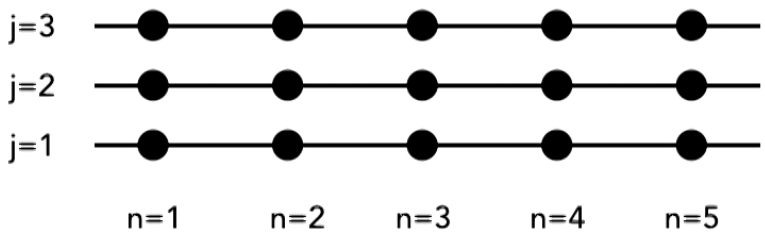
Form of Hamiltonian

$$H = \sum_n H_n^{(\text{slice})} + T^{(\text{grid})} + V$$

$$T^{(\text{grid})} = -\frac{1}{2a^2} \sum_{nj} (c_{nj}^\dagger c_{n+1,j} - 2n_{nj} + c_{n+1,j}^\dagger c_{nj})$$

Grid kinetic energy: hop without changing orbital j *

Can use higher-order discrete deriv. to reduce error in a



* assuming uncontracted basis set

Form of Hamiltonian

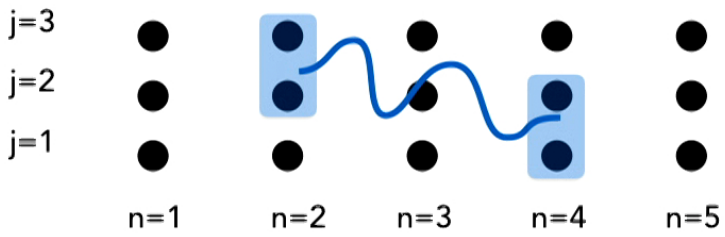
$$H = \sum_n H_n^{(\text{slice})} + T^{(\text{grid})} + V$$

$$V = \sum_{nn'} \sum_{ijkl} V_{mjk}^{nil} (c_{ni}^\dagger c_{nl})(c_{mj}^\dagger c_{mk})$$

Operators $c^\dagger$ and c paired within rungs

Consists of $N_z^2 N_{\text{orb}}^4$ terms ($\ll N^4$)

Can get even better scaling with compression (matrix product operator) techniques

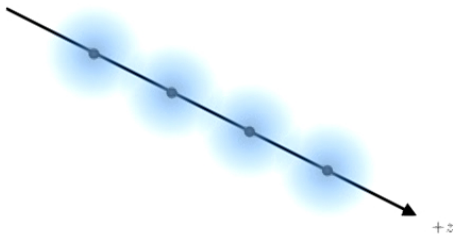


Hydrogen chains

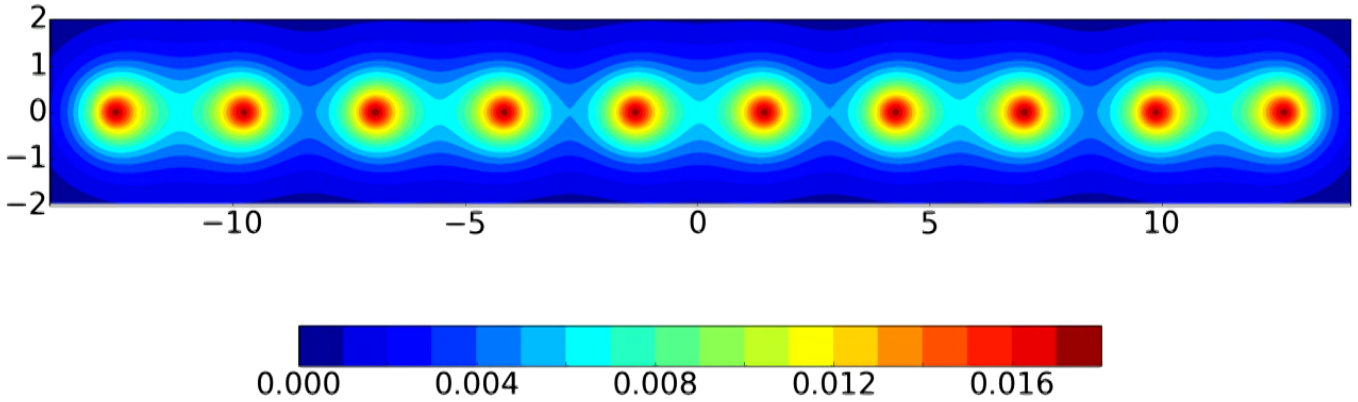
Electronic structure of hydrogen chains with fixed nuclei

Simple, but can explore

- strong correlation
- basis set effects
- extended systems (thermodynamic limit)

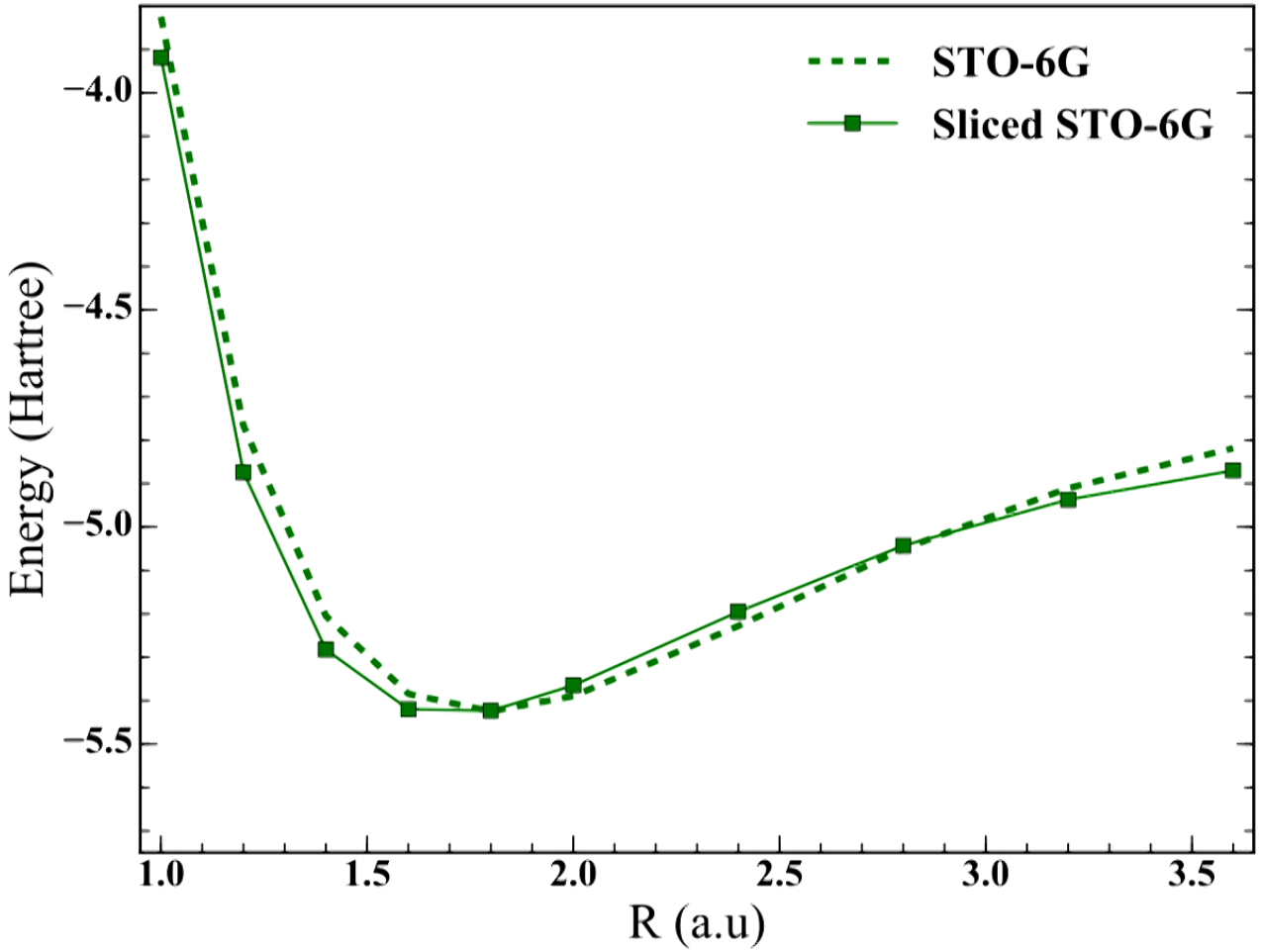


Density plot – chain of 10 hydrogen atoms

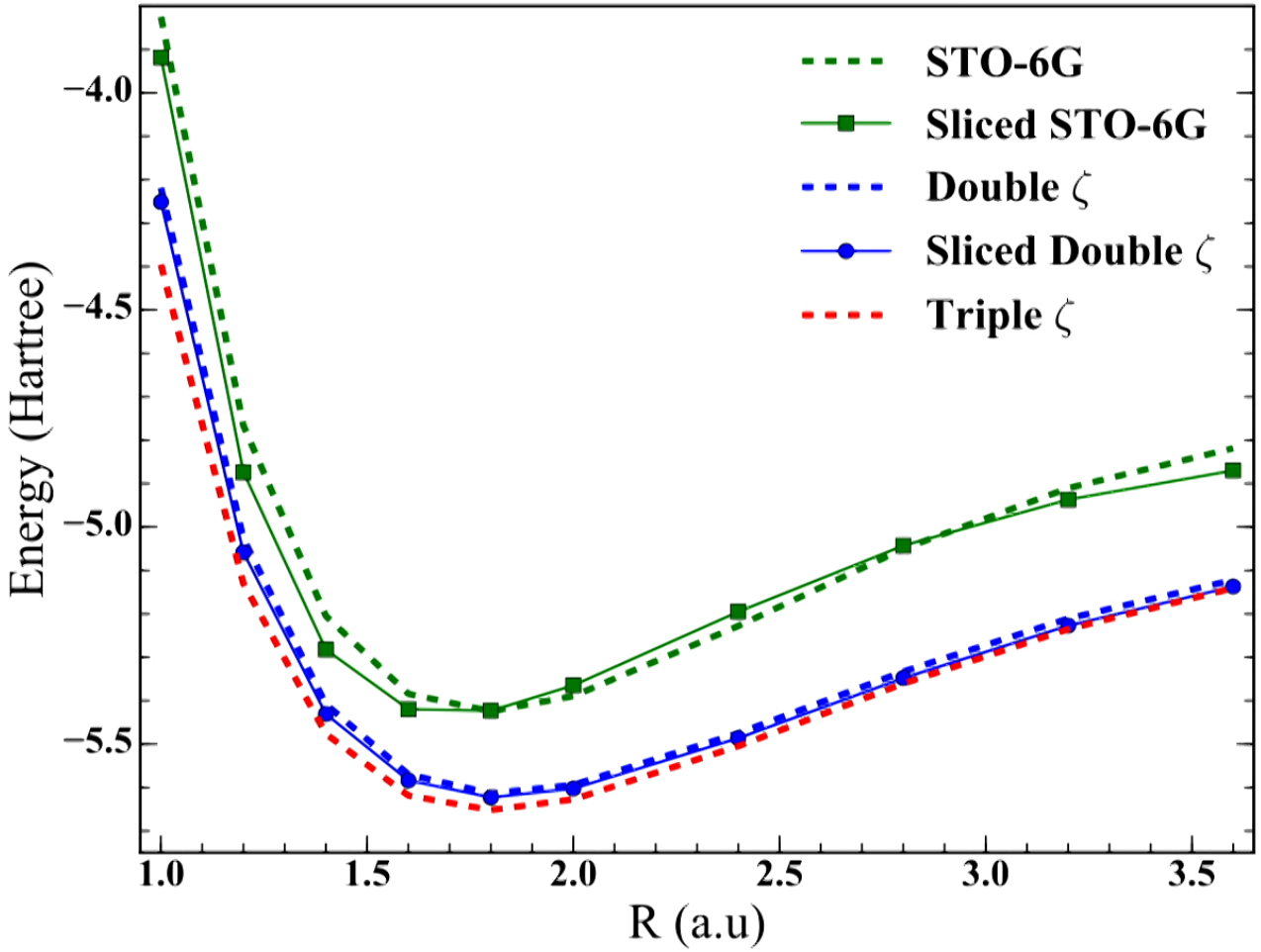


Spacing R=2.8; "sliced" cc-pvDZ basis

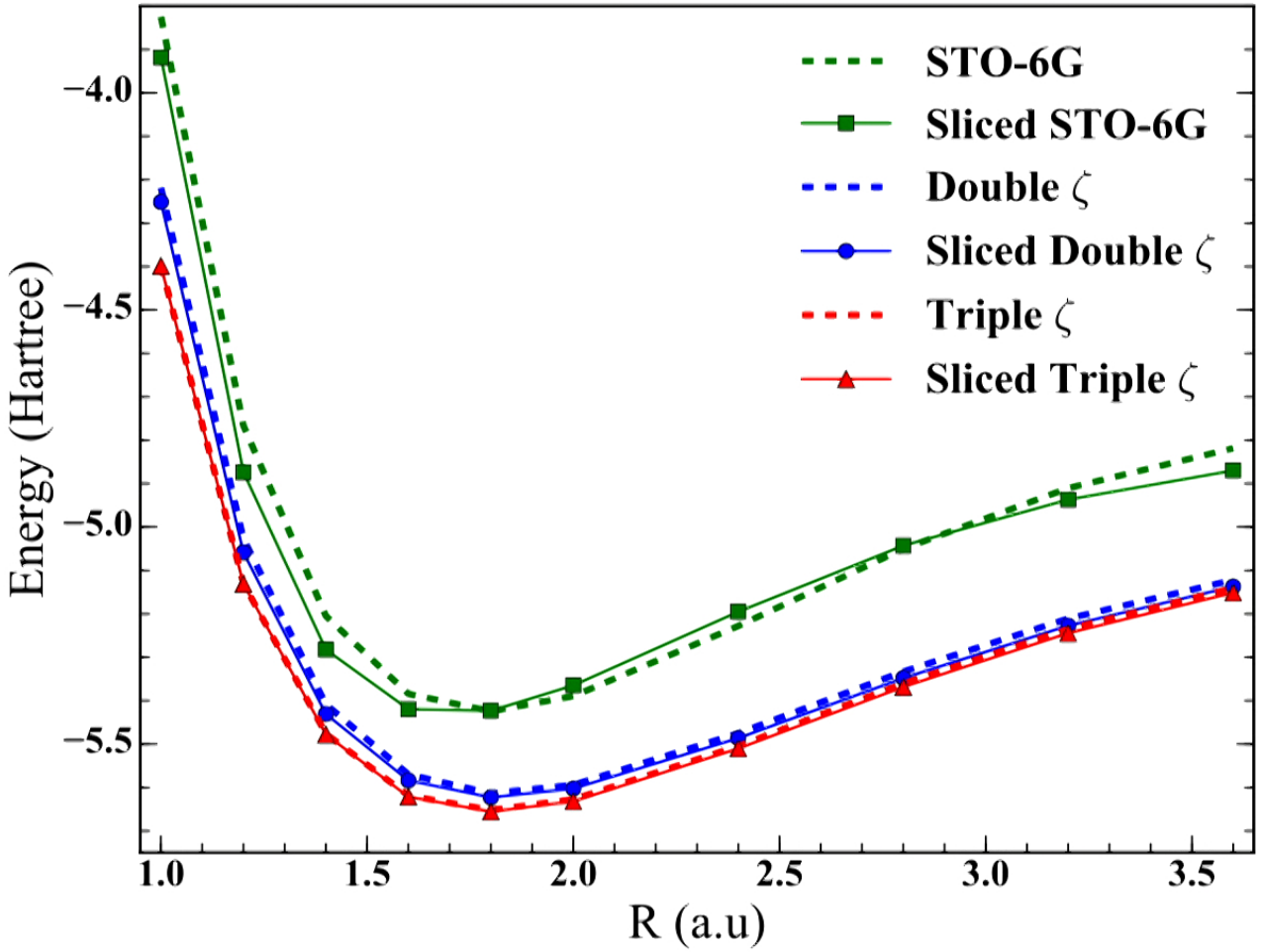
Chains of N_a = 10 hydrogen atoms, spacing R (fixed nuclei)



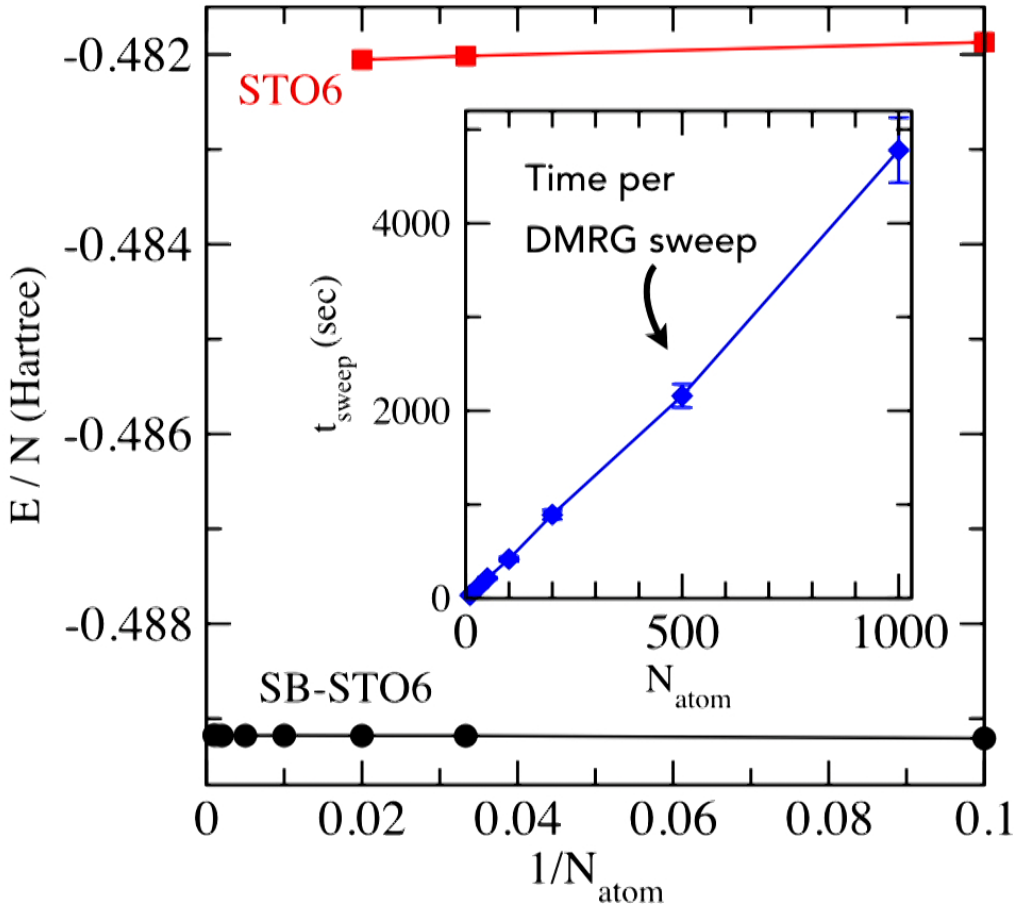
Chains of N_a = 10 hydrogen atoms, spacing R (fixed nuclei)



Chains of N_a = 10 hydrogen atoms, spacing R (fixed nuclei)



Linear scaling to 1000 hydrogen atoms (in minimal basis)



Scaling

Different slices *defined* to be orthogonal

$\Longrightarrow$ number of interaction terms defining Hamiltonian scales as N_z^2

Using matrix product operator (MPO) technology, can compress interactions further

Matrix size basically *independent* of system size.

Final algorithm scales linearly ($\sim N_z$)

Compression of Long-Range Interactions

3. SVD right-hand matrix to get X matrix (*efficiently*)

$$\begin{bmatrix} W_{12}^{(p)} & W_{13}^{(p)} & \cdots \\ W_{22}^{(p)} & W_{23}^{(p)} & \cdots \\ \vdots & & \\ V_{p,p} & V_{p,p+1} & \cdots \end{bmatrix} = X^{(p+1)} W^{(p+1)}$$

4. X matrices relate different U matrices to each other

$$\begin{bmatrix} U^{(p)} & \\ & 1 \end{bmatrix} X^{(p+1)} = U^{(p+1)}$$

Summary & Future Directions

- Grid approach convenient, natural for DMRG in 1D continuum (non-relativistic)
- Extending approach to 3D by attaching transverse basis functions extremely powerful for chemistry
- Straightforward to apply advanced DMRG techniques: infinite & parallel DMRG
- Higher-Z atoms in progress, should work well

Stoudenmire, White, arxiv: 1702.03650

Form of Hamiltonian

$$H = \sum_n H_n^{(\text{slice})} + T^{(\text{grid})} + V$$

$$H_n^{(\text{slice})} = \sum_{ij} t_n^{ij} c_{ni}^\dagger c_{nj} + \sum_{ijkl} V_n^{ijkl} c_{ni}^\dagger c_{nj}^\dagger c_{nk} c_{nl}$$

Full complexity of orbital basis, but confined to each slice

$(N_{\text{orb}})^4$ terms but N_{orb} is small