What would you do with the Exact Functional?
Probing the limits of density functional theory (DFT)

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In this talk:

We have extended the powerful density matrix renormalization group (DMRG) to solve continuum electronic systems in 1d.

One key application is studying density functional theory (DFT)—we can compute the exact functional.

Which limitations of DFT come from approximations?

Which are fundamental?
Outline:

• DMRG for continuum systems

• Exact density functional theory with DMRG

• Applications:
  ‣ Gaps in DFT
  ‣ Convergence of the Kohn-Sham equations
What is DMRG?

“It is at the moment the closest to an ultimate weapon as one can dream of.” — T. Giamarchi

- Controlled, essentially exact results
- Linear scaling with system size (in 1d)
- Full access to wavefunction
- Dynamics, finite temperature
- Parallelizable*

1d and narrow 2d systems

*Stoudenmire, White, PRB 87 155137, (2013)
How does DMRG work?

Lattice sites

Many-body wavefunction
How does DMRG work?

Freeze out all but a small piece of wavefunction
How does DMRG work?

Solve Schrödinger equation exactly for remaining piece

\[ \tilde{H} |\tilde{\Psi}\rangle = \tilde{E} |\tilde{\Psi}\rangle \]
How does DMRG work?

Shift exposed region, keeping only the most important states in the basis
How does DMRG work?

Shift exposed region, keeping only the most important states in the basis
Example DMRG Calculation

Video available online: http://youtu.be/0zi4qUnSqe0
DMRG for continuum systems
Grid basis

Need discrete degrees of freedom

Simplest approach is discretize real space:

\[ T = -\frac{1}{2} \int_x c^\dagger(x) \frac{\partial^2}{\partial x^2} c(x) \]

\[ \simeq -\frac{1}{2a^2} \sum_j (c_{j+1}^\dagger c_j - 2n_j + c_{j+1}^\dagger c_j) \]

Not atomic lattice sites, but “grid sites”
Converge results to $a \to 0$ limit…

Grid error—1d hydrogen atom:

\[ \text{Err.} \sim \frac{1}{a^{1.2}} \]
Hamiltonian

Want to study ‘uncontrived’ 1d physics

\[ \hat{H} = -\frac{1}{2} \sum_{\sigma} \int_x \psi^{\dagger}_\sigma(x) \frac{\partial^2}{\partial x^2} \psi_\sigma(x) \]

\[ + \frac{1}{2} \int_{x, x'} v_{ee}(x - x') \hat{n}(x) \hat{n}(x') \]

\[ + \int_x v(x) \hat{n}(x) \]
Hamiltonian

Want to study ‘uncontrived’ 1d physics

\[
\hat{H} = -\frac{1}{2a^2} \sum_{\sigma,j} \left( c_{\sigma j}^\dagger c_{\sigma j+1} - 2n_{\sigma j} + c_{\sigma j+1}^\dagger c_{\sigma j} \right) \\
+ \frac{1}{2} \sum_{i,j} v_{i j}^{i j} n_i (n_j - \delta_{i j}) \\
+ \sum_{j} v^j n_j
\]
Hamiltonian

What to choose for \( v(x), v_{ee}(x - x') \)?

1d matter:

\[
    v(x) = \sum_a v_a(x - x_a) = \sum_a -Z v_{ee}(x - x_a)
\]

Also we choose:

\[
    v_{ee}(x - x') = e^{-|x-x'|}
\]
Why hasn’t DMRG been applied to these systems before?

- Cost of long-range interactions
- Poor convergence—separation of energy scales
• Cost of long-range interactions

Normally DMRG scales $\propto N^2$, with this approach $\propto N^2 \times N = N^3$

Disaster for the continuum! ($N \sim 1000$)
• Cost of long-range interactions

Fortunately solution recently proposed:

By writing Hamiltonian as a product of “transfer matrices”* at each site, can represent arbitrary strings of operators.

Choosing strings of operator $\lambda \hat{I}$ produces exponentially decaying interactions.

* a matrix product operator (MPO)
• Cost of long-range interactions

Bottom line:
Cost of exponential interactions can be made same as next-neighbor

Can approximate power-laws as sum of exponentials:

\[
\frac{1}{|i - j|^{\alpha}} \approx \sum_p \chi_p \lambda_p^{i-j}
\]

Crosswhite, Doherty, Vidal, PRB 78 035116, (2008)
Why hasn’t DMRG been applied to these systems before?

- Poor convergence—separation of energy scales
• Poor convergence—separation of energy scales

At least 3 widely varying energy scales in our systems:

Grid kinetic energy ($\sim 1/a^2$)

\[ \downarrow \]

\[ \downarrow \]

Density fluctuation ($U$)

\[ \downarrow \]

\[ \downarrow \]

Spin fluctuation ($t^2/U$)
• Poor convergence—separation of energy scales

Unusual situation for DMRG:

Typically concerned about cost of “keeping enough states” for good accuracy.

Here number of states ~100 (small) but number of sweeps needed can be ~1000 or more.
• Poor convergence—separation of energy scales

Solution: make better initial state.

From grid point of view, system very dilute:

For small region, only handful of orbitals contribute to wavefunction.
• Poor convergence—separation of energy scales

Create coarse-graining mapping that projects all but these orbitals

Apply maps to Hamiltonian

Use DMRG at each scale and apply maps in reverse
Apply maps to Hamiltonian

Use DMRG at each scale and apply maps in reverse
Apply maps to Hamiltonian

$H_0$

Use DMRG at each scale and apply maps in reverse
Apply maps to Hamiltonian

Use DMRG at each scale and apply maps in reverse
Apply maps to Hamiltonian

Use DMRG at each scale and apply maps in reverse
Demonstration:
Demonstration:
Demonstration:
Demonstration:
Demonstration:
Demonstration:
DMRG for continuum systems

Summary: powerful tool to solve broad class of continuum 1d systems essentially exactly.

Today: DFT, but exciting possible applications for 1d cold atom/molecule experiment.

+ Minimal approximation of Hamiltonian required
+ Exploit DMRG’s abilities to simulate:
  ‣ Real-time dynamics
  ‣ Finite $T$ effects

Stoudenmire, Wagner, Burke, White, PRL 109, 056402 (2012)
Application #1: Computing Gaps in DFT
Lightning DFT overview...
Density functional theory (DFT)

Often where “rubber meets the road” in condensed matter / materials physics / chemistry.

Recent application:

Enhanced bulk topological gap in graphene coupled to heavy adatoms

Density functional theory (DFT)

Outputs a band structure, but what does it mean for an interacting system?

Spin-orbit coupling. As Fig. 2(a) illustrates, the Dirac cones characteristic of pure graphene indeed remain massless—despite the reduced translation symmetry, conventional gapped phases are not stabilized here, consistent with the intuition developed in the single-adatom case above.

Indium does, however, electron-dope graphene and shifts the Fermi level $E_F$ to 0.95 eV above the Dirac points. From the adatom's local density of states (LDOS) displayed in Fig. 2(a), one can see that indium's $5p$ orbitals lie almost entirely above $E_F$, implying that the $5p$ electron in neutral indium nearly completely transfers to graphene. (The charge of an indium adatom is $\frac{8}{8}$ from the Bader charge division scheme.)

Note that the relatively diffuse $p_z$ LDOS indicates that this orbital hybridizes more strongly with graphene compared to the $p_{x,y}$ orbitals. Replacing indium with thallium, again without spin-orbit coupling, leads to the band structure and LDOS shown in Fig. 2(d). Clearly the electronic structure is modified very little by this substitution; importantly, the Dirac cones remain massless with thallium as well.

Thus any gap opening at the Dirac points must originate from spin-orbit coupling. Figure 2(b) displays the band structure and LDOS for spin-orbit-coupled indium on graphene. Note the sizable spin-orbit splitting in the LDOS for the $p_{x,y}$ orbitals. More remarkably, a gap $\Delta\approx7$ meV now appears at the Dirac points, which already exceeds the spin-orbit-induced gap in pure graphene $\Delta\approx7-11$ by several orders of magnitude. The analogous results for thallium—whose atomic mass is nearly twice that of indium—are still more striking. As Fig. 2(e) illustrates, $p$-orbital splittings of order 1 eV are now evident in the LDOS, and a gap $\Delta\approx21$ meV opens at the Dirac points. We emphasize that these results apply for adatom coverages of only $6.25\%$.

To explore the dependence of $\Delta$ on the adatom coverage, we additionally investigated systems with one adatom in $\frac{5}{8}$, $\frac{7}{8}$, and $\frac{10}{8}$ supercells. (For $N$ supercells with $N$ a multiple of 3, the Dirac points reside at zero momentum and can thus hybridize and gap out even without spin-orbit coupling. We therefore ignore such geometries.) The values of $\Delta$ along with the Fermi level $E_F$ computed for the coverages we studied appear.
Density functional theory (DFT)

DFT an exact reformulation of quantum mechanics using density instead of wavefunction:

\[ E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \]

\[ E[n] = \min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle \]

“one of the greatest free lunches ever” — K. Burke
Density functional theory (DFT)

Rigorous foundation is the Hohenberg-Kohn theorem:

\[ \hat{H} = \hat{T} + \hat{V}_{ee} + \int_x v(x) \hat{n}(x) \]

\[ v(x) \longrightarrow \psi(\{x_j\}) \longrightarrow n(x) \]
Density functional theory (DFT)

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HK '64
Density functional theory (DFT)

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HK ’64
Density functional theory (DFT)

\( n(x) \rightarrow v(x) \) mapping holds for each type of interaction, including none:

\[
\hat{H} = \hat{T} + \hat{V}_{ee} + \int \! v(x) \, \hat{n}(x) \quad \text{(1)}
\]

\[
\hat{H}_s = \hat{T} + \int \! v_s(x) \, \hat{n}(x) \quad \text{(2)}
\]

Non-interacting system called "Kohn-Sham system". Defined to have same density as interacting one.
Easy to find *exact* Kohn-Sham potential if you have exact density already:
Easy to find exact Kohn-Sham potential if you have exact density already:

\[ n(x) \]

\[ v(x) \]

Exact KS potential \( v_s(x) \)
Here’s how:

1. Start with guessed Kohn-Sham potential and solve non-interacting problem.

2. Compare resulting density to exact (interacting system) density.

3. Update potential: attempt to reduce
   \[ \Delta n(x) = n_{\text{trial}}(x) - n(x) \]
KS Potential Demo Calculation:

\[ n^{\text{exact}} \quad n^{\text{trial}} \quad \psi_s^{\text{trial}} \]
KS Potential Demo Calculation:

- $n_{\text{exact}}$
- $n_{\text{trial}}$
- $\psi_{s}^{\text{trial}}$
KS Potential Demo Calculation:

\[ n^{\text{exact}} \]  \[ n^{\text{trial}} \]  \[ \psi_s^{\text{trial}} \]
KS Potential Demo Calculation:

\[ n_{\text{exact}} \quad n_{\text{trial}} \quad \psi_{s}^{\text{trial}} \]
KS Potential Demo Calculation:

\[ n^\text{exact}, \quad n^\text{trial}, \quad \psi_s^\text{trial} \]
KS Potential Demo Calculation:

\[ n_{\text{exact}}, \quad n_{\text{trial}}, \quad \psi_{s}^{\text{trial}} \]
KS Potential Demo Calculation:

- Green line: $n^{\text{exact}}$
- Red line: $n^{\text{trial}}$
- Blue line: $\psi^{\text{trial}}$

Graph showing the comparison of exact and trial potentials.
In DFT literature, divide KS potential into original $v(x)$ plus correction

$$v_s(x) \overset{\text{def}}{=} v(x) + v_{\text{HXC}}(x)$$

Mean-field-like picture:

$$\hat{H}_s = \hat{T} + \int x v_{\text{HXC}}(x) \hat{n}(x) + \int x v(x) \hat{n}(x)$$

Accounts for missing interactions
Is DFT a mean-field theory?

**No:** exact theory gives exact energy and ground-state density

**Yes:** using any other properties of KS system is a type of approximation
One such approximation: band gap $\approx$ real gap

Exact charge gap

$$E_g = I - A$$

$$I = E_{N-1} - E_N$$

$$A = E_N - E_{N+1}$$

KS band gap

$\pi$
Computing interacting charge gap

\[ n(x) \quad n_{\uparrow}(x) \quad n_{\downarrow}(x) \]

\[ N = 40 \]

Charge Gap: \[ E_g = E_{N+1} - 2E_N + E_{N-1} \]
Computing interacting charge gap

\[ n(x) \]

\[ n_{\uparrow}(x) \]

\[ n_{\downarrow}(x) \]

\[ N = 39 \]

Charge Gap: \[ E_g = E_{N+1} - 2E_N + E_{N-1} \]
Computing interacting charge gap

Charge Gap: $E_g = E_{N+1} - 2E_N + E_{N-1}$
1. Compute exact density of N-electron system.

2. Obtain (exact) Kohn-Sham potential and read off Kohn-Sham gap
Weakly correlated systems: H$_2$ chains

Chain of H$_2$ molecules, model band insulator

- Fixed H$_2$ equil length 1.26
- Parameter: bond length “b”
H$_2$ chains (40 atoms)

\[ n(x) \]

\[ \frac{v(x)}{4} \]

\[ b = 1.26 \]
H$_2$ chains

(40 atoms)

\[ n(x) \]

\[ \frac{v(x)}{4} \]

b = 1.54
H$_2$ chains

\[ b = 1.94 \]
$\text{H}_2 \text{ chains}$

(40 atoms)

\[ n(x) \]

\[ \frac{v(x)}{4} \]

\[ b = 2.34 \]
Extrapolate all results to thermodynamic limit.

![Graph showing the relationship between charge gap and inverse number of atoms.](image)
H$_2$ chains

![Graph showing the relationship between bond length and charge gap. The graph is labeled "Exact Gap." The x-axis represents bond length, ranging from 1.25 to 2.75, while the y-axis represents charge gap, ranging from 0 to 0.4. The graph shows a positive correlation between bond length and charge gap.]
H$_2$ chains

![Graph showing the relationship between bond length and charge gap for $H_2$ chains.](#)

- **Exact Gap**
- **KS Band Gap**
Expect KS system gapped since even # electrons in unit cell

Extra missing piece called derivative discontinuity,* absent from many approximate functionals

Also check standard approx’s:
Strong correlated systems: H chains

Chain of H atoms, model
Mott insulator

parameter: bond length “b”
$H$ chains

40 atoms

$n(x)$

$v(x)$

$\frac{v(x)}{4}$

$b = 1.0$
H chains

$\frac{n(x)}{4}$

$\frac{v(x)}{4}$

$b = 2.0$

(40 atoms)
H chains

(40 atoms)

\[ n(x) \]

\[ v(x) / 4 \]

\[ b = 3.0 \]
H chains

(40 atoms)

\[ n(x) \]

\[ v(x) / 4 \]

\[ b = 4.0 \]
H chains

![Graph showing the relationship between bond length and charge gap. The line labeled 'Exact Gap' increases as the bond length increases.]
Similarity to 1d Hubbard model:

- **Exact Gap**
- **Exponential opening**
- **Linear for larger gaps**
H chains

![Graph showing the relationship between bond length and charge gap. The graph has a y-axis labeled "Charge Gap" and an x-axis labeled "Bond Length." Two lines are plotted: one for "Exact Gap" and another for "KS Band Gap." The "Exact Gap" line starts near zero at a bond length of 1.2 and gradually increases as the bond length increases. The "KS Band Gap" line is not shown in this description.]
H chains Mott insulators, one electron per unit cell

\[ \rightarrow \text{ lowest band of Kohn-Sham system half full} \]

Not failure of DFT per se—taking KS band gap an uncontrolled approximation
But comparing to LDA yields another twist…

(Unrestricted) LDA approx spontaneously breaks spin symmetry:

well-known “spin contamination” effect
Unrestricted LDA gap “better” than exact KS gap
Future work on gaps:

- Benchmark gaps with standard approx’s (Hybrids, LDA+U)
- Benchmark newer approx’s (range-separated hybrids)
- Obtain argument for generality of ULDA gap, useful approach for more realistic systems?
Application #2: 
Convergence of KS Equations
Recall last section:

Interacting sys. \[ \hat{H} = \hat{T} + \hat{V}_{ee} + \int_x v(x) \hat{n}(x) \]

Exact density \[ n(x) \]

"inversion"

Exact KS system \[ \hat{H}_s = \hat{T} + \int_x v_s(x) \hat{n}(x) \]

Gaps, etc.
But in real DFT applications:

Replace

$\mathbf{Trial\ density: \ n_j(x)}$

$\mathbf{n_{j+1}(x)}$

Kohn-Sham Equations

New KS system: $v_s^{(j)}$
But in real DFT applications:

Replace

Trial density: \( n_j(x) \)

\( n_{j+1}(x) \)

Kohn-Sham Equations

New KS system: \( \nu_s^{(j)} \)
Trial density: $n_j(x)$

New KS system: $v_s^{(j)}$

Recall: $v_s(x) = v(x) + v_{HXC}(x)$

Definition of $v_{HXC}(x)$
Obtain KS potential supporting $n_j(x)$
(saw this before)

no interactions

$v_s[n_j](x)$
Obtain interacting-system potential supporting $n_j(x)$

with interactions

$v[n_j](x)$
\[ \nu_{\text{HXC}}[n_j](x) = \nu_s[n_j](x) - \nu[n_j](x) \]

new “mean-field” correction to potential

New Kohn-Sham system:

\[ \hat{H}_s = \hat{T} + \int_x \nu_{\text{HXC}}[n_j](x)\hat{n}(x) + \int_x \nu(x)\hat{n}(x) \]

Solve to get new trial density…
Only new ingredient is “interacting inversion”, requires solving many interacting systems.

Being able to compute both:

\[ v_s[n](x) \]
\[ v[n](x) \]

Means having the “exact functional”
Exact functional

Often discussed as a closed-form analytic expression:

Our perspective: exact functional is an algorithm
What’s the application?

Learn how DFT behaves with exact functional. Any failures are fundamental. Otherwise they are failures of approximations.
Convergence

Do the KS equations always converge using the exact functional?

Test calculations using DMRG on small chains:

![Graph showing input and output densities for a one-dimensional, strongly correlated four-atom system.](image-url)
Convergence

One step of the KS equations

Already looks to overshoot…
Is damping enough to fix?

\[ n_\lambda(x) = \lambda n_{j+1}(x) + (1 - \lambda) n_j(x) \]
Convergence

Test 1: weakly correlated H₂ molecule

Damping helps, but not required:
Convergence

Test 2: strongly correlated \( \text{H}_2 \) molecule

Convergence requires \( \lambda < 0.5 \)
Convergence

Is damping always enough?

Yes! Can prove via linear response that energy always goes down for small enough damping.

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

Combined with convexity of exact functional, guarantees convergence.
Future Directions
Gaps are an example where exact Kohn-Sham system fails to reproduce exact properties.

What about transport?

Common approx: \( G(k, \omega) \rightarrow G^{KS}(k, \omega) \)

Yields exact transport properties of single-impurity Anderson model!

Continuum models?

Combine METTS* algorithm with continuum. Test thermal DFT approximations, cold atoms systems at finite T.

- DMRG/QMC hybrid
- Quantum Monte Carlo with no sign problem
- (Does have the “DMRG problem”)

\[ |1\rangle = |\uparrow\rangle|\downarrow\rangle|\downarrow\rangle|\uparrow\rangle \]

\[ |\phi_1\rangle \propto e^{-\beta H/2} |1\rangle \]

\[ \langle \phi_1|\hat{A}|\phi_1\rangle \]

*White, PRL 102, 190601 (2009)
Stoudenmire, White, NJP 12, 055026 (2010)
Combine METTS* algorithm with continuum. Test thermal DFT approximations, cold atoms systems at finite T.

- DMRG/QMC hybrid
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- (Does have the “DMRG problem”)

\[ |2⟩ = |↑⟩|↓⟩|↑⟩|↓⟩ \]

\[ |φ_1⟩ \propto e^{-βH/2} |1⟩ \]

*White, PRL 102, 190601 (2009)
Stoudenmire, White, NJP 12, 055026 (2010)
Compute lattice models using exact natural orbitals, DFT (Kohn-Sham) orbitals. Compare to continuum. (Good student project.)
Compute lattice models using exact natural orbitals, DFT (Kohn-Sham) orbitals. Compare to continuum. (Good student project.)
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Summary

- Can extend DMRG to solve continuum 1d systems.
- Computing exact quantities appearing in density functional gives insight into gaps, KS equations.
- Much more to explore including:
  - Quasi-1d cold atom/molecule systems
  - Transport approx’s in DFT
  - Continuum to lattice mapping