Quantum chemistry and materials simulation in the age of entanglement

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The last time I did an experiment

the little kids had to show me what to do.
What we want to understand (I) biocatalysis

\[ \text{H}_2\text{O} + 4e^- + nh\nu \rightarrow \text{H}_2 + \text{O}_2 \]

photosynthesis

\[ \text{N}_2 + 8\text{H}^+ + 8e^- + 16\text{ATP} \rightarrow 2\text{NH}_3 + \text{H}_2 + 16\text{ADP} + 16\text{P}_i \]

nitrogen fixation

how does Nature perform remarkable chemistry under ambient conditions?
What we want to understand (II) molecular materials

how do we make materials with molecular tailorability that rival or exceed their traditional semiconductors?
What we want to understand (III) high temperature superconductivity

1986: cuprates, $T_c = 135K$
2008: iron-based, $T_c = 55K$

don’t know what is going on but not for a lack of theories!

can we understand and predict superconductivity from a quantitative microscopic level?
Quantum mechanics is the foundation of chemistry

The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known ...

Dirac (1929)

the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.
Quantum mechanics

\[ H \psi = E \psi \]

H is a differential operator

single particle (e.g. electron in H atom) \( \psi(\mathbf{r}) \) (orbital)

\[ |\psi(\mathbf{r})|^2 \]

probability distribution of electron in space

energies of transitions between different orbitals can be measured by spectroscopy.

fine structure constant: theory (QED) expt agree to p.p.b.
Many particle QM

classical world

observe

can observe 1st ball’s position independently of 2nd ball’s position

quantum world

observe

observed value of 1st position depends on observed value of 2nd position

Einstein did not like this “spooky action at a distance”, but it can be observed. QM of many components involves joint probability amplitudes
many particle wavefunctions

\[ \Psi(r_1, r_2, \ldots r_n) \]

simultaneous probability (amplitude) of n electrons

wavefunction is high-dim object

Quantum simulation (quantum chemistry) appears exponentially hard as number of electrons increases. Just storing the wavefunction seems impossible!
Doing the best you can: Pople

Basis (spatial resolution)

one electron at a time

increasing accuracy and increasing complexity

Treating more electrons explicitly

HF  Doubles  Triples  N-tuples
but this view of many-particle QM is depressing

[The Schrodinger equation] cannot be solved accurately when the number of particles exceeds about 10. No computer existing, or that will ever exist, can break this barrier because it is a catastrophe of dimension ...  

Pines and Laughlin (2000)

in general the many-electron wave function $\Psi$
... for a system of $N$ electrons is not a legitimate scientific concept [for large $N$] 

Kohn (Nobel lecture, 1998)
Density Functional Theory?
also known as, “Giving Up”

“for systems of very many electrons where wave function methods encounter and are stopped by the exponential wall”

kohn-sham density functional theory

Kohn

solve for each particle’s behaviour independently, add “correlations” with fudge-factor “exchange-correlation functional”

\[ E[\rho] = E_{mf}[\rho] + E_{xc}[\rho] \]

DFT revolutionized usage of quantum chemistry. For a while it seemed there would be nothing else!
but there are many problems

functionals capture “average” interaction effects
does not cancel repulsion of single electron: feels repulsion of itself!

Difficulties with:

<table>
<thead>
<tr>
<th>Multicenter bonds</th>
<th>Charge transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excited states</td>
<td>Transition metals</td>
</tr>
<tr>
<td>Spin states</td>
<td>Dispersion</td>
</tr>
</tbody>
</table>

etc. etc. etc.

Radically improving DFT appears extremely challenging or impossible

New efforts to understand many-electron wavefunctions and renaissance in rigorous quantum simulations
illusion of complexity

nature does not explore all possibilities

exponential complexity is not real
physical many-electron wavefunctions

\[ \Psi(r_1, r_2, \ldots, r_n) \]

simultaneous probability (amplitude) of n electrons

but not concerned with arbitrary quantum states

\[ H \Psi(r_1, \ldots, r_n) = E \Psi(r_1, \ldots, r_n) \]

ground and low-lying quantum states of Hamiltonians with physical interactions
Local realism recovered

We do observe locality (local realism) in our lives!

Physical quantum states only support limited long-range entanglement.

For ground-states this reflects the limited interactions in the Hamiltonian.

If we divide system into inner and outer regions, only degrees of freedom on the boundary are “entangled”. Surface “Area Law” of entanglement.
General argument

Hastings: (from Lieb-Robinson bounds)

\[ |\Phi\rangle \quad \text{product state (unentangled state)} \]

true ground-state \[ \exp(-\beta H)|\Phi\rangle \]

but Hamiltonian applied finite \[ O(1/\text{Gap}) \] times

only limited amount of entanglement generated
Mathematics of entanglement

\[ \Psi(n_1, n_2) = A(n_1)A(n_2) \]

\[ \Psi(n_1, n_2) = \sum_{i} A(n_1, i)A(n_2, i) \]

low entanglement (physical states): \textbf{small number} of terms
Tensor networks

\[
\Psi(n_1, n_2, n_3) = A(n_1)A(n_2)A(n_3)
\]

entangled

\[
\Psi(n_1, n_2, n_3) = \sum_{i j} A(n_1, i)A(n_2, i, j)A(n_3, j)
\]

replace scalar “classical” probabilities by “tensor” quantum probabilities and contract in some pattern: tensor network

Nishino, Wen, Vidal, Cirac, Verstraete
Tensor networks and Lego

tensor networks: physical wavefunctions constructed by contracting local tensor probabilities together

**polynomial space complexity** because need not explicitly consider joint probabilities

Computation involves contraction of the graph can be hard, but polynomial time approximation algorithms in physically relevant cases
Simple example

$H_{50}$ symmetric bond-stretch (50,50)  active space $10^{28}$

$$\Psi(s_1, s_2, \ldots s_k) = \sum_{\{\alpha\}} A(s_1, \alpha_1) A(s_2, \alpha_2, \alpha_3) \ldots A(s_k, \alpha_{k-1})$$

<table>
<thead>
<tr>
<th>$r/r_e$</th>
<th>$M=250$</th>
<th>$M=500$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-0.41914</td>
<td>-0.41919</td>
</tr>
<tr>
<td>1.6</td>
<td>-0.65718</td>
<td>-0.65719</td>
</tr>
<tr>
<td>2.0</td>
<td>-0.91789</td>
<td>-0.91789</td>
</tr>
<tr>
<td>3.2</td>
<td>-2.67195</td>
<td>-2.67195</td>
</tr>
</tbody>
</table>

can solve Schrödinger equation even in $10^{28}$ dimensional space
Fundamental physics

Tensor networks are a new language of QM. They are having an impact in many fundamental areas of physics.

e.g. natural successor to the renormalization group language of physics from 70’s

RG: describe in terms of collective behaviour of successively larger groups of molecules, removing microscopic detail
Tensor network as RG

physical degrees of freedom

Density matrix RG
White (1993)

renormalized degrees of freedom

RG flow

traditional RG is a theory of linear (or tree) tensor networks, but tensor network allow more general flow of information
Quantum phases

classical phases

solid, liquid, gas ...

quantum phases

metal, insulator, superconductor, magnet, anti-ferromagnet, spin-liquid, flux phase, topological insulator ...

As tensor networks are believed to cover all “physical states”, classify phases according to mathematics of TNS.
Tensor networks and phases

Wavefunction with symmetry transform in a simple way under symmetry operations

$$\Psi(r, r' \ldots) = e^{i\phi} \Psi(Sr, Sr' \ldots)$$

Different phases related to representations of the symmetry group

Projective symmetry group (Wen), includes traditional phases and topological phases
bioinorganic systems

active site of biological processes such as photosynthesis and nitrogen fixation: complex clusters of transition metals
tensor networks in biology

without tensor networks, electronic states (which govern catalysis) were simply not computable – “guessed” from fitting poor spectroscopic data


Tensor network simulation: 10’s to 100’s of states on vibrational energy scales

Crossings of electronic states are ubiquitous in large metalloenzyme clusters

Mn4CaO5 water-splitting complex: Kurashige, Yanai, Chan, Nature Chem (2013)

Central role of non-adiabaticity in bioinorganic chemistry?
Molecular materials

Molecular crystal structure governs function, but ...

“One of the continuing scandals in the physical sciences is that it remains impossible to predict the structure of even the simplest crystalline solids from their chemical composition”


Challenges

Global sampling of molecular conformations

Accurate energy functions

“accurate energy models ... prove to be the most challenging aspect of successful crystal structure prediction”

Report from CSP2010 (Crystal Structure Prediction competition)
Polymorph energy scale

Molecular crystal polymorphs often separated by ~1.0 kJ/mol!

Can we compute crystal lattice energies to better than 1 kJ/mol?
Theory and *revised* exptal lattice energies

**Final theor. lattice energy:** $55.97 \pm 0.76 \pm 0.1 \text{ kJ/mol}$

**Exptal lattice energy:** 51-53 kJ/mol!

**Revise exptal lattice energy:** $55.3 \pm 2 \text{ kJ/mol}$!

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Theoretical lattice energy accurate to 0.76 kJ/mol
i.e. **now possible to reach the polymorph energy scale**

Good agreement with revised expt., but theor. lattice energies **more accurate** than exptal counterparts

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Yang, Hu, Usvyat, Matthews, Schuetz, Chan, Science (2014)
Superconductivity: 2D Hubbard model of cuprates

Cu $d^9$ tetragonal: one active orbital per CuO$_2$ unit:
Each CuO$_2$ unit is a single orbital “site” in a Hubbard model
Converged 2D Hubbard phase diagram

Different methods now give consistent results!

Energies per site as a function of interaction U, half-filling

<table>
<thead>
<tr>
<th>U</th>
<th>DMET</th>
<th>DMRG</th>
<th>AFQMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-0.8611</td>
<td>-</td>
<td>-0.8603</td>
</tr>
<tr>
<td>6</td>
<td>-0.6567</td>
<td>-</td>
<td>-0.6568</td>
</tr>
<tr>
<td>8</td>
<td>-0.5237</td>
<td>-0.5247</td>
<td>-0.5248</td>
</tr>
<tr>
<td>12</td>
<td>-0.3685</td>
<td>-0.3696</td>
<td>-</td>
</tr>
</tbody>
</table>

Energies per site agree to 0.1-0.3%

Simons collaboration led by Millis; benchmarking project led by Gull and White
Superconductivity at 0K

Hubbard model phase diagram from DMET $4 \times 2$ calculations ($T=0K$)

AF phase

SC phase

metal

AF phase boundary

d-wave SC phase boundary
Conclusions

Complexity of quantum mechanics is often an illusion.

Tensor networks provide a natural parametrization of physical quantum states.

This new language is not only changing fundamental physics, but enabling rigorous many-particle quantum mechanical simulations of complex materials.