Title: Tensor network methods for quantum chemistry

Speakers: Steven White

Collection: Tensor Networks: from Simulations to Holography III

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Abstract: The search for applications of quantum computers has highlighted the field of quantum chemistry, where one can also apply tensor network methods. There are several challenges in getting useful results for molecules compared to simulating a model Hamiltonian in condensed matter physics. The first issue is in descretizing continuum space to get a finite Hamiltonian which is amenable to tensor network techniques. Another is the need for high accuracy, particularly in energies, to compare with experiments. I will give an overview of the approaches used in this field, and then focus on our work using grid and wavelet-based discretizations coupled with DMRG methods.

# Tensor Networks and Quantum Chem

### **Google's Quantum Computer Achieves Chemistry Milestone**

A downsized version of the company's Sycamore chip performed a record-breaking simulation of a chemical reaction

Scientific American

Quantum computers are making quantum chemistry famous!

Drug design, new materials, \$\$

#### What about using tensor networks for simulating quantum chemistry?

Renormalization-group approach for electronic structure

Steven R. White, John W. Wilkins, and Kenneth G. Wilson Phys. Rev. Lett. **56**, 412 – Published 3 February 1986 I have been thinking about this field since grad school.

#### <u>Outline</u>

- Overview of quantum chemistry
- Our work using wavelets and DMRG







Hamiltonian and Energy scales
$$H = -\frac{1}{2} \sum_{i} \nabla_i^2 + \sum_{\alpha,i} \frac{-Z_{\alpha}}{|\vec{r}_i - \vec{R}_{\alpha}|} + \frac{1}{2} \sum_{i,j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$
N electrons, N<sub>a</sub> nucle $1/a^2$  $Z/a$  $1/a$ Spin-orbit, phonons, etc treated perturbatively $1/a^2$  $Z/a$  $1/a$ Putting H on a grid, spacing  $a$ 

KE ensures  $\psi(r_1, r_2, ...)$  is generally very smooth (not a field theory!)

except for cusp singularities at fixed  $R_{\alpha}$  and in relative coords when  $r_i = r_j$   $e^{-Z|r|}$ The first two terms are one particle, "easy".

The long-range part of the two-el 1/r is crucial for charge neutrality, but it couples many electrons at once.

The short range part is reduced by 3D volume element  $r^2 dr$ .

Both effects suggest mean-field treatment: Hartree Fock, and density functional theory. Underlying both is a single Fermion determinant.

DFT cleverly interpolates QMC correlation energies of an interacting el gas, plus exact sum rules, etc—works fine for many molecules and solids.

Strongly correlated is usually synonymous with "DFT doesn't work"



## Strong correlation methods

<u>Nearly weakly correlated</u>: perturbation theory, coupled cluster, configuration interaction (diag within few-excitation subspace) <u>Strongly correlated but small</u> (exact diag) Quantum Monte Carlo (but sign problem) DMRG (fairly small or ID) We would love to add PEPS to this list! (Garnet Chan)

# Mapping the continuum to a discrete Hamiltonian

•Almost all electronic structure methods use a basis

- •<u>Plane waves</u>: standard for solids (periodic box). Analytic integrals
- ⇒Requires smoothing out the nuclear cusps (pseudopotential). Nonlocality: volume law
- •Atom centered Gaussians
  - Highly adapted to each atom. Analytic integrals. 5-10 Gaussians to give  $e^{-Z|r|}$  very accurately, so excellent at nuclear cusp.
  - ➡<u>Nonorthogonal</u>, orthogonalizing makes them nonlocal (somewhat)
  - $\rightarrow$  Two-electron interaction has four indices  $V_{ijkl}$
- •Hamiltonian:  $\sum_{ij\sigma} H_{ij}^1 c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} c_{i\sigma}^{\dagger} c_{j\sigma'}^{\dagger} c_{k\sigma'} c_{l\sigma}$

• Most correlation methods start from this Hamiltonian

•(Usually they start by rotating basis to Hartree Fock orbitals)



 $\{\phi_i(\vec{r})\}$ 

Quantum chemistry DMRG (White and Martin, 1999, T. Xiang, Garnet Chan..

•<u>Complementary operators:</u> complexity  $N^5m^3 \rightarrow N^3m^3 + N^4m^2$ 

 $V_{ijkl} c_i^{\dagger} c_j^{\dagger} c_k c_l \rightarrow c_i^{\dagger} O_i$   $O_i = V_{ijkl} c_j^{\dagger} c_k c_l$  with i in left block, j,k,l in right block •White and Martin: ~25 Gaussians, transformed basis to HF molecular orbitals, to

treat one stretched water molecule

•Progress in two decades: ~100 active orbitals, selected from bigger Gaussian basis

•Only treat valence levels ("active space"): truncation or integrate out other orbs



Impressive calculations of the oxygen evolving complex, responsible for photosynthesis (Chan's group) [technical note: split localization]

Still very far from what we can simulate with local models

# **Going beyond QCDMRG**

- Our main effort has focused on improving the construction of H, allowing DMR and PEPs to work as well as in Hubbard models
  - •Better locality (Area Law)
  - •Reduced complexity of the two electron interaction  $V_{ijkl}$

Our first two approaches used ID grid representations

- <u>ID grids for toy continuum models</u>
  - Up to 100 pseudoatoms—4000 lattice sites
  - Grid gives interactions as  $V_{ii}$
  - Key to success was MPO compression
  - Useful as a toy system to understand DFT (Kieron Burke)
- Sliced basis sets (real hydrogen chains)
  - Use a 1D grid for the long direction
  - Use Gaussians for transverse directions (1-12 Gaussians)
  - For long chains, nicely surpasses QCDMRG (linear scaling in length, 1000 atoms!)









### Improving our grids: MERA and wavelets

•Our ultimate goal is to generate very coarse, very accurate 3D grids for use with DMRG and PEPS. Can we use MERA to <u>decimate</u> our grids?

•At small spacing, KE dominates. So think first about single-particle framework, ID



### Simplest MERA layer

The same diagram can represent the usual tensor product space or a much simpler direct sum space. Same idea as a Fourier transform vs Fourier transforming the fermion creation operators

How do we choose the disentanglers and isometries (2x2 unitaries)? Make the states we throw out (deta) orthogonal to low order bely namials. Then the states

states we throw out (dots) orthogonal to low order polynomials. Then the states

we keep represent all smooth functions.

This recipe generates **Daubechies' famous wavelets** 

Thus:

Wavelet technology can help us get coarse grids
MERA technology can help make better wavelets







Ternary gates allow for symmetric, compact wavelets—with binary gates, impossible

(a) Site-centered symmetric





 $b_i$ 

#### Gausslets—a variation on our ternary wavelets with analytic i

Instead of using the scale-invariant functions, apply the wavelet transform once Gaussians, with an extra "orthogonalizer" layer in between [White, J. Chem. Phys. 147, 244102 (2017)]



0

-2

0

"Gausslet"

2

Exactly orthonormal Polynomial completeness to 10th order Integrates like a  $\delta$ -function to 20th order

the bottom layer for further MERA

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### **Diagonal Approximations with gausslets**

 Suppose we have a function G(x) that we place on grid points, with <G(x-i)|G(x-j)> = δij, with polynomial completeness, and a polynomial <u>delta-function property</u>:

$$\int dx \ G(x-j)\phi(x) = \phi(j) \mathbf{k} \ \mathbf{\Phi} \ \mathbf{a} \ \mathbf{polynomial}$$

•<u>One particle potential</u>: as part of Schrodinger eqn, let  $\Psi(x)=U(x) \Phi(x)$ . Standard derivation:  $\Psi = (G(x-i)|\Psi(x))$ , etc, gives standard result,  $\Psi = U = U = U = 0$ 

•<u>Diagonal approx</u>:  $\Psi(x) = U(x) \varphi(x)$  evaluated at x=i gives  $\Psi_i = \Psi(i) = U(i) \varphi(i) = Ui \varphi_i$  so replace Uij  $\Rightarrow$  Ui  $\delta_{ij}$ , and this also

solves the Schrodinger equation. A non-standard approx, but it converges very rapidly to the continuum result as the spacing goes to zero

•<u>Two particle terms</u>: essentially the same, Vijkl  $\Rightarrow \delta$ ij  $\delta$ kl Vik

Thus, a gausslet basis has a  $V_{ii}$  interaction just like a grid.







### **3D variable-grid gausslet bases**

- How do we make a 3D gausslet? Easy:  $G_{3D}(x, y, z) = G(x)G(y)G(z)$
- These live on a 3D distorted grid. Spacings: near nuclei, ~0.5 Bohr, edges of atoms: ~4 Bohr
- Working with a basis has a key advantage over a grid: we can throw in extra functions to better represent singularities, orthogonalizing them to the gausslets. We now do this, adding in some Gaussians







#### **Results:** Gausslet basis-DMRG, H<sub>10</sub> chain



Results from many state of the art classical



Our first results with MSG-DMRG



MSG-DMRG is arguably now the best of these methods for H-chains



### Conclusions

- Quantum chemistry and electronic structure is a fruitful area for tensor network methods—but as a mature area, it is also challenging to have an impact
- We have focused on the simplest aspect: setting up decent Hamiltonians for DMRG and tensor networks. MERA and its connection to wavelets allowed us to set up our gausslet bases. For hydrogen chains, our gausslet-DMRG gives stateof-the-art results.
- At the single particle level, we are focusing now on larger Z atoms, adding Gaussians to the gausslet bases. We are also exploring further decimations with corrections to the interaction terms to further reduce the Hamiltonian size. A key constraint is maintaining a diagonal representation.
- The ultimate goal is to make bases with, say, 50 sites per atom, with simple Hamiltonians, which we use with PEPS for broad classes of molecules and solids.

