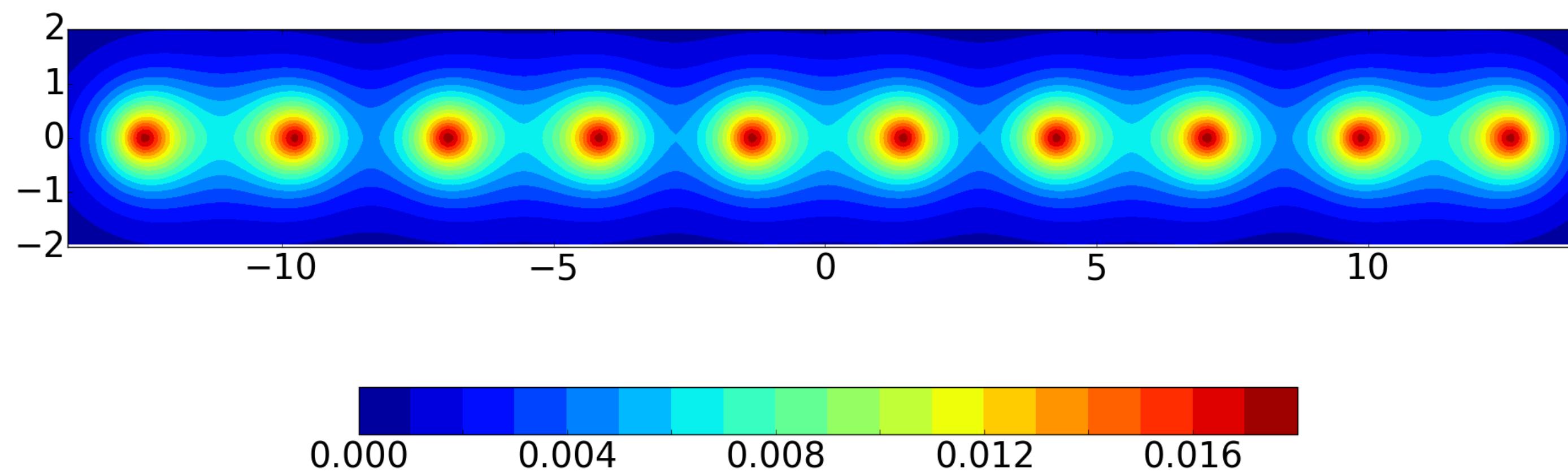


Sliced basis DMRG



Collaborator: Miles Stoudenmire (soon to join the Flatiron Institute of the Simons Foundation)

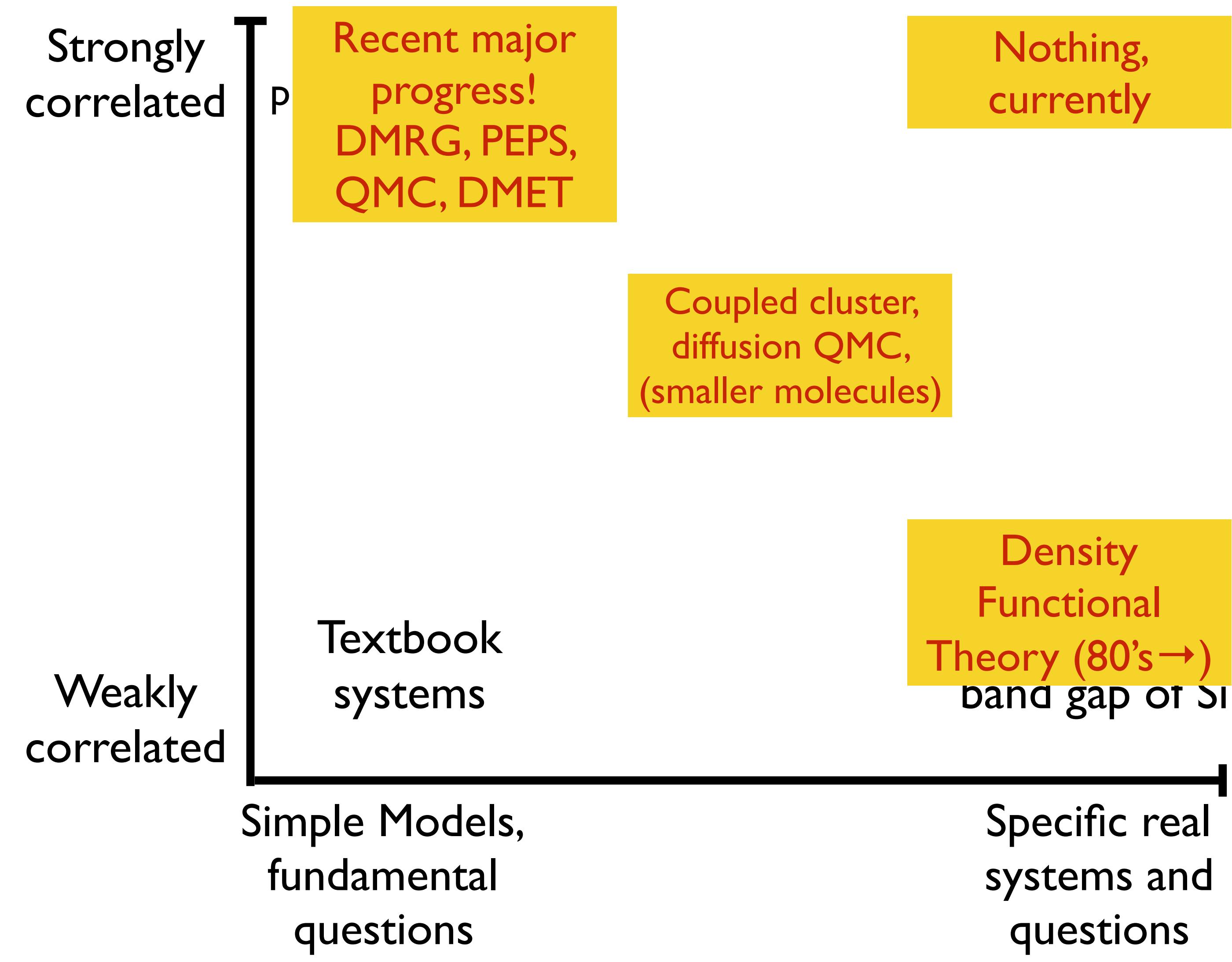
Thanks to the Simons Foundation, and the DOE

Calculations done using ITensor (itensor.org)



Solving the many electron Schrödinger Eqn

Strong Correlation versus accurate continuum electronic structure/chemistry

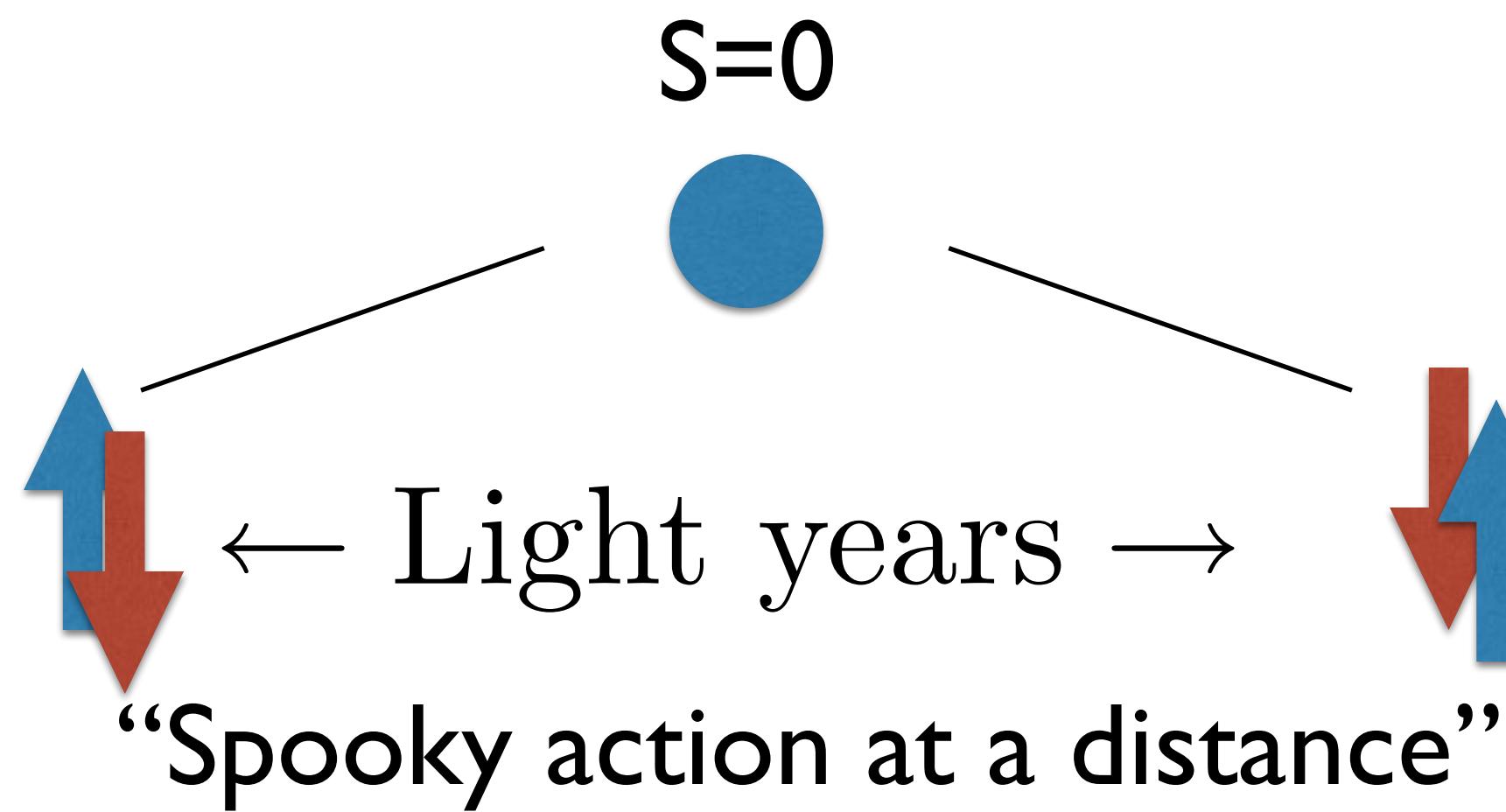


One of the nicer tools to try to get to the upper right corner is quantum chemistry DMRG. A key weakness of QCDMRG is poor scaling of the computation time with the system size N .

Sliced Basis DMRG is a modification of QCDMRG that dramatically improves the scaling with N for chain-like systems—all the way to linear scaling in the length.

DMRG and tensor networks are low entanglement approximations

Einstein Poldosky Rosen paradox

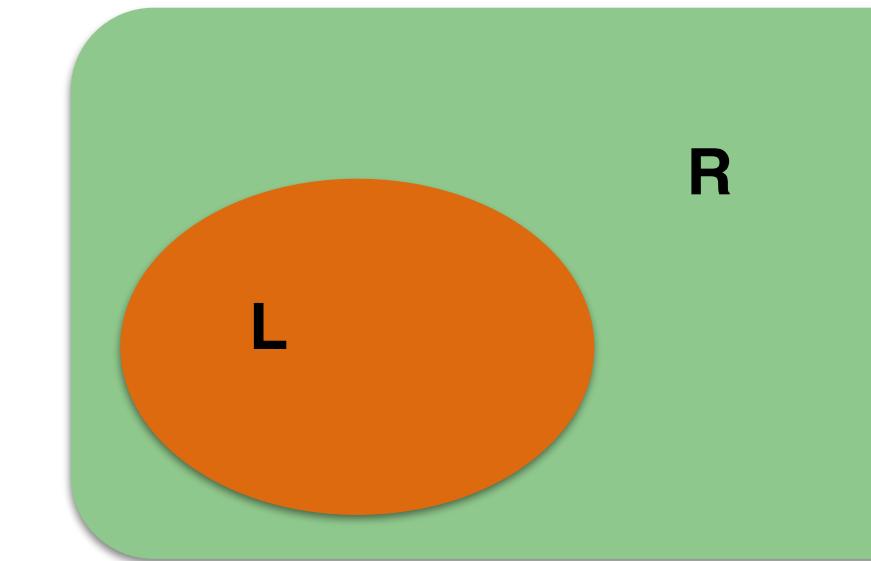


$$\frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle| - |\downarrow\rangle|\uparrow\rangle)$$

What is entanglement?

Entanglement is present when the wavefunction is the sum of different distinct pieces, each a product of parts which are separated in space

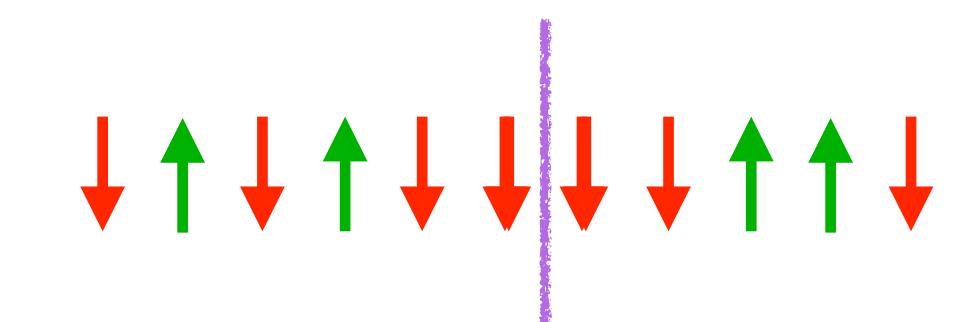
The von Neumann entanglement entropy is the log of the number of pieces. Singlet: $S_{VN} = \ln 2$



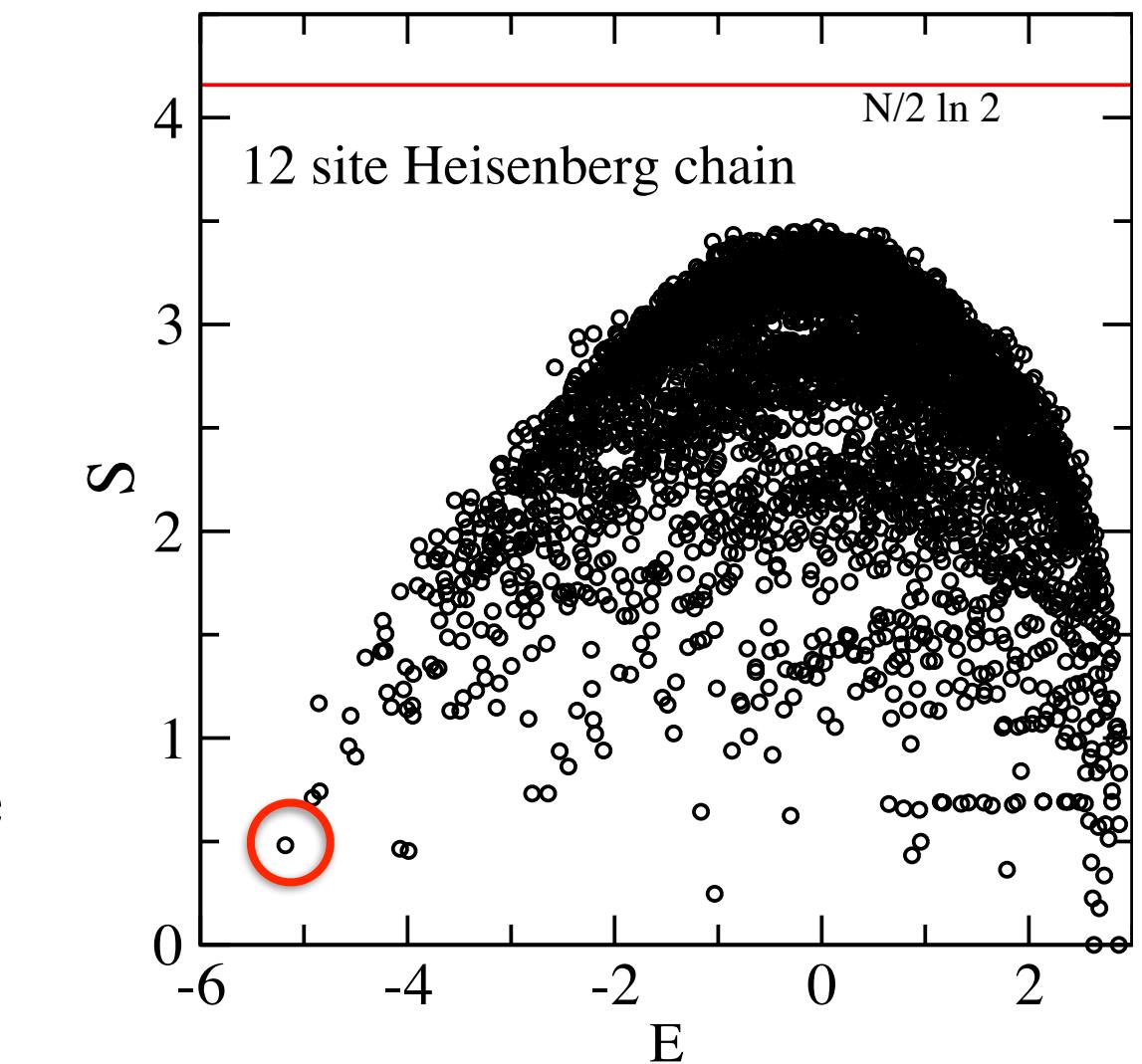
It turns out it is very interesting to look at S where there is no separation between the two parts—say, cutting a lattice spin model into two arbitrary parts

How should S depend on the size of L ?

- The answer: For eigenstates of most realistic Hamiltonians
 - Ground states obey an **Area Law**
 - Highly excited states obey a **Volume Law**



Von Neumann Entanglement entropy S for every eigenstate (system divided in center)



What are Tensor Network States?

A tensor network state is a factorization of a wavefunction into a product of matrices or tensors:

$$\Psi(s_1, s_2) = \sum_{\alpha} A(s_1, \alpha) B(\alpha, s_2) \text{ or}$$

$$\Psi(s_1, s_2, s_3) = \sum_{\alpha\beta} A(s_1, \alpha) B(\alpha, s_2, \beta) C(\beta, s_3)$$

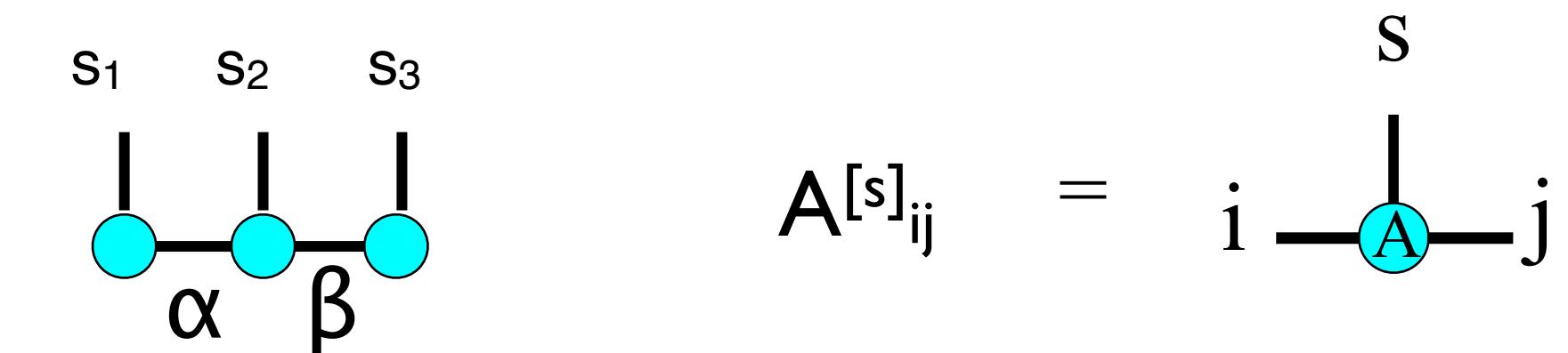
The extra “internal” indices **encode entanglement**

$$|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$$

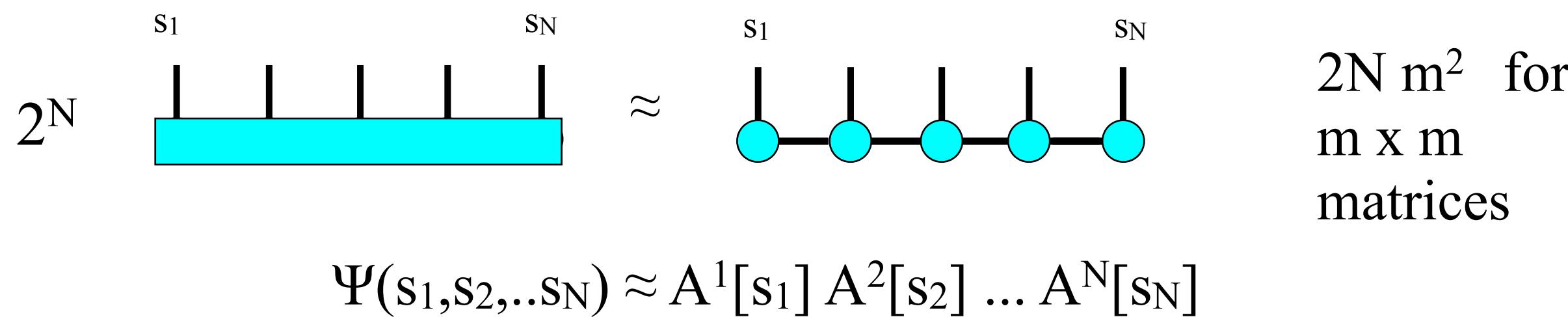
$\alpha=1$ $\alpha=2$

Usually each tensor has one “physical” index s_i . Complicated TN’s can also have extra tensors with no physical indices to organize entanglement.

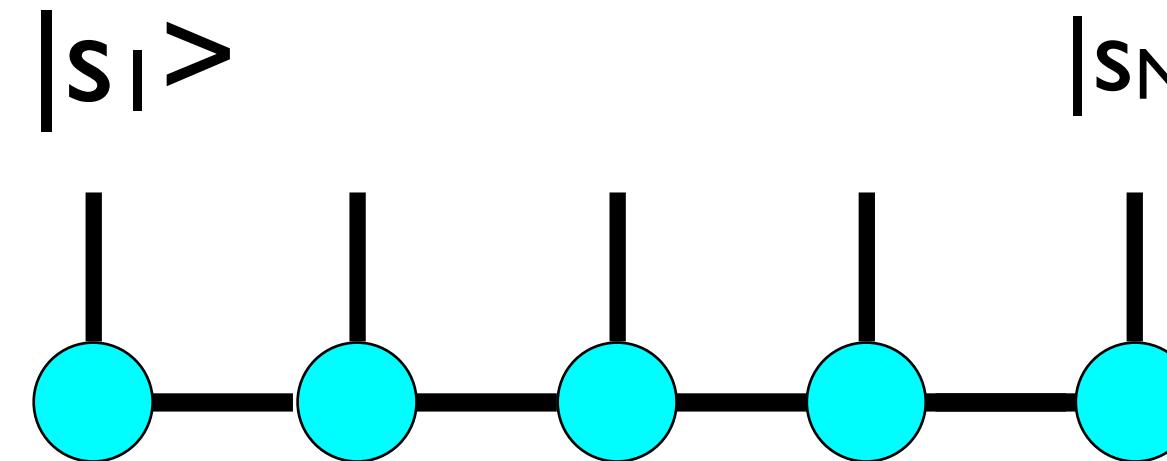
Diagrams: connected indices are internal lines, summed over.



The density matrix renormalization group (DMRG) is based on a special tensor network state called a matrix product state.



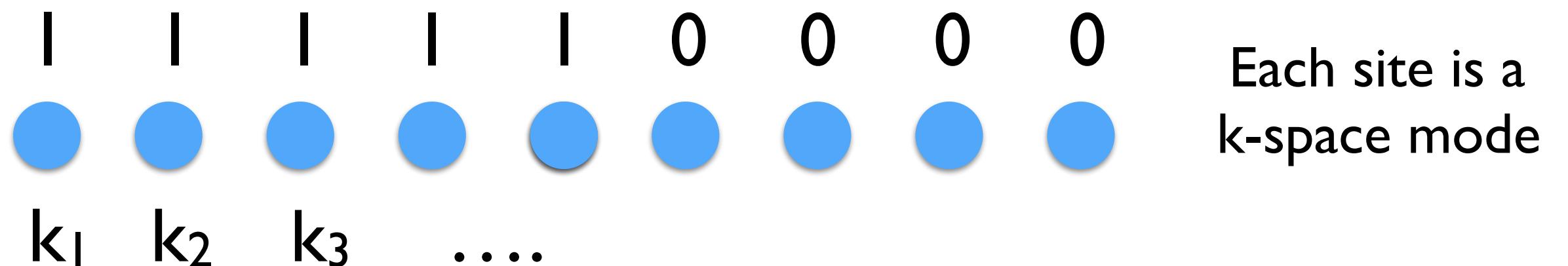
DMRG for a typical 1D model: a Hubbard chain



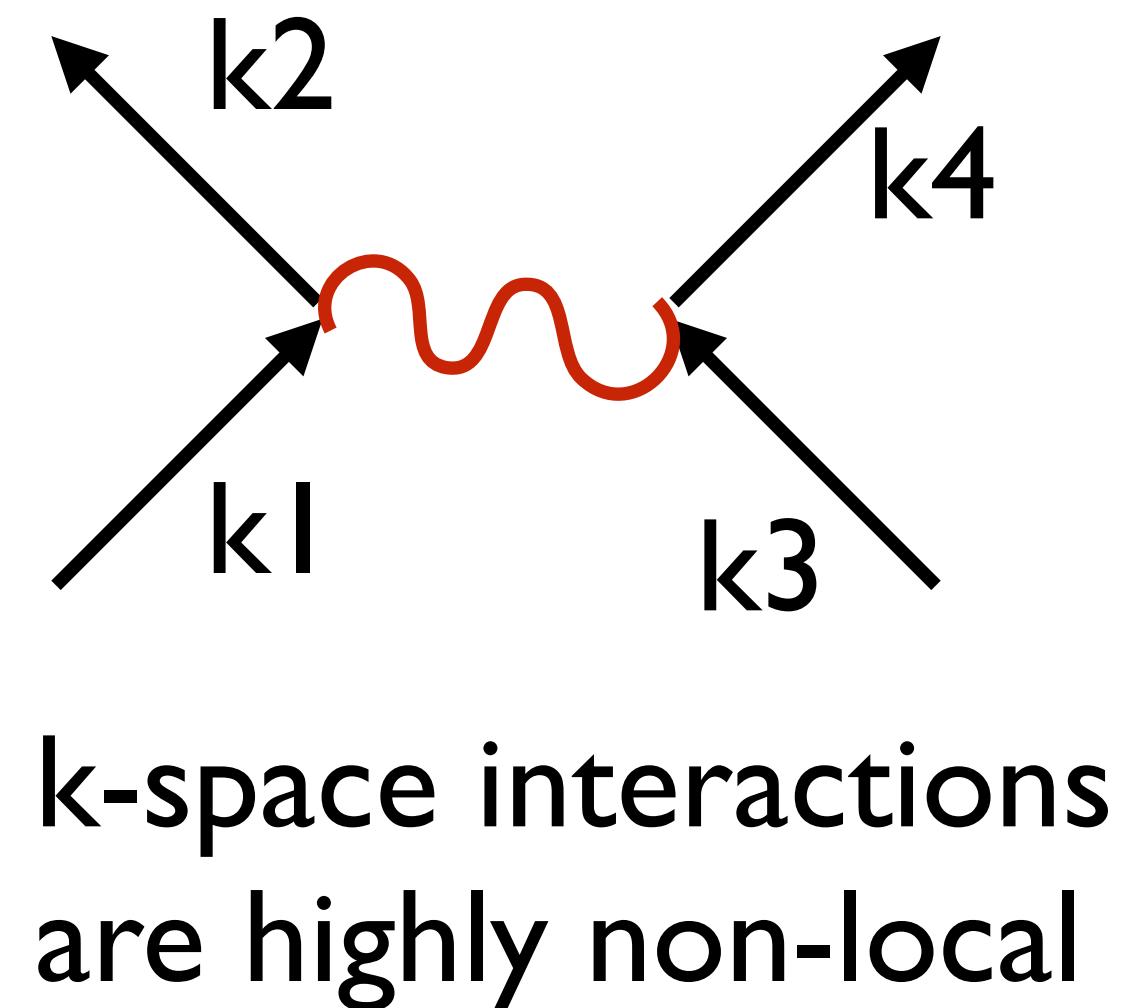
1. Optimize energy over the tensors
2. Calculation time linear in length
3. Accuracy roughly exponential in matrix size
—because of the entanglement area law.

Why not try DMRG in k-space??

- The $U=0$ state is a product state



- The entanglement entropy is zero for $U=0$, so $m=1$ is perfect.
- The area law is formulated in real-space, not k-space. The non-locality in k-space gives a **volume law** for any nonzero U .
- In tests on the 2D Hubbard model in k-space (Ehler and Noack), for any interesting interaction size U/t , the volume law from k-space dominates and the method is not useful

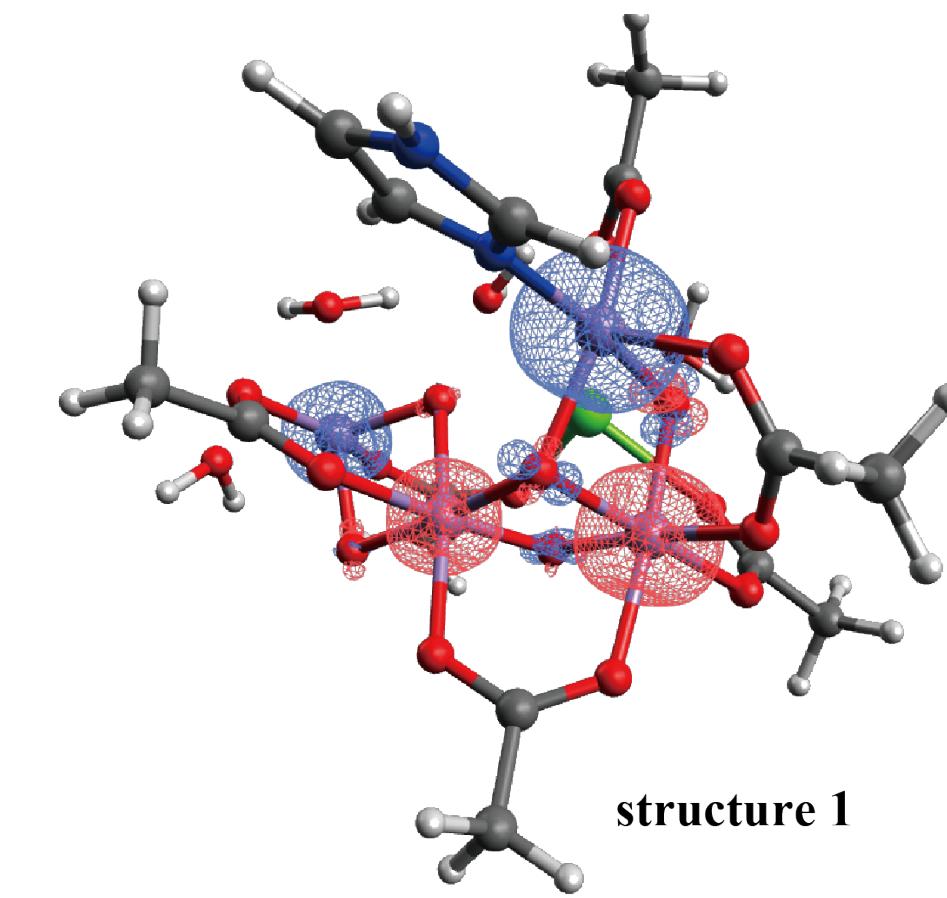
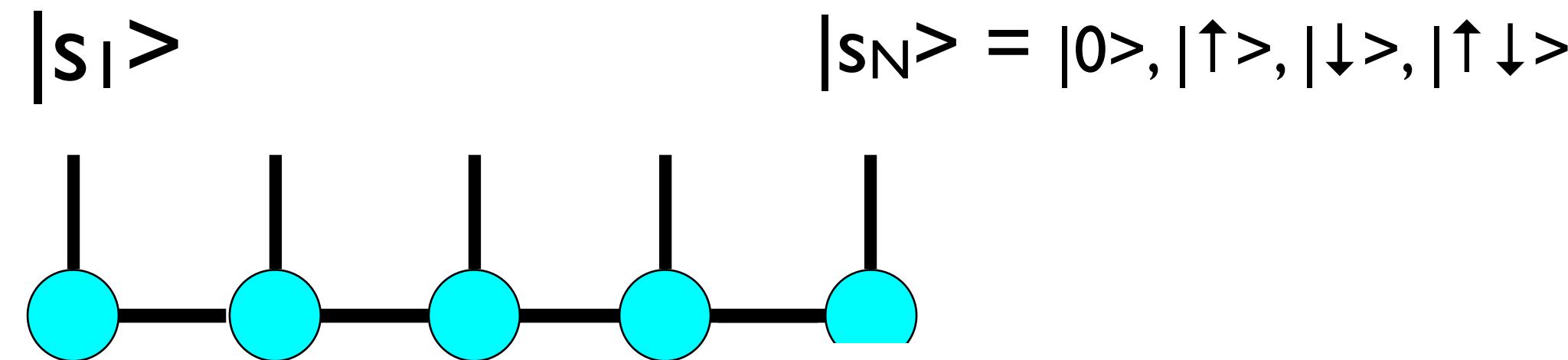


Conclusion: do DMRG in real space!

Quantum chemistry DMRG

SRW and R. L. Martin, J. Chem. Phys. 110, 4127 (1999).
Turned into a standard QC tool mostly by Chan's group

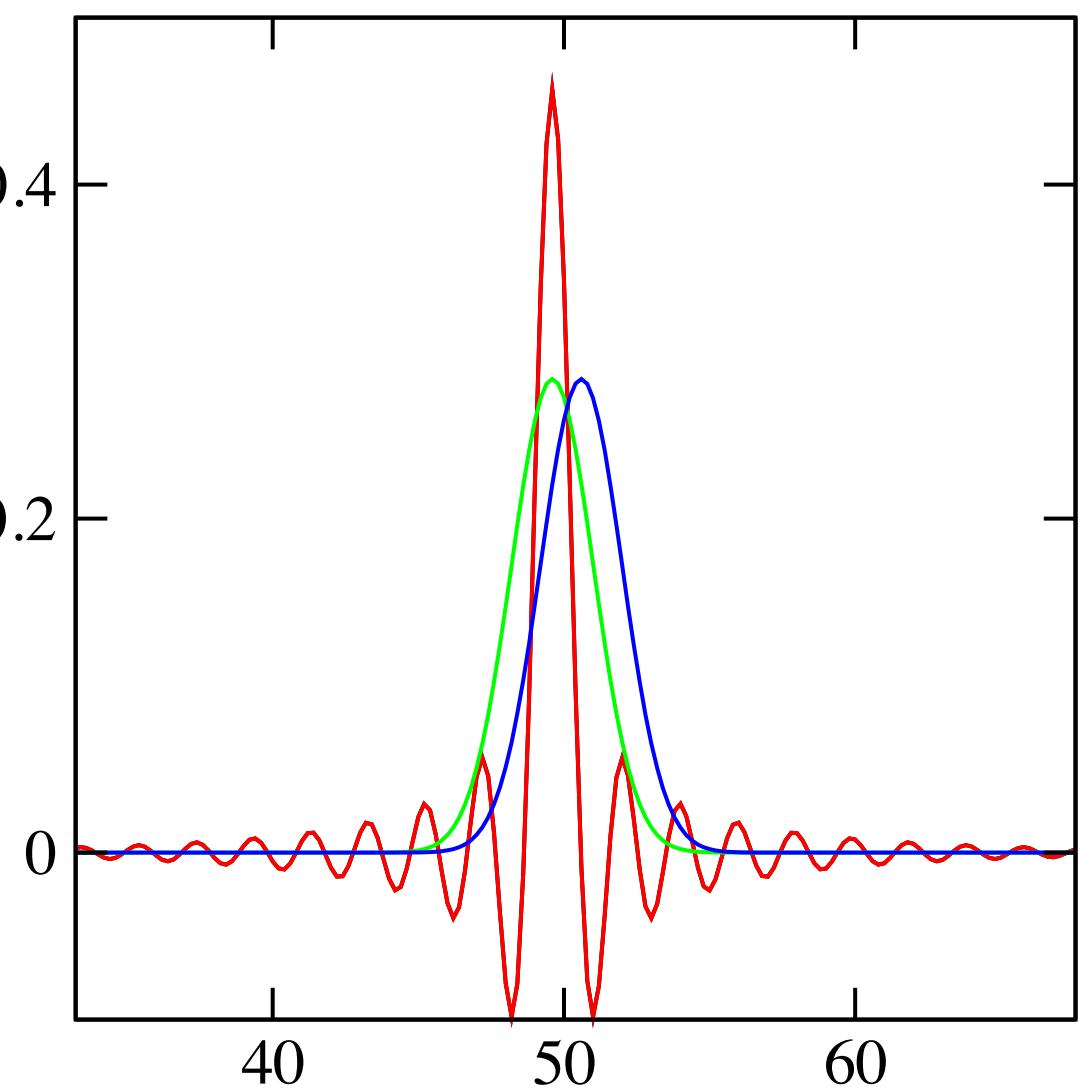
- In a standard Gaussian basis, perform HF and transform to the orthogonal HF basis.
- Choose an ordering for the orbitals to make it look like a 1D chain
- In principle, then do standard DMRG
- To deal with the many terms in the two electron interaction V_{ijkl} , there are tricks utilizing special sums of operators
- Final calculation time: $\sim N^3$ (dominant part)
- Area Law: the HF orbitals are extended across the system, like k-space states.
 $m=1$ gives the HF state (like $U=0$ Hubbard), but for post-HF this version of QCDMRG only works well for small molecules
- Some form of localization of the orbitals is crucial to do larger systems
- Chan's group recommends split localization: rotate within the HF-occupied space and separately within the unoccupied space to localize the orbitals, but non-split localization is also good.



Reliable calculations
of the oxygen
evolving complex,
responsible for
photosynthesis
(Chan's group)

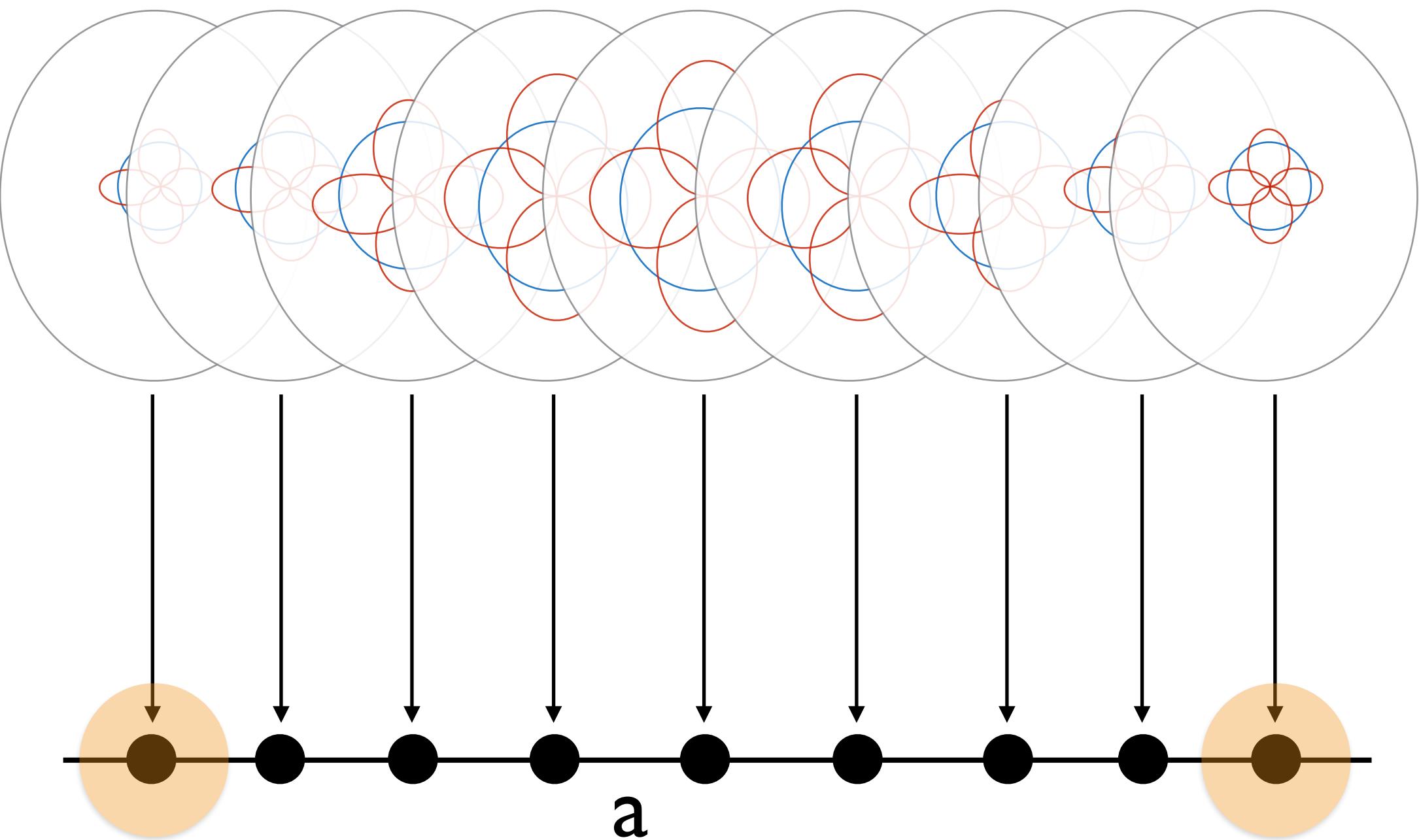
Problems with QCDMRG

- Area Law: how localized can you make the basis? Sometimes not very, even without splitting into occupied and unoccupied spaces.
Worse when basis is more complete.
- The nonlocality may increases entanglement (how much?)
- Computational cost: two electron interaction has $O(N^4)$ terms, V_{ijkl}
This limits QCDMRG limited to ~ 100 -200 active basis functions,
whereas for a Hubbard chain we can do tens of thousands of sites
- For long systems, truncations of the V_{ijkl} can improve scaling—
quadratic scaling DMRG (Hachmann, et al, J. Chem. Phys. 125 (2006), 144101)
- But what if the basis were completely localized, as in a real-space
grid?? This would drop V_{ijkl} to $O(N^2)$: $i=l$ and $j=k$, and
potentially cure other problems...



Array of evenly spaced gaussians, orthogonalized and maximally localized

Sliced Basis Approach to Quantum Chemistry with DMRG



In one direction (z), use a fine grid, spacing a
($a=0.1$ or 0.2 Bohr)

In x,y directions, use 2D Gaussians based on
a standard 3D basis.

E.M. Stoudenmire and Steven R. White,
PRL, to appear

A grid has two key advantages:

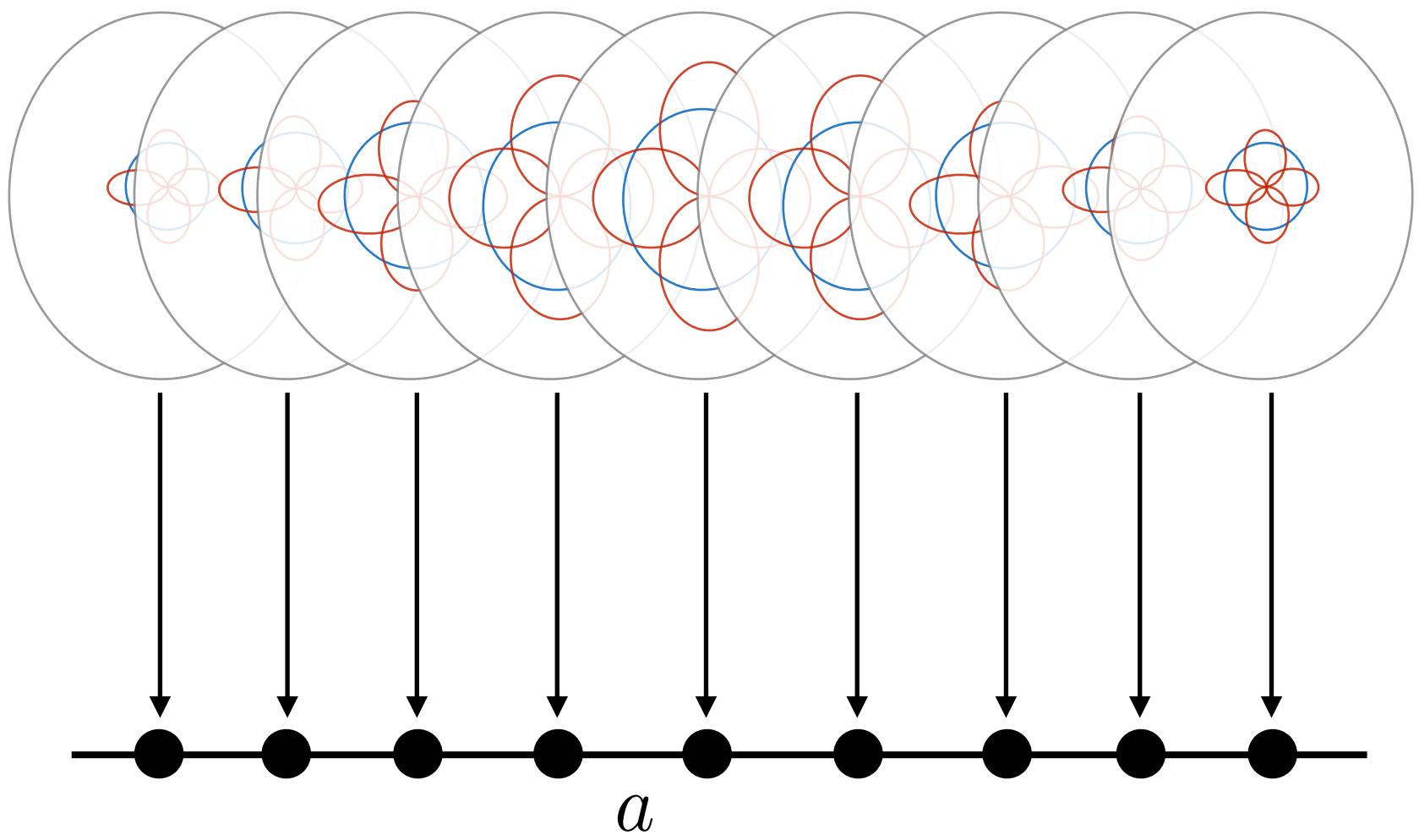
- I. Fewer interaction terms
2. Clearly obeys area law

It has two minor disadvantages:

- I. More basis states
2. Higher energy kinetic terms
 $\sim 1/a^2$ cause some stiffness

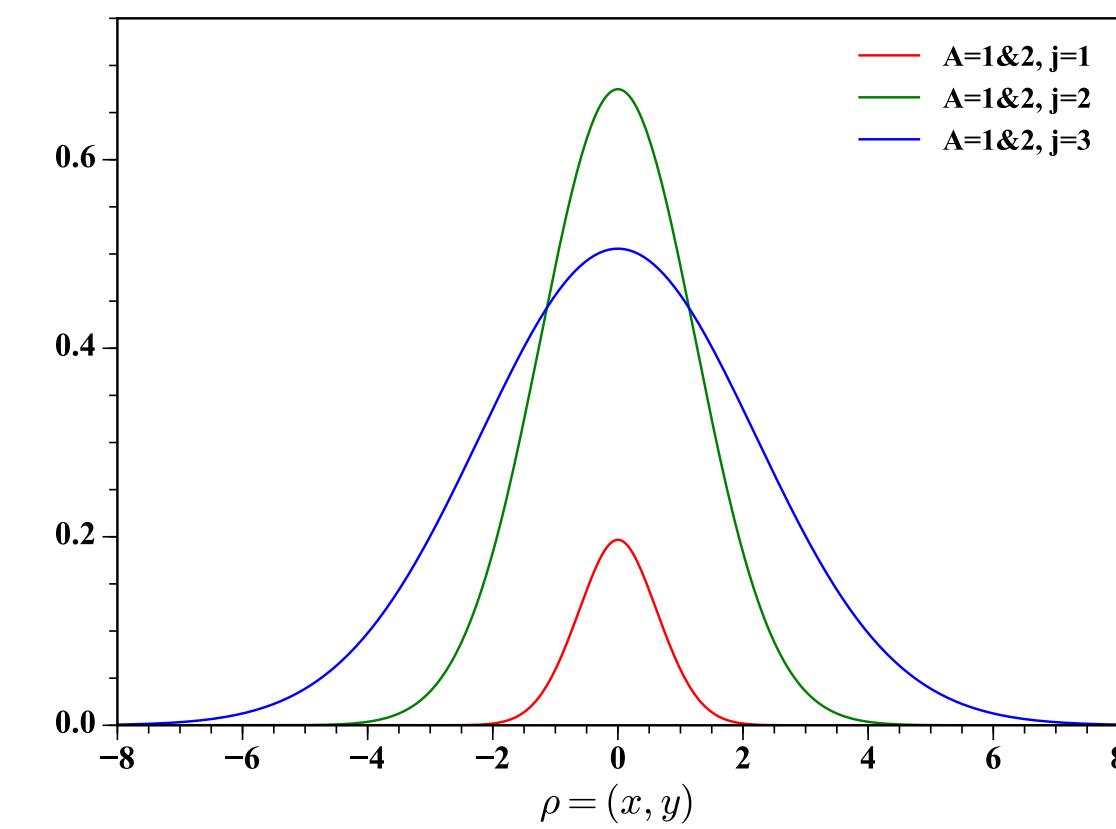
Sliced “basis functions”

$$\phi_{nj}(\vec{r}) = \delta^{1/2}(z - z_n) \varphi_{nj}(x, y)$$



Functions on different slices
automatically orthogonal
Same slice: orthogonalize

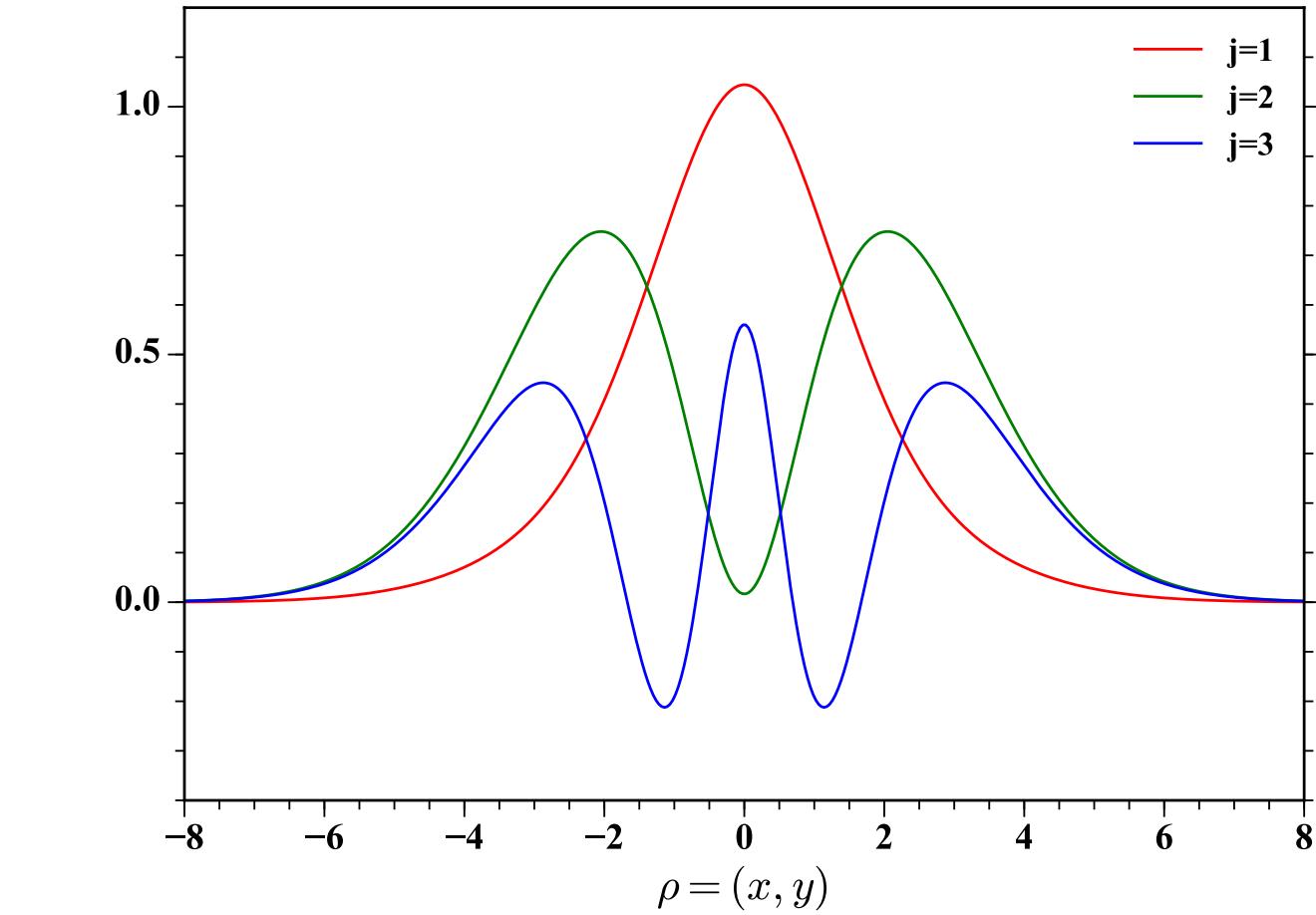
Example: H_2 molecule, slice through bond



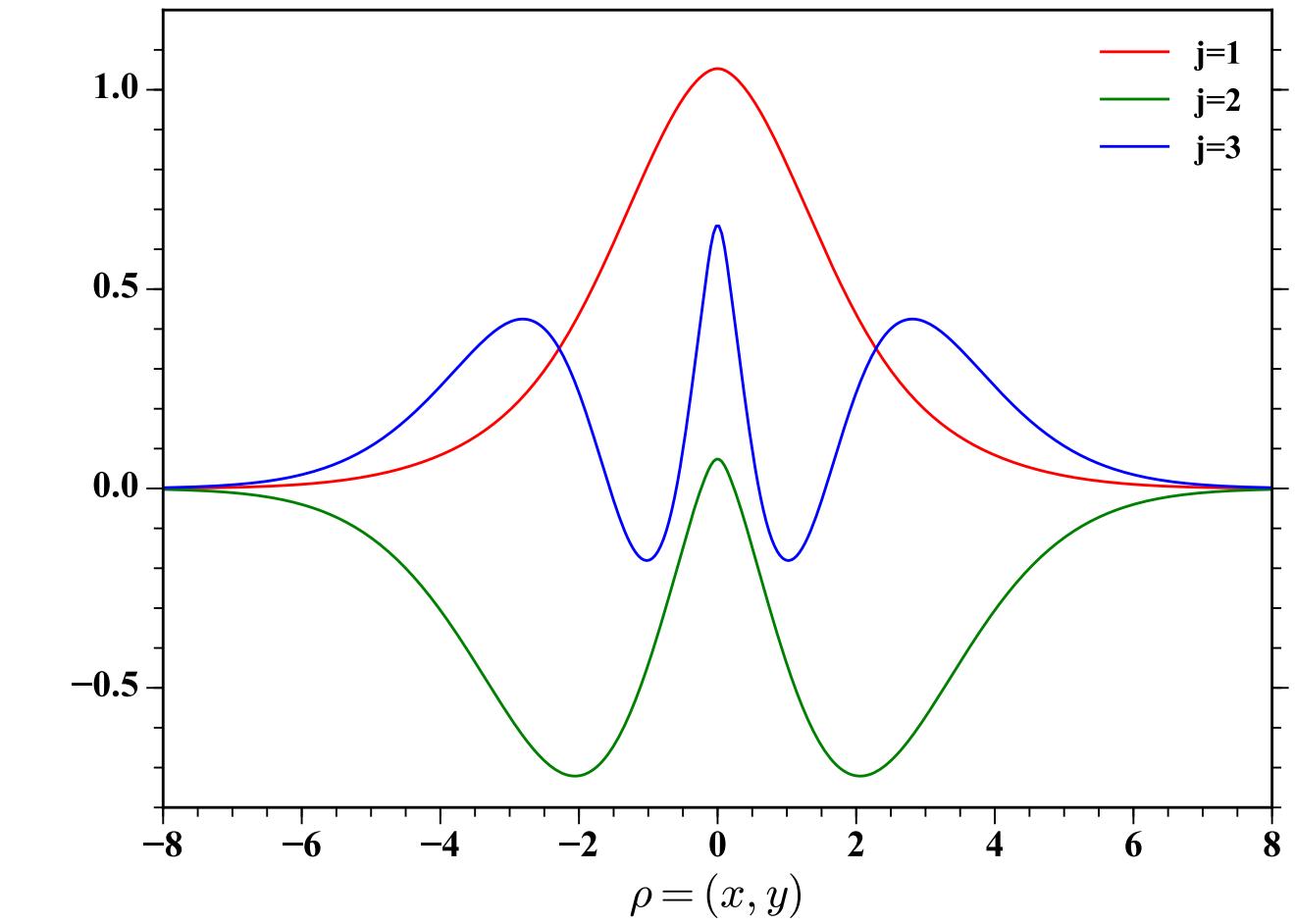
Original transverse
gaussians

Orbitals taken from
cc-pvTZ, S orbitals only

Transverse S
functions



Orthogonalized
and contracted



Slice through nucleus

Constructing the Hamiltonian

For z-direction kinetic energy, use finite difference approx (4th order)

Other terms involve integrals. The 2 el. Coulomb is the most difficult

$$V_{ijkl} = \int_{\mathbf{r}_1, \mathbf{r}_2} \frac{\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_k(\mathbf{r}_2)\phi_l(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

With sliced basis, i and l must be on same slice, similarly j and k.

This reduces the number V's down to $(N_{\text{slice}})^2$

Compression: Just with the slicing, we reduce the computational scaling by a factor of N: $N^3 \rightarrow N^2$.

However, the V matrix is smoothly decaying at large separation. Can it be compressed, and the compression utilized in the DMRG algorithm? Yes!

[General compression approach in QCDMRG: Chan, Keselman, Nakatani, Li, and White, J. Chem. Phys. 145, 014102 (2016).]

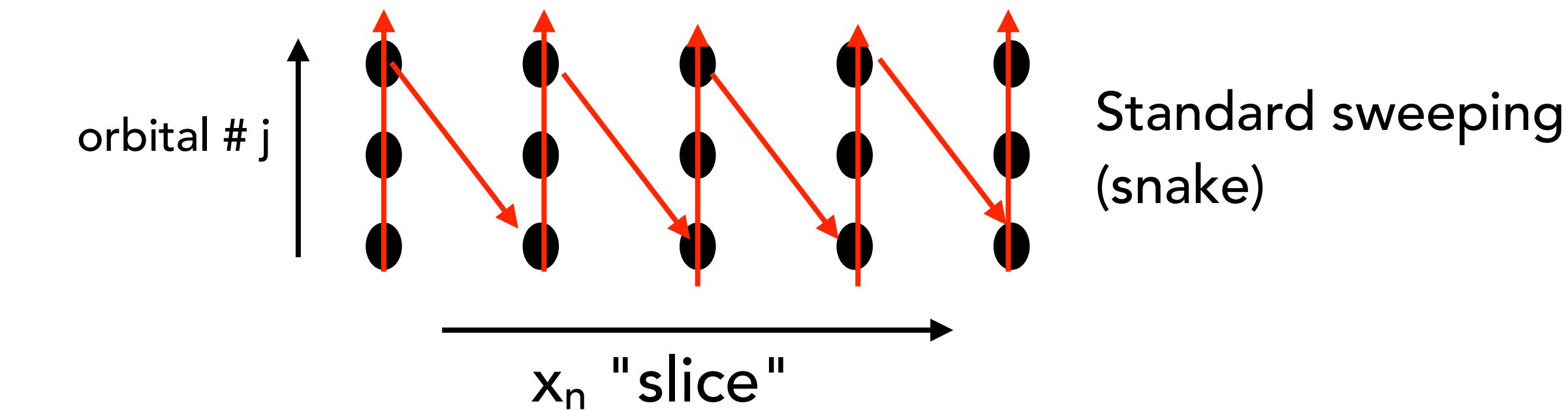
$$V(z, z') =$$

SVD
Sharp along diagonal

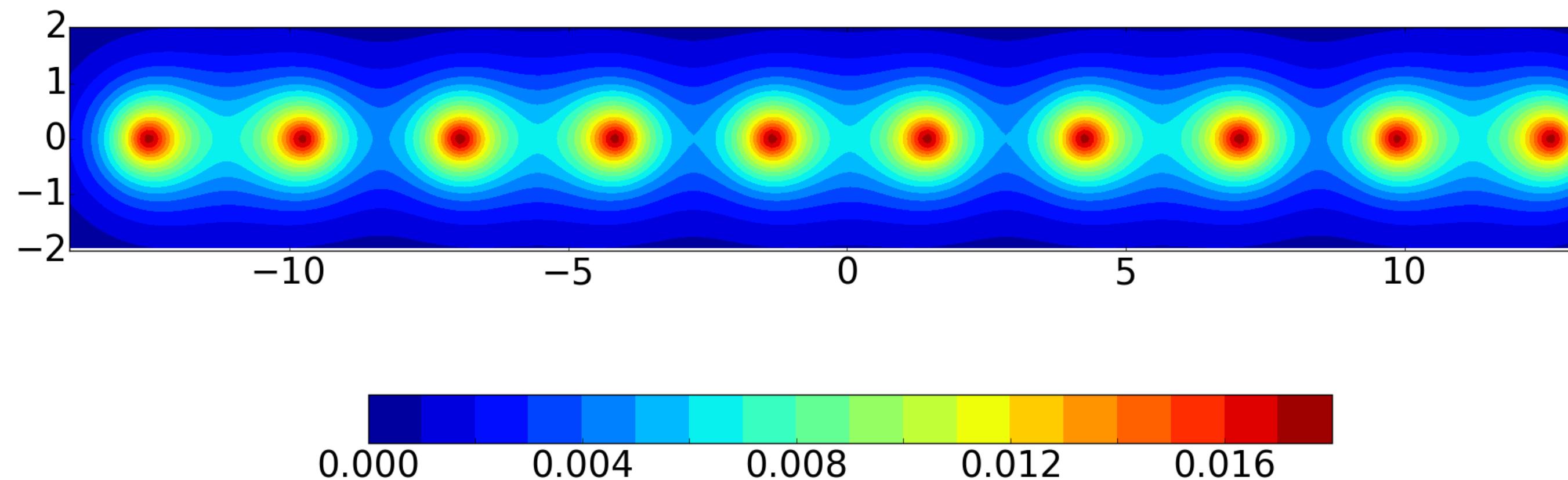
The compression tool in DMRG is an SVD, keeping only some singular values, but here the sharp behavior along the diagonal makes a standard SVD on V useless.

However, a more complicated off-diagonal SVD method can be used to compress V. This method translates to DMRG using matrix product operator technology. Final result: $N^3 \rightarrow N$

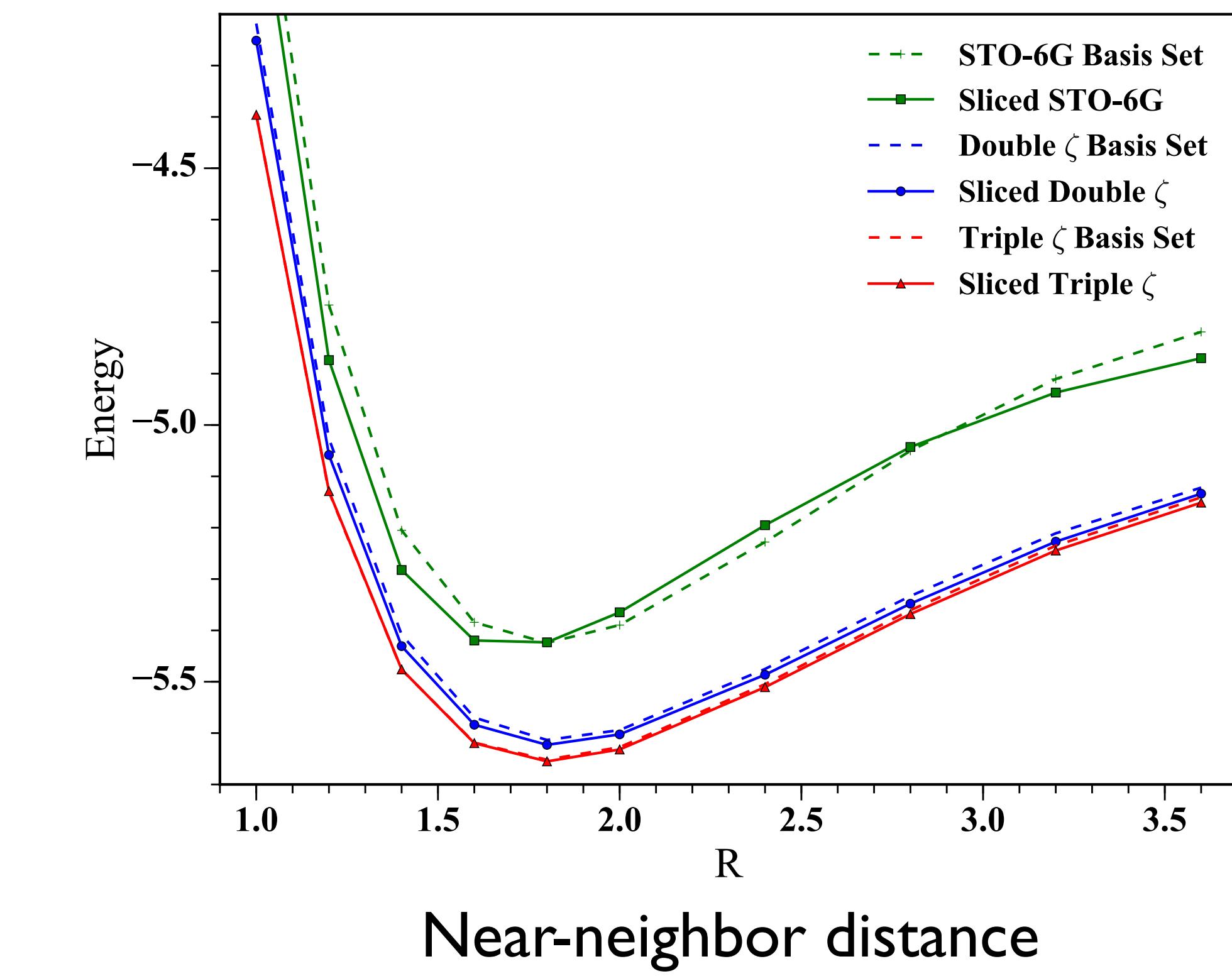
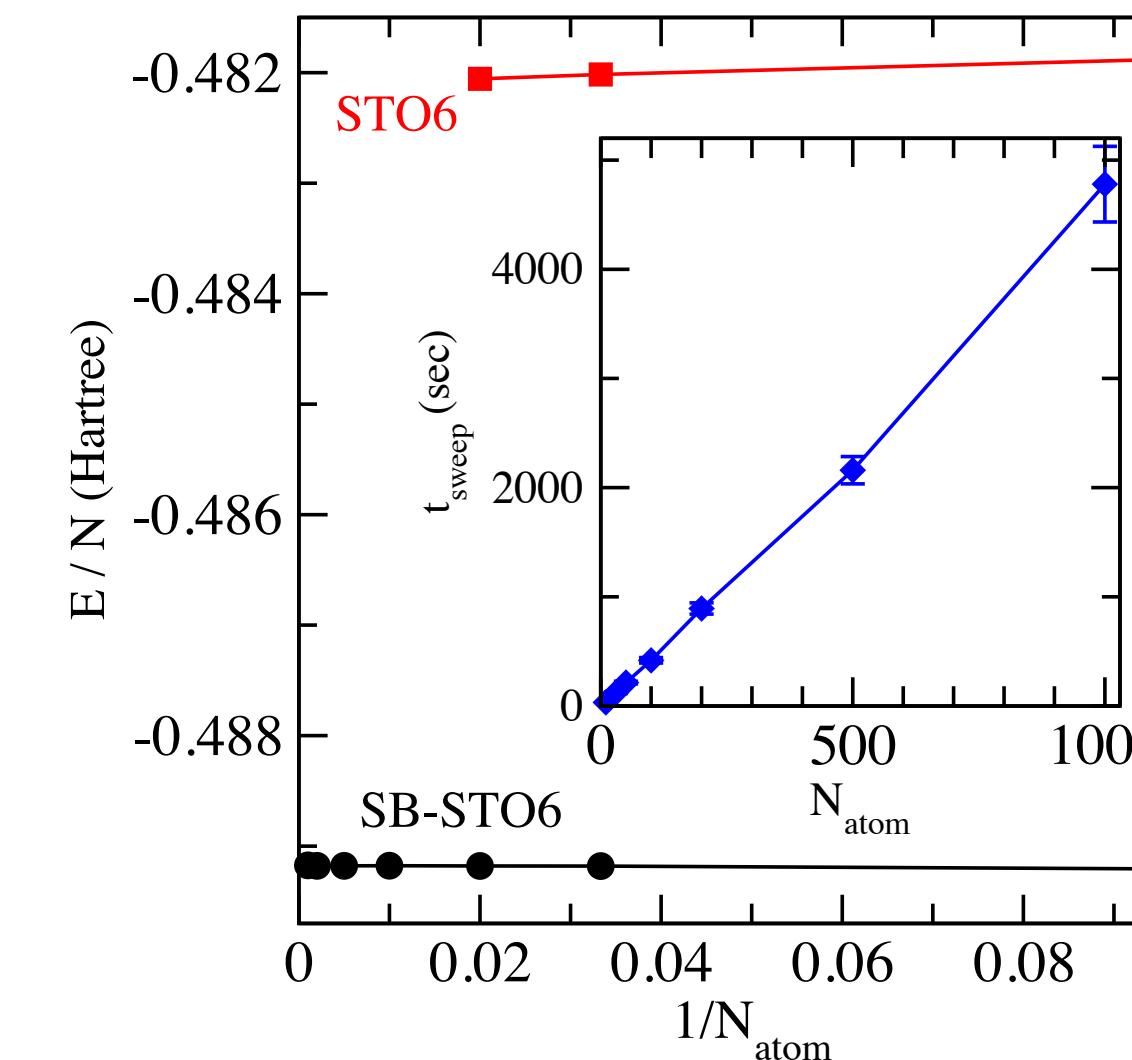
In the end, to DMRG this looks like a long multi-leg ladder Hubbard model, and our standard software (ITensor) can be used with little change.



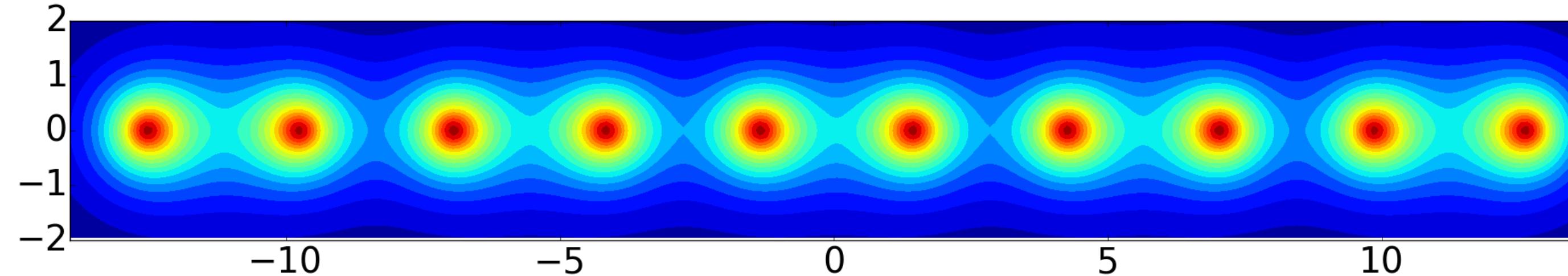
Application: Hydrogen Chains (Simons Collaboration, Shiwei's talk)



Computation time:
Linear scaling, starting at
small N ;
1000 atoms on a desktop
sub-mH accuracy within a
minimal basis



Dimerization of the hydrogen chain

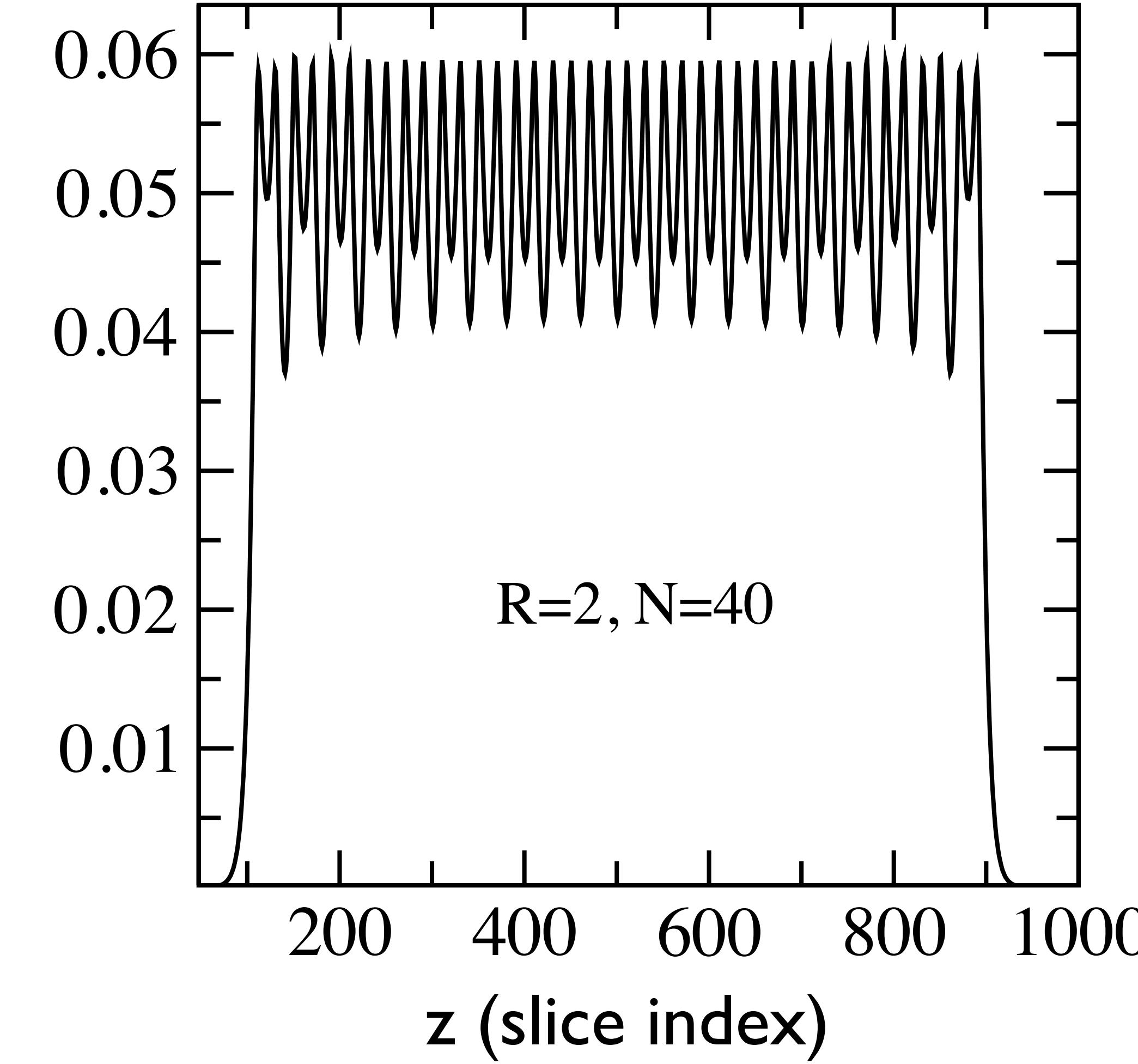
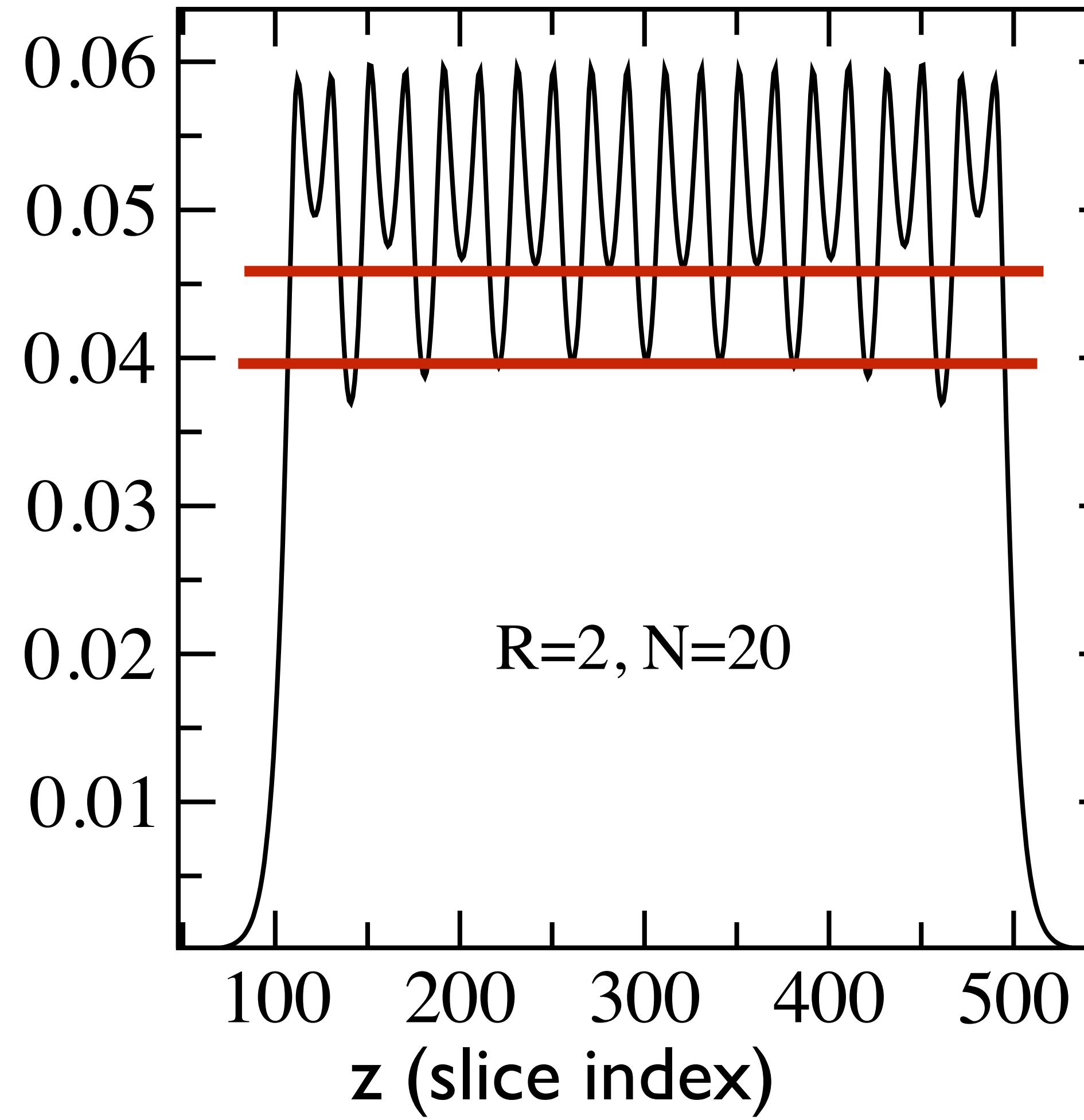


Electron density in a plane containing the nuclei

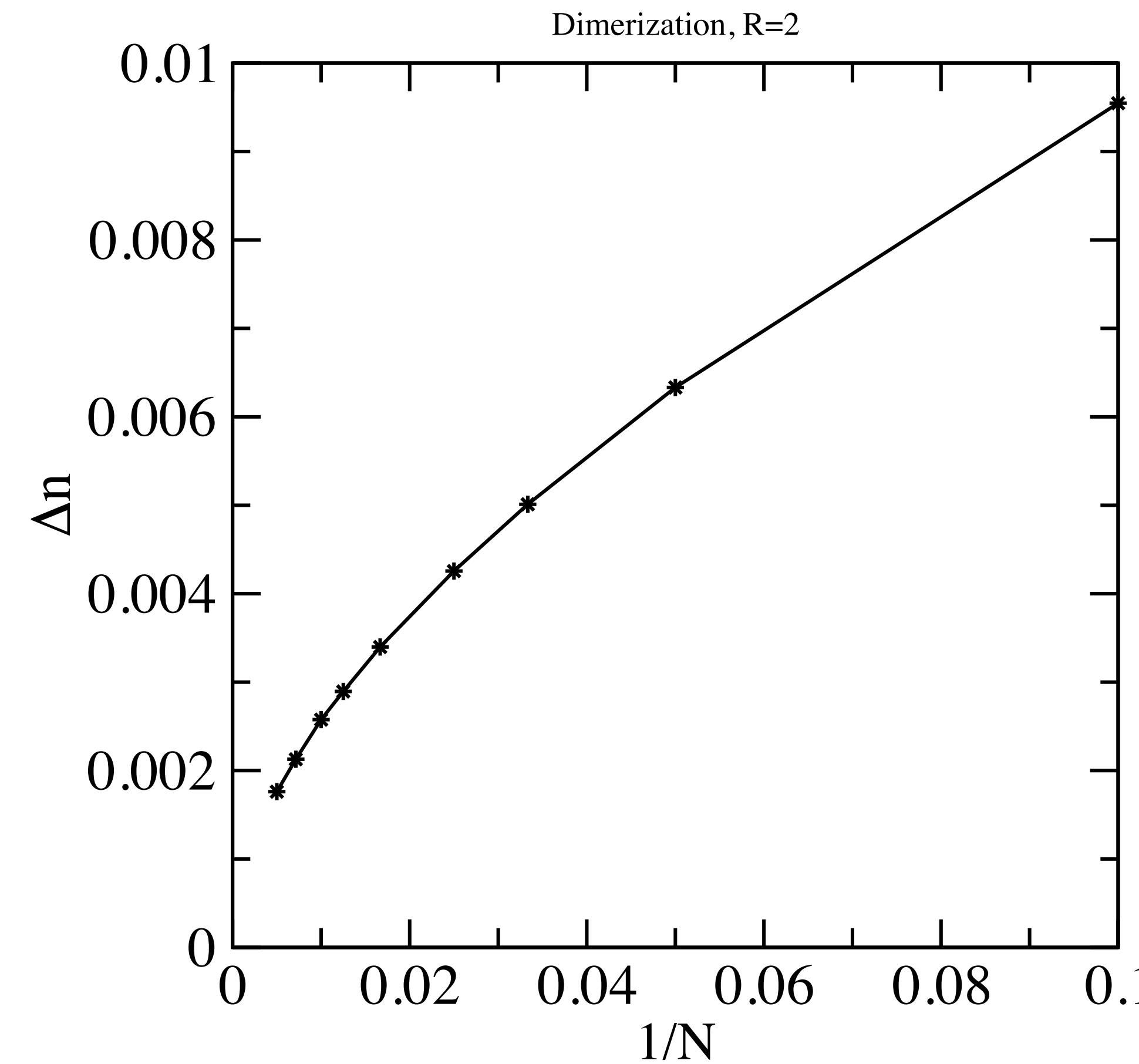
- In the thermodynamic limit, does the dimerization of the electron density remain finite—a true broken symmetry?
 - Since it is a discrete symmetry (translation), breaking it in 1D is possible
 - Simple models: half-filled Hubbard chain—there is no bond density between sites, but an analogous quantity is the bond hopping. Does not break symmetry.
 - Heisenberg chain: The analogous quantity is $\langle S_i S_{i+1} \rangle$ —it does break symmetry if you add a big enough next neighbor exchange $J' > 0.24 J$
 - If the symmetry is not broken, in both models the behavior is critical—power law decay of the dimerization away from open ends, power law correlations.
 - Only an accurate simulation can tell what phase the hydrogen chain is in.

Dimerization of the hydrogen chain (minimal sliced basis)

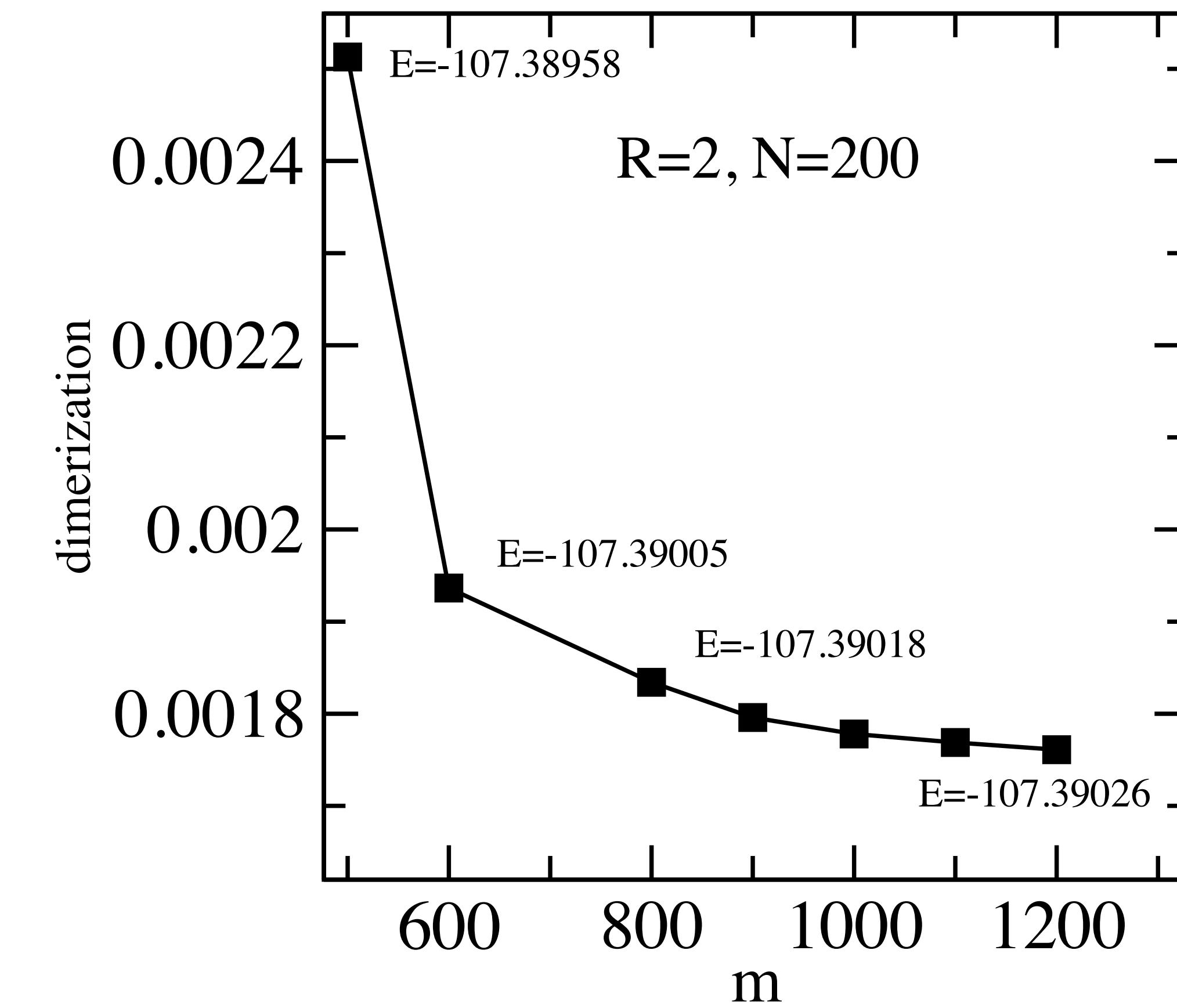
Integrated density over a slice



Dimerization of the hydrogen chain (minimal sliced basis)

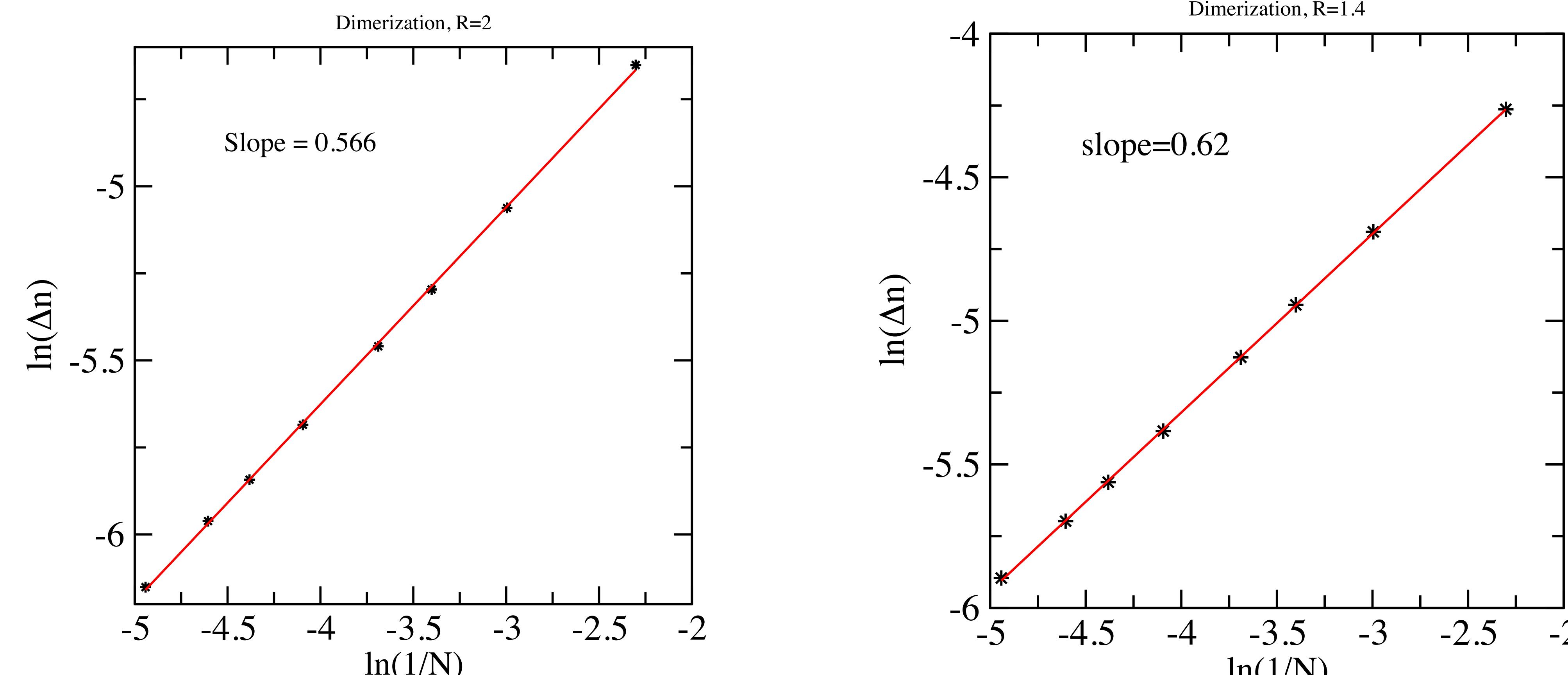


Dimerization in the center
versus length



Extremely high accuracy in E
is needed to get the
dimerization converged

Dimerization of the hydrogen chain (minimal sliced basis)



Analytic slope for the
Heisenberg model: $1/2$

Conclusion: at moderate to large separation, the dimerization is not a broken symmetry: just power law decay away from the edges—like in the n. n. models.

Sliced basis DMRG

- Details of how you set up the basis can be crucial in doing electronic structure with DMRG/tensor networks
- For DMRG, the sliced basis approach represents significant progress for chain systems: using the combination of locality and a type of compression, we achieve linear scaling with very high accuracy (within the basis).
- There are lots of routes to further development. We need to do higher Z, less linear systems, to start.
- For hydrogen chains, we can directly study the critical behavior of the dimerization.