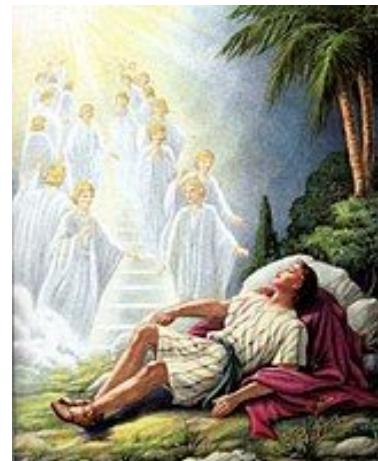


# How Quantum Computing Can Transform Quantum Chemistry and Physics

Quantum Mechanical Heaven =  
Quantum Computers!?



Chemical Accuracy	
Rung 5	Double hybrid +dependence on virtual orbitals
Rung 4	Hybrid +dependence on occupied orbitals
Rung 3	Meta-GGA +dependence on kinetic energy
Rung 2	GGA +dependence on density gradient
Rung 1	LDA dependence on local density
Hartree World	

computational cost ↑

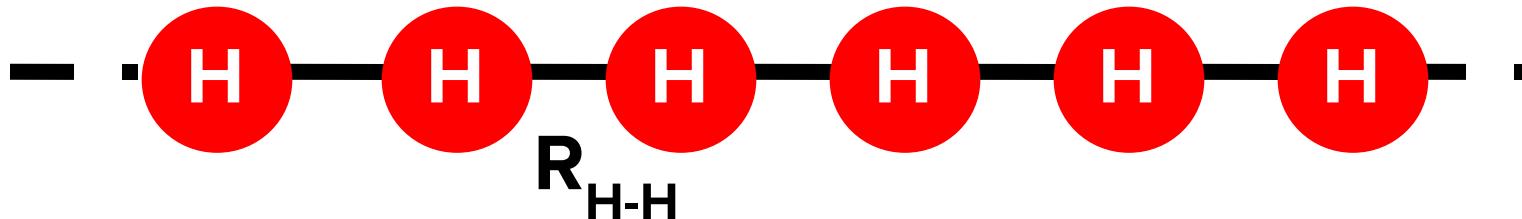
**PROF. BRENDA RUBENSTEIN**  
**Joukowsky Family Assist. Prof. of Chemistry**  
*Dartmouth/Brown Quantum Winter School 2020*



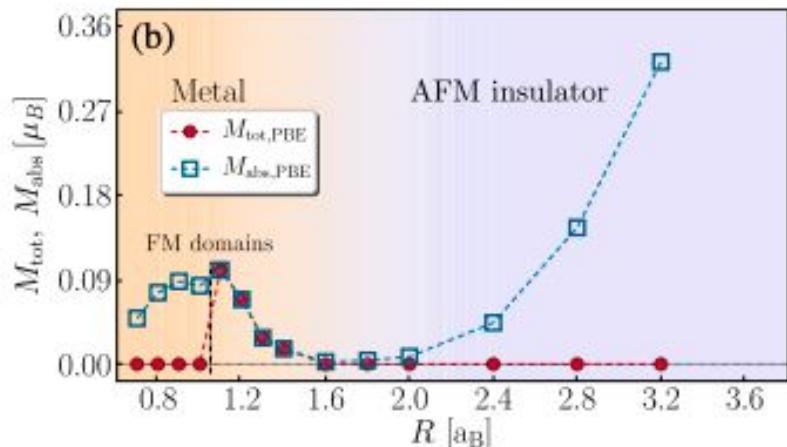
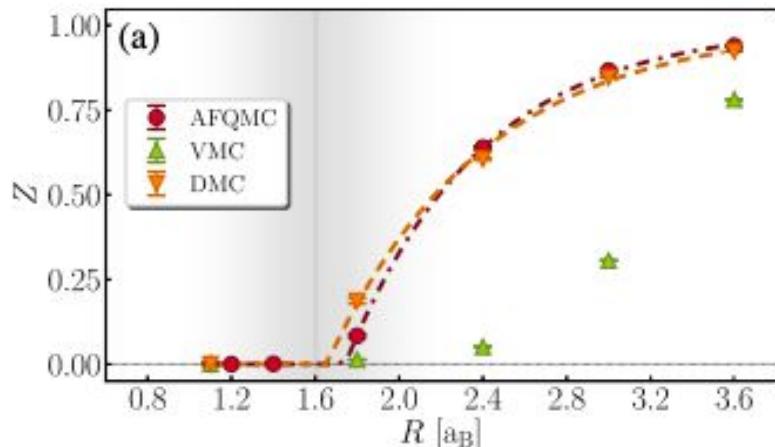
BROWN

# CHALLENGING QUANTUM PROBLEMS

## Hydrogen Chains!

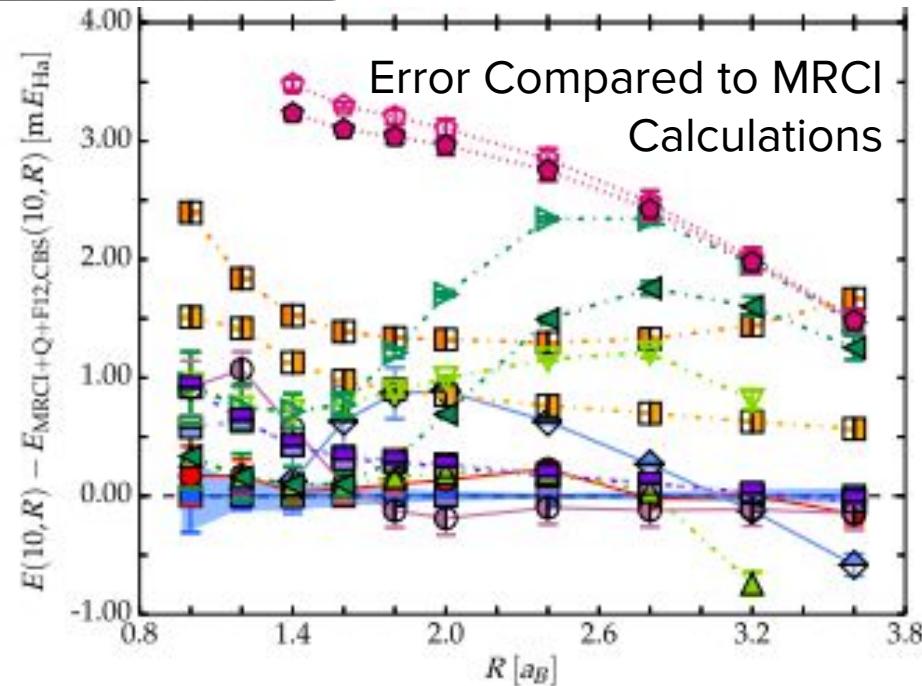
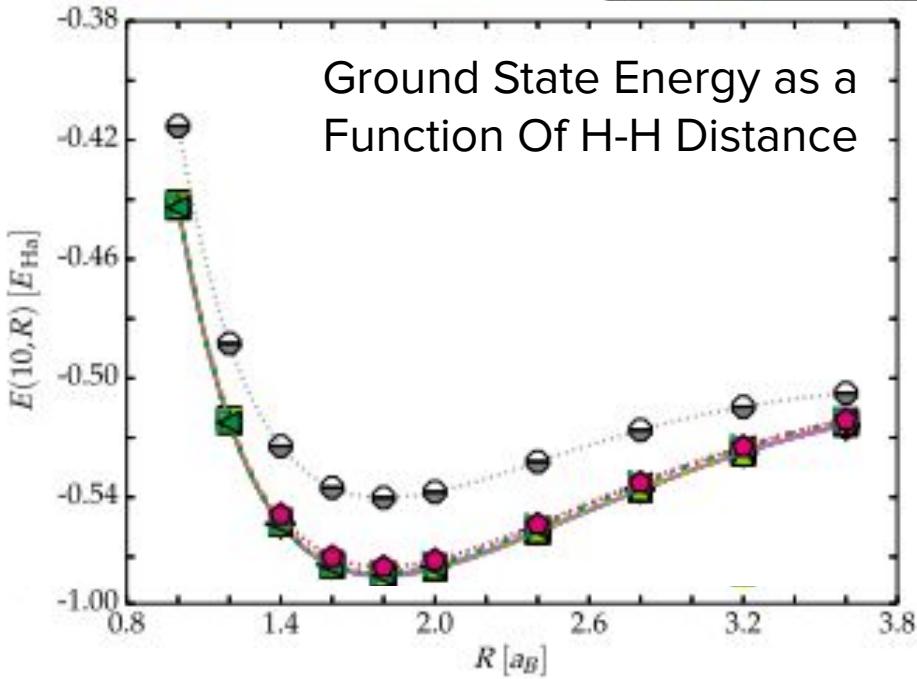
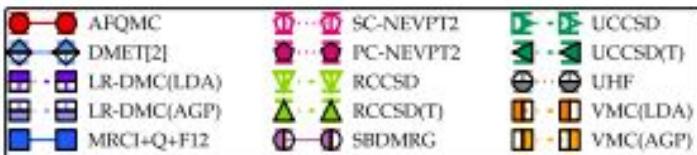


### Metal Insulator Transition



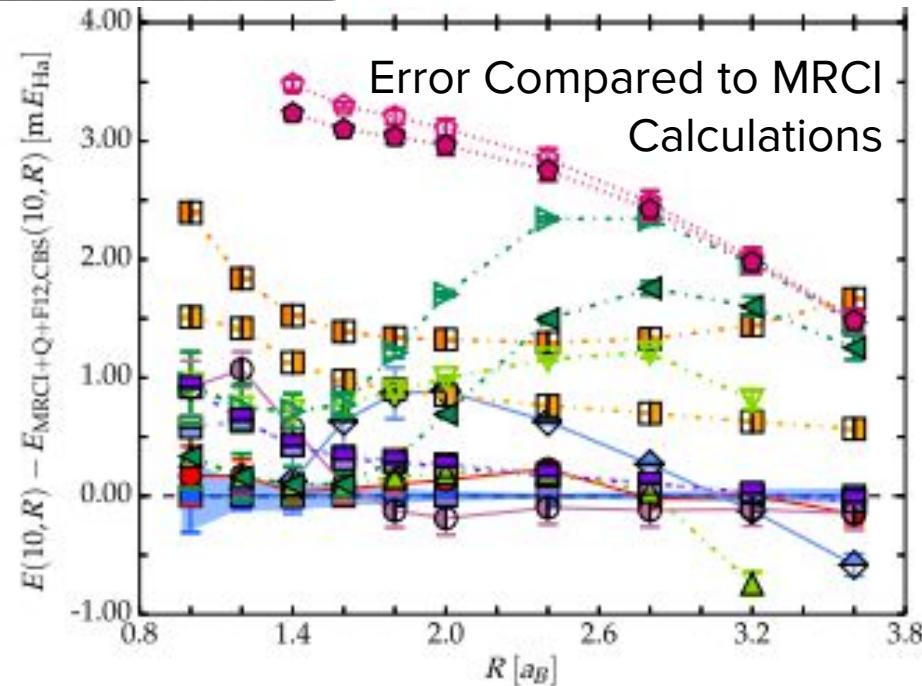
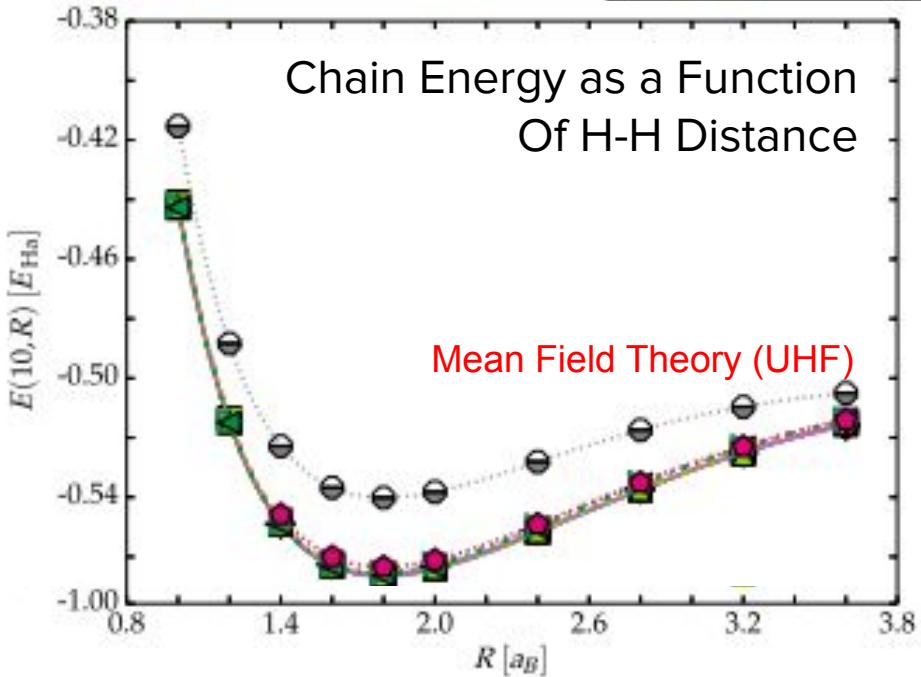
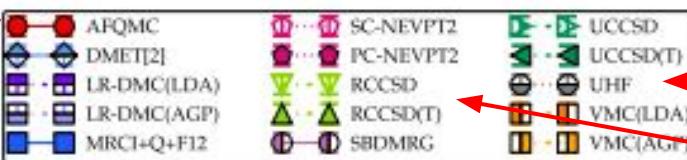
# CHALLENGING QUANTUM PROBLEMS

## Hydrogen Chains!



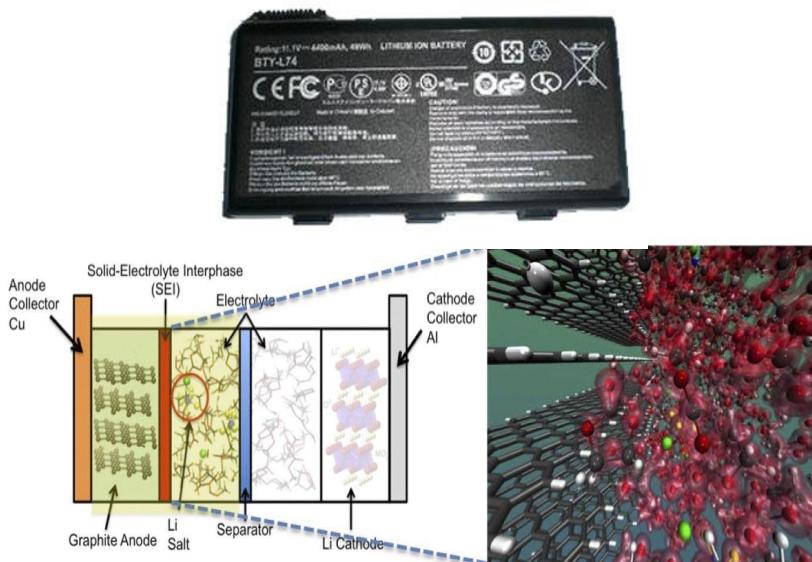
# CHALLENGING QUANTUM PROBLEMS

Hydrogen Chains!



# DESIGNING MATERIALS OF TOMORROW, TODAY

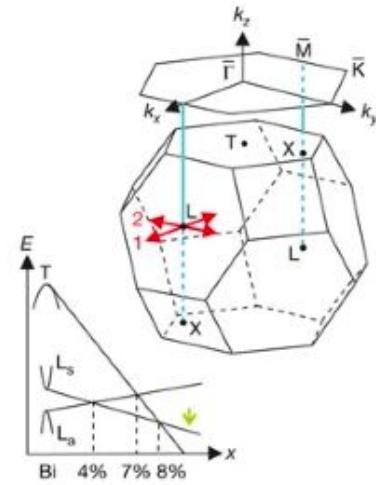
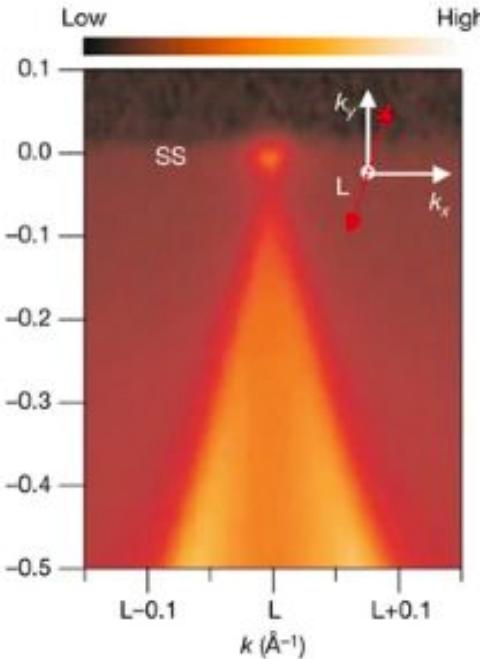
## Batteries



**How do we make batteries with high energy densities and shorter discharge times?**

M. Ong et al., *J. Phys. Chem. B*, 2015.

## Topological Insulators



**Can we predict and design new topological insulators?**

D. Hsieh et al., *Nature*, 2008.

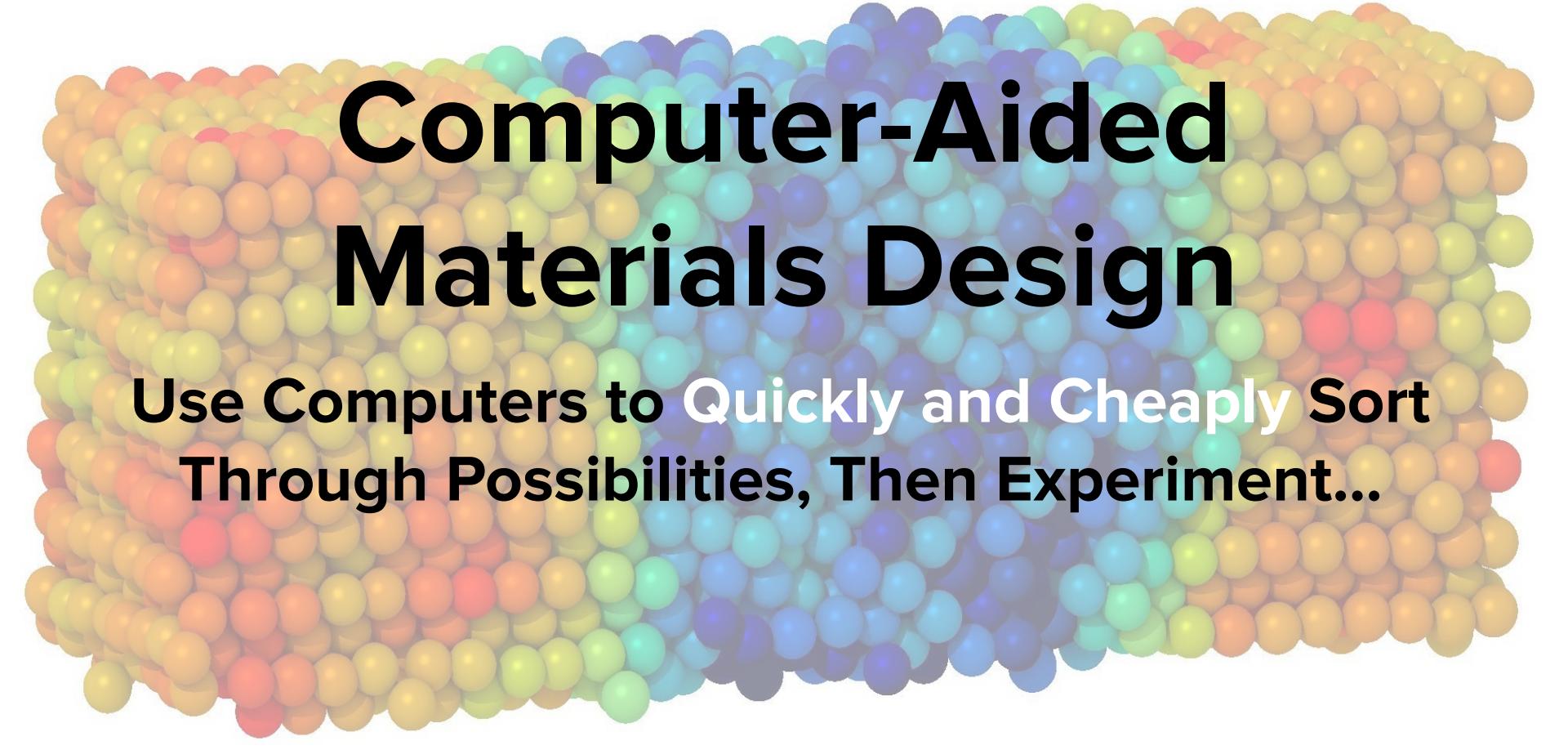
THE “OLD” WAY OF DOING THINGS

# Experimentation!

BUT, Experiments Cost \$\$\$\$\$\$ and Require  
People, Sometimes *Many, Many* People



THE “NEW” WAY OF DOING THINGS



# Computer-Aided Materials Design

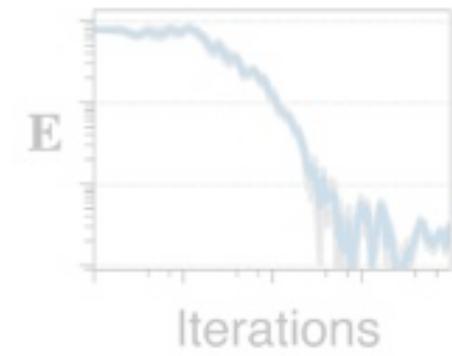
**Use Computers to Quickly and Cheaply Sort  
Through Possibilities, Then Experiment...**

THE “*NEW, NEW*” WAY OF DOING THINGS

# Machine Learning Quantum Mechanics

Use Machine Learning to *Directly Predict Properties*  
*or Accelerate Computation,*  
Then Experiment...

$$r_j \sim |\psi_\theta|^2$$



# COMPUTER-AIDED MATERIALS DESIGN



1 Candidate Molecules/Materials  
*(aka, Good Guesses)*



2 Simulation



Synthesis 4

3 Screened Candidates  
*(aka, Better Guesses)*



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# TODAY'S SIMULATIONS

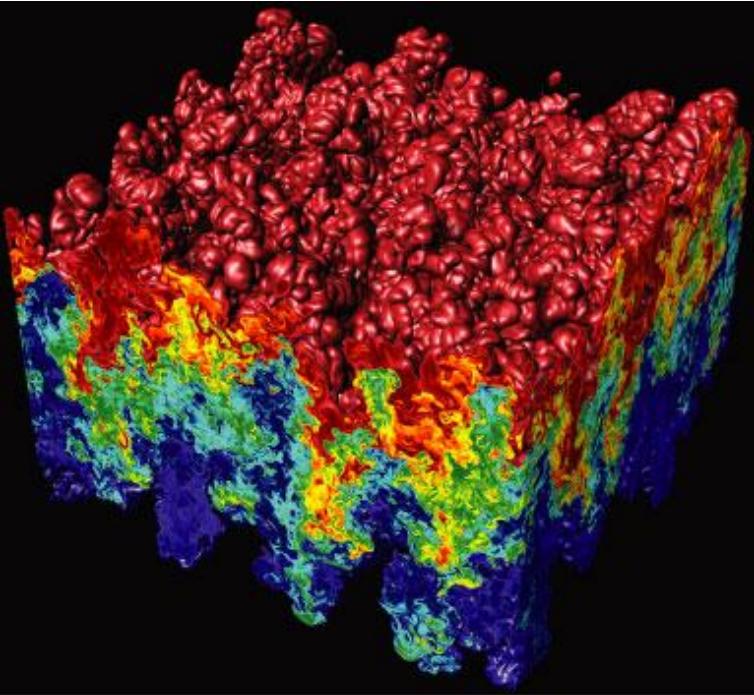
## Molecular Dynamics Meets Hydrodynamics



Fred Streitz,  
LLNL Computational  
Physicist,  
2007 Gordon Bell Prize  
Recipient.



IBM Blue Gene,  
104 Racks, 596 TFlops, 2007.



Over 1 Trillion Particles,  
Visualization of the Onset of the  
Kelvin-Helmholtz Instability, 2007.



BROWN

# THE SCHRODINGER EQUATION (SWE)

Still a Challenge for Theorists

You may have been taught that the Schrodinger Equation is a recipe for solving problems in quantum mechanics.

$$\mathcal{H}\Psi = E\Psi$$



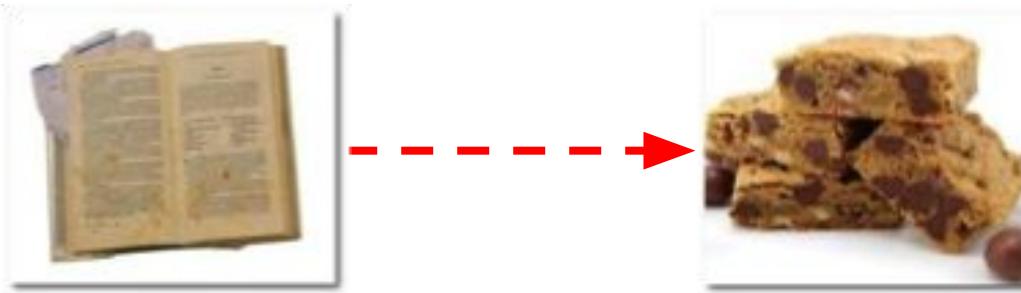
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# THE SCHRODINGER EQUATION (SWE)

Still a Challenge for Theorists

You may have been taught that the Schrodinger Equation is a recipe for solving problems in quantum mechanics.

$$\mathcal{H}\Psi = E\Psi$$



**BUT, it only tells us what equation we should be solving, NOT how to solve it accurately in a computationally tractable amount of time!**

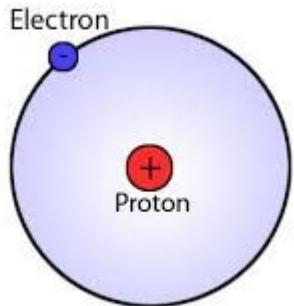


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# SOLVING THE ONE-ELECTRON SWE

What You're Misleadingly Taught!

**What We're Used To**  
The One-Body Case



Hydrogen Atom (1e, 1p)

Hydrogen Atom  
Hamiltonian

$$\hat{H} = -\frac{1}{2} \nabla^2 - \frac{1}{|\vec{r} - \vec{R}|}$$

Kinetic  
Energy  
of Electron

Electron-  
Nuclear  
Interaction

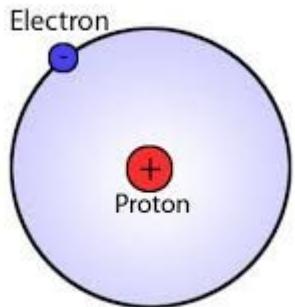


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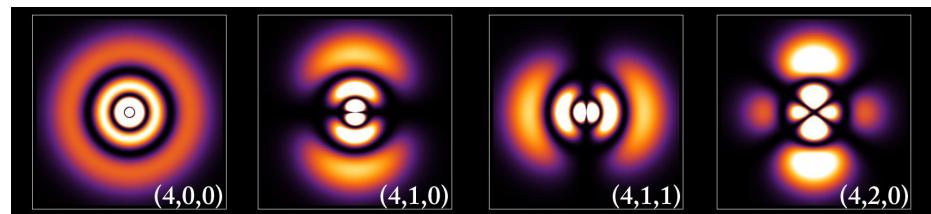


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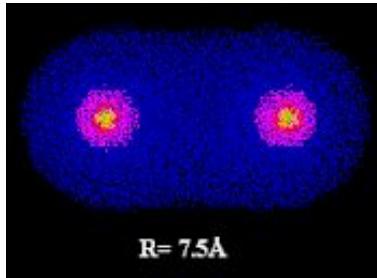
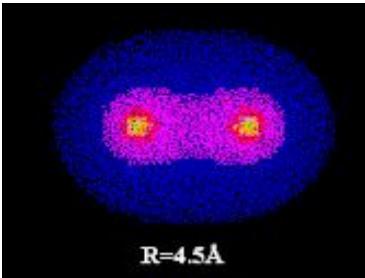
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# SOLVING THE ONE-ELECTRON SWE

What We Actually Need to Solve!

**Most of Physics!**

The Many-Body Case



Molecular  
Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i < j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,a=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} + \sum_{a < b=1}^N \frac{1}{|\mathbf{R}_a - \mathbf{R}_b|}$$

Hydrogen Molecule (2e, 2p)



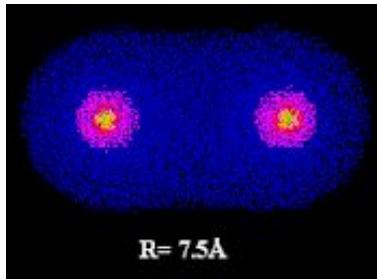
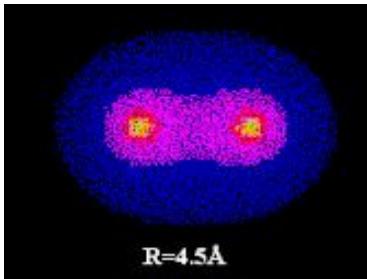
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Electron-Electron Interaction!

Internuclear Interaction!



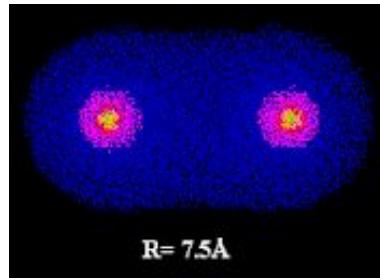
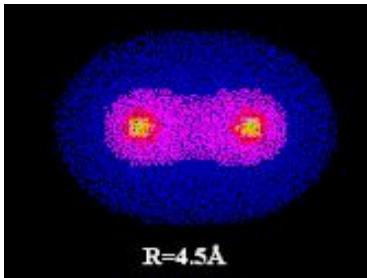
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# SOLVING THE ONE-ELECTRON SWE

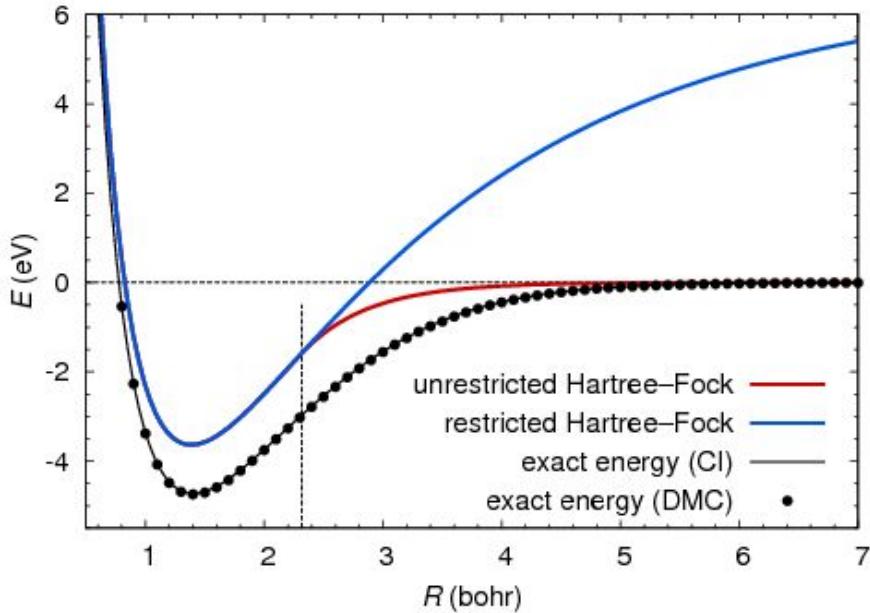
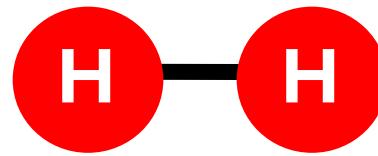
What We Actually Need to Solve!

**Most of Physics!**

The Many-Body Case



Hydrogen Molecule (2e, 2p)



# THE PROBLEM: E-E INTERACTION

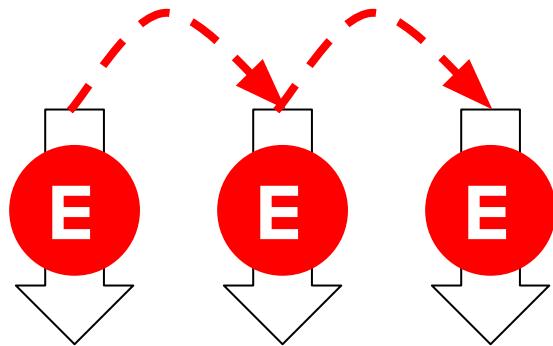
Correlated, Coordinated Electrons

## Molecular Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \boxed{\sum_{i < j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}} \\ - \sum_{i,a=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{R}_a|} + \sum_{a < b=1}^N \frac{1}{|\mathbf{R}_a - \mathbf{R}_b|}$$

Electron-  
Electron  
Interaction!

## How Electrons Actually Behave



(Well, Not Quite This  
Dramatically...)

## Key Point:

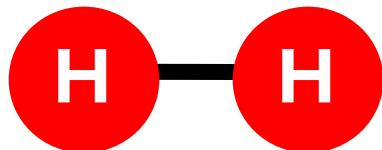
Electrons Behave in a **Correlated Fashion**, Especially *d*- and *f*- Electrons

# EXACT DIAGONALIZATION (ED)

The Most Straightforward, Most Accurate Technique

1. Determine Many-Electron States of the System

(2 electrons,  
2 orbitals)



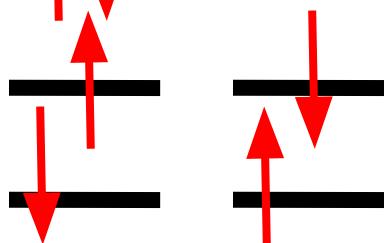
State 1



State 2



State 3



State 4



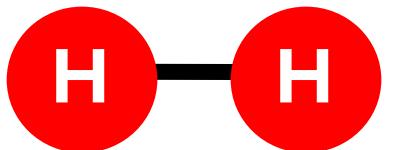
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# EXACT DIAGONALIZATION (ED)

The Most Straightforward, Most Accurate Technique

1. Determine Many-Electron States of the System

(2 electrons,  
2 orbitals)



2. Construct Hamiltonian  
Based Upon Those States

State 1



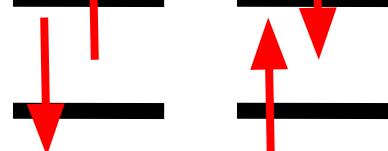
State 2



State 3



State 4



$$\hat{H}\Psi = E\Psi$$
$$\hat{H} = \begin{pmatrix} h_{1,1} & h_{1,2} & h_{1,3} & h_{1,4} \\ h_{2,1} & h_{2,2} & h_{2,3} & h_{2,4} \\ h_{3,1} & h_{3,2} & h_{3,3} & h_{3,4} \\ h_{4,1} & h_{4,2} & h_{3,4} & h_{4,4} \end{pmatrix}$$



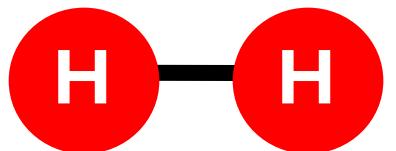
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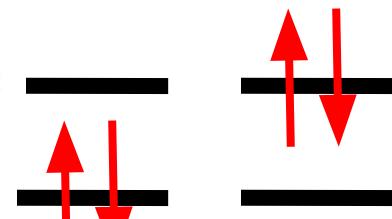
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$$|\Psi_1\rangle = |\psi_2\bar{\psi}_2\rangle$$



$$|\Psi_2\rangle = |\psi_1\bar{\psi}_1\rangle$$



$$|\Psi_3\rangle = |\psi_1\bar{\psi}_2\rangle$$



$$|\Psi_4\rangle = |\psi_2\bar{\psi}_1\rangle$$

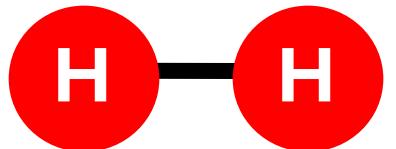


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$$|\Psi\rangle = c_1|\Psi_1\rangle + c_2|\Psi_2\rangle + c_3|\Psi_3\rangle + c_4|\Psi_4\rangle$$

$$|\Psi_1\rangle = |\psi_2\bar{\psi}_2\rangle$$



$$|\Psi_2\rangle = |\psi_1\bar{\psi}_1\rangle$$



$$|\Psi_3\rangle = |\psi_1\bar{\psi}_2\rangle$$

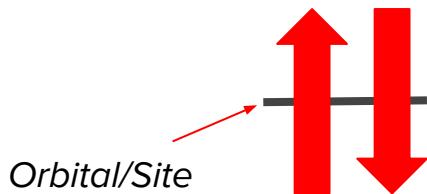


$$|\Psi_4\rangle = |\psi_2\bar{\psi}_1\rangle$$



# SOLVING THE SWE EXACTLY

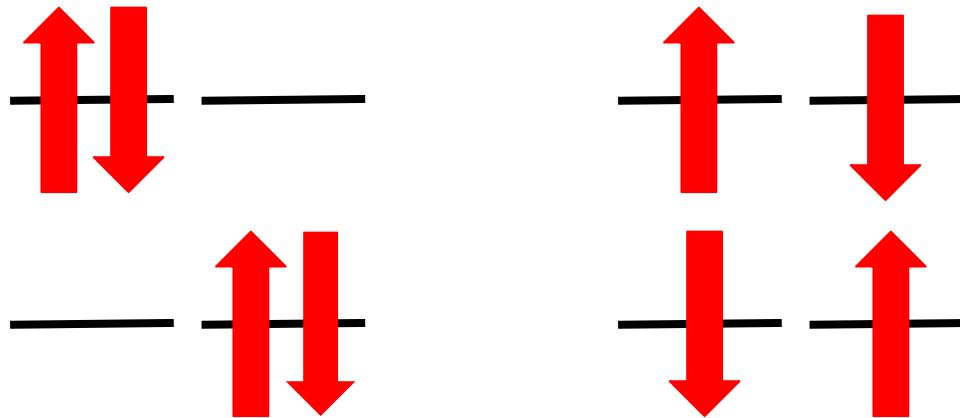
Solving the Schrodinger Equation exactly is theoretically straightforward: just enumerate all of the possible states.



**Consider 2 Electrons in 1 Orbital:  
1 State**

# SOLVING THE SWE EXACTLY

Solving the Schrodinger Equation exactly is theoretically straightforward: just enumerate all of the possible states.



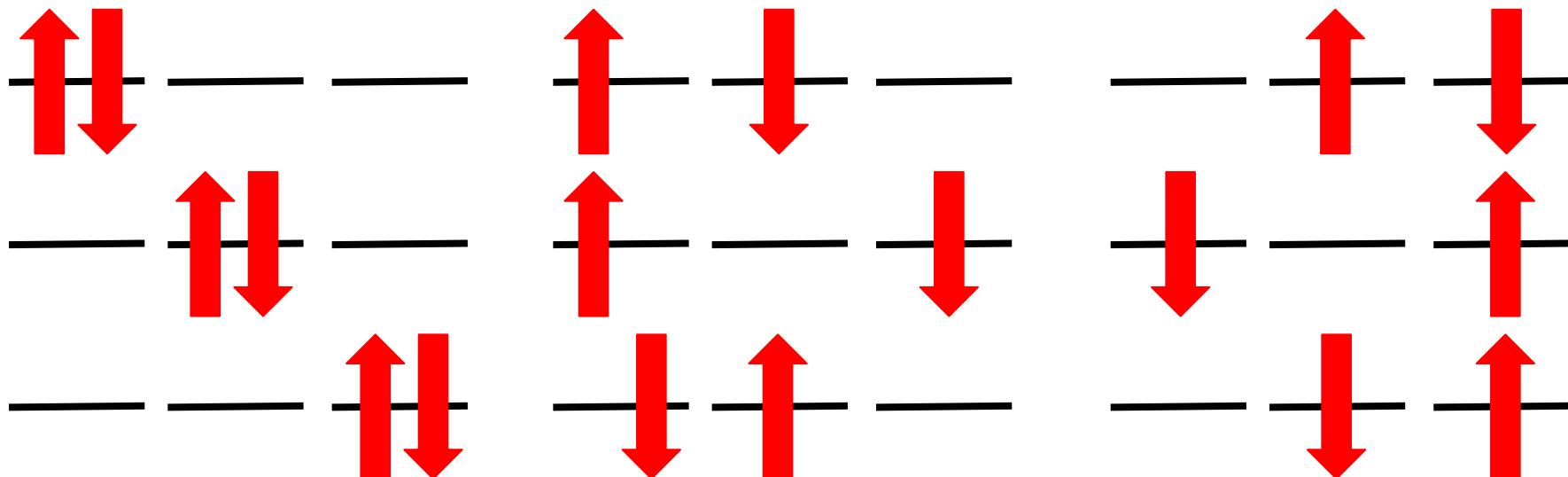
**Consider 2 Electrons in 2 Orbitals:  
4 States**



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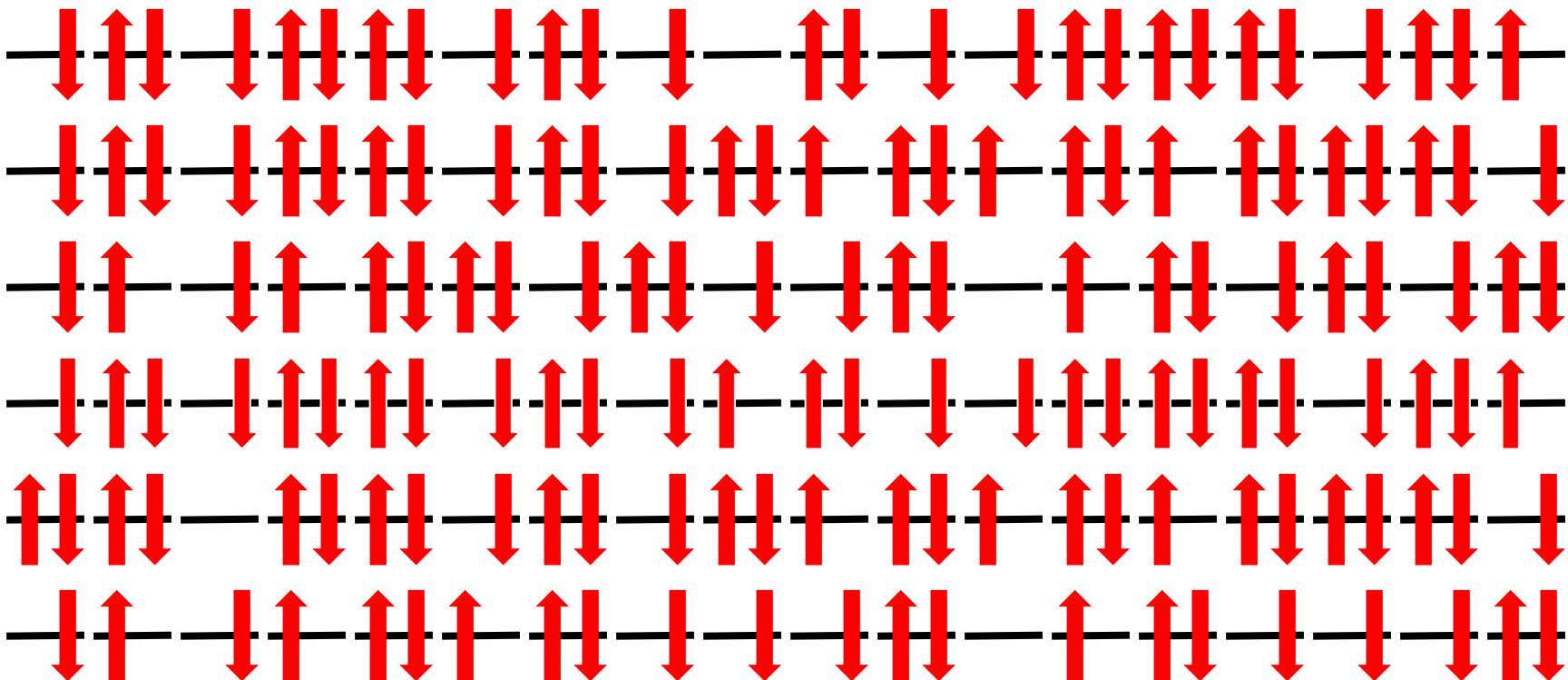
# SOLVING THE SWE EXACTLY

Solving the Schrodinger Equation exactly is theoretically straightforward: just enumerate all of the possible states.



Consider 2 Electrons in 3 Orbitals:  
**9 States**

# SOLVING THE SWE EXACTLY





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# SOLVING THE SWE EXACTLY

Solving the Schrodinger Equation exactly is theoretically straightforward: just enumerate all of the possible states.

**Consider  $N$  Electrons in  $M$  Orbitals:  
An Exponential Number of States!**

It just isn't **practically feasible** to enumerate all states and solve the equation, even with the fastest computers in the world!



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# SOLVING THE SWE EXACTLY

Solving the Schrodinger Equation exactly is theoretically straightforward: just enumerate all of the possible states.

**Consider  $N$  Electrons in  $M$  Orbitals:  
An Exponential Number of States!**

$$\binom{2M}{N} = \frac{(2M)!}{(2M - N)!N!}$$

It just isn't **practically feasible** to enumerate all states and solve the equation, even with the fastest computers in the world!

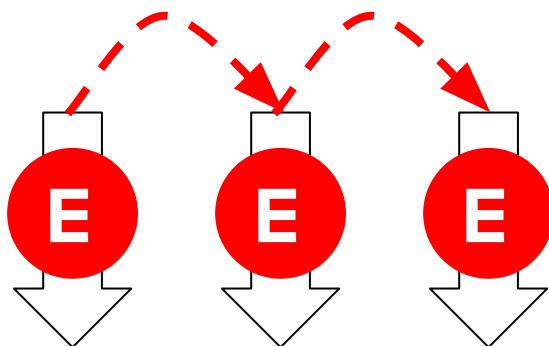


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# ONE FRUITFUL APPROXIMATION

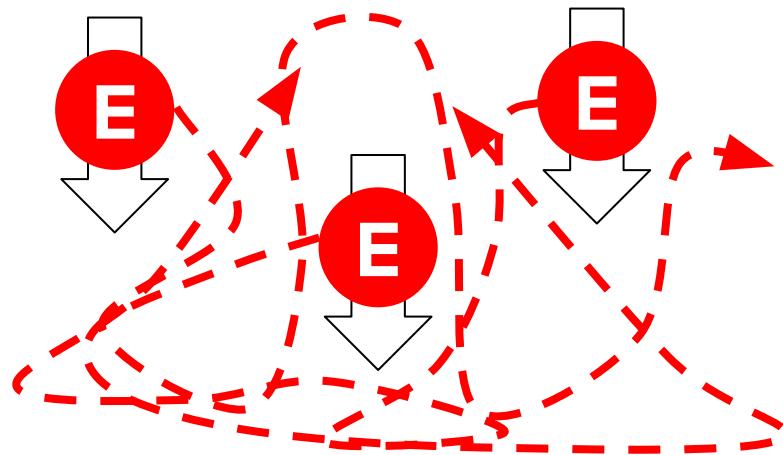
## Mean Field Theory (Including Density Functional Theory)

### How Electrons Actually Behave



(Perhaps Not As  
Dramatically...)

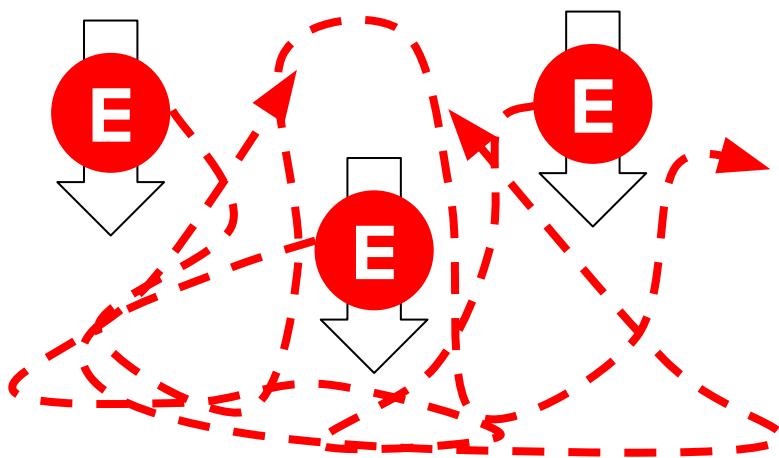
### How Mean Field Theories *Think* Electrons Behave



# ONE FRUITFUL APPROXIMATION

## Mean Field Theory (Including Density Functional Theory)

How Mean Field Theories  
*Think* Electrons Behave

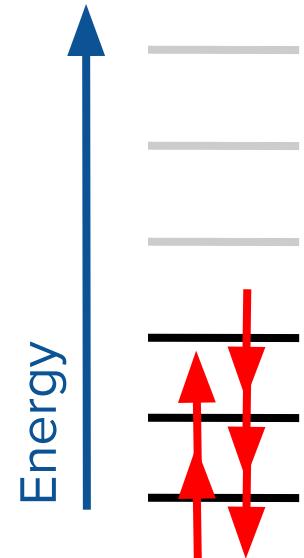


## Hartree Fock Theory

Find The BEST Single Determinant

$$|\Psi_{HF}\rangle = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3\dots\psi_N\bar{\psi}_N\rangle$$

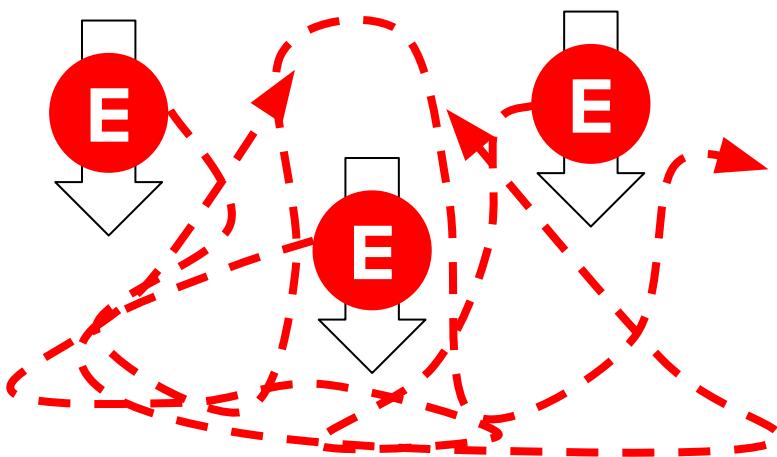
By Finding the Orbitals That  
Give the Lowest Energy



# ONE FRUITFUL APPROXIMATION

## Mean Field Theory (Including Density Functional Theory)

**How Mean Field Theories  
Think Electrons Behave**



## Hartree Fock Theory

Find The BEST Single Determinant

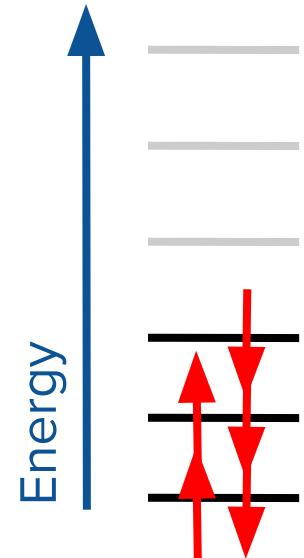
$$|\Psi_{HF}\rangle = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3\dots\psi_N\bar{\psi}_N\rangle$$

By Finding the Orbitals That  
Give the Lowest Energy

$$E_0 = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle$$

$$\boxed{\hat{f}(i)}\psi(r_i) = \epsilon\psi(r_i)$$

$$\hat{f}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^K \frac{Z_K}{r_{iA}} + \hat{v}^{HF}(i)$$





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# A VERY FRUITFUL APPROXIMATION

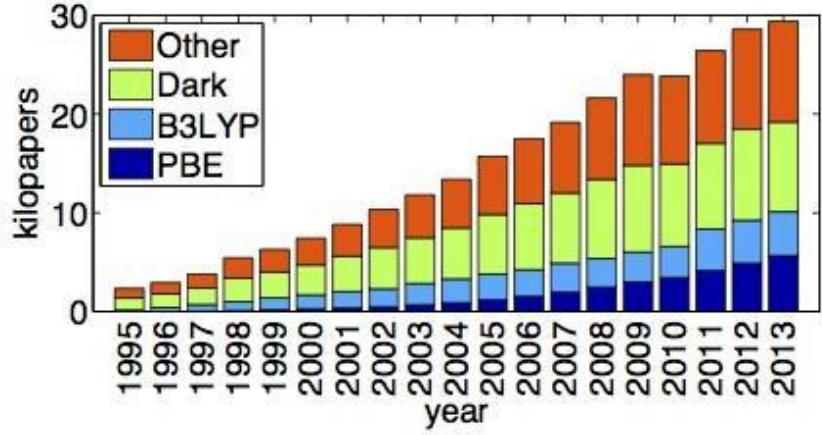
## Mean Field Theory (Including Density Functional Theory)



**Walter Kohn, Recipient of the 1998 Nobel Prize**

*"for his development of the density-functional theory"*

**Publications Mentioning DFT in Title**

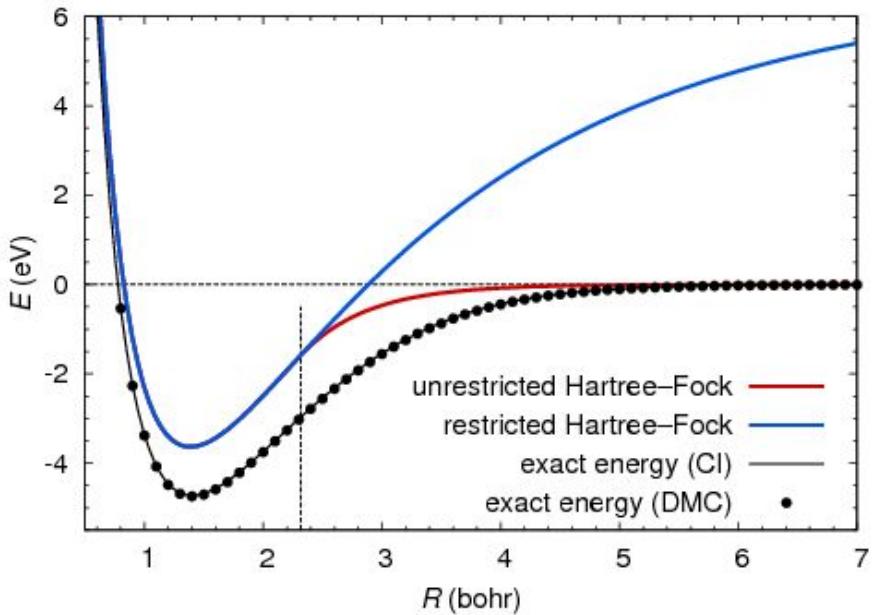
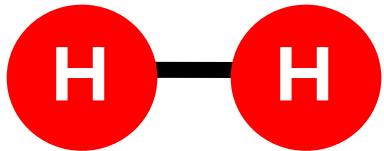




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# ONE FRUITFUL APPROXIMATION

That Can Be Very Wrong Sometimes....

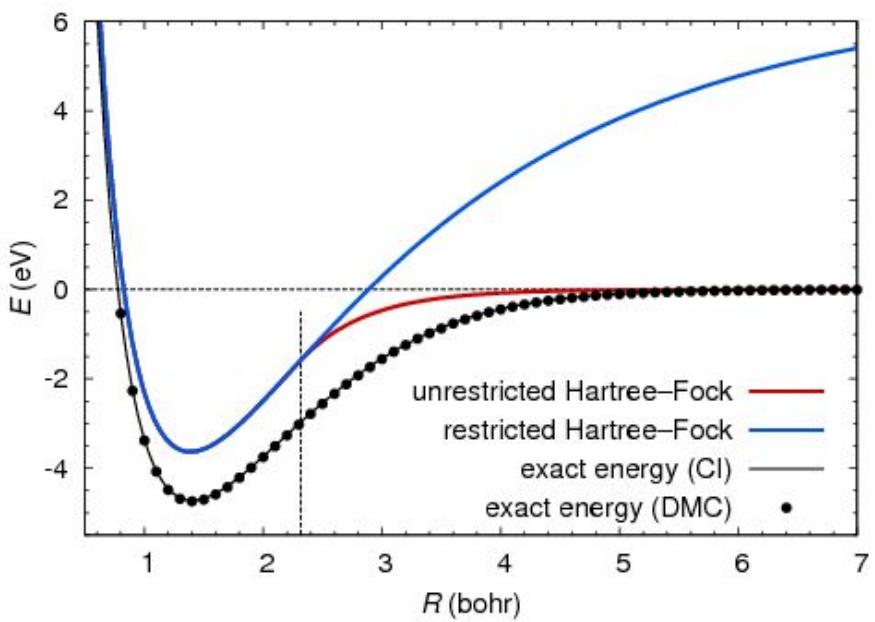
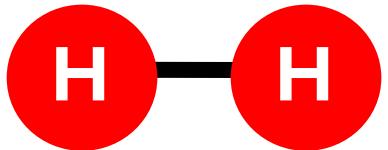




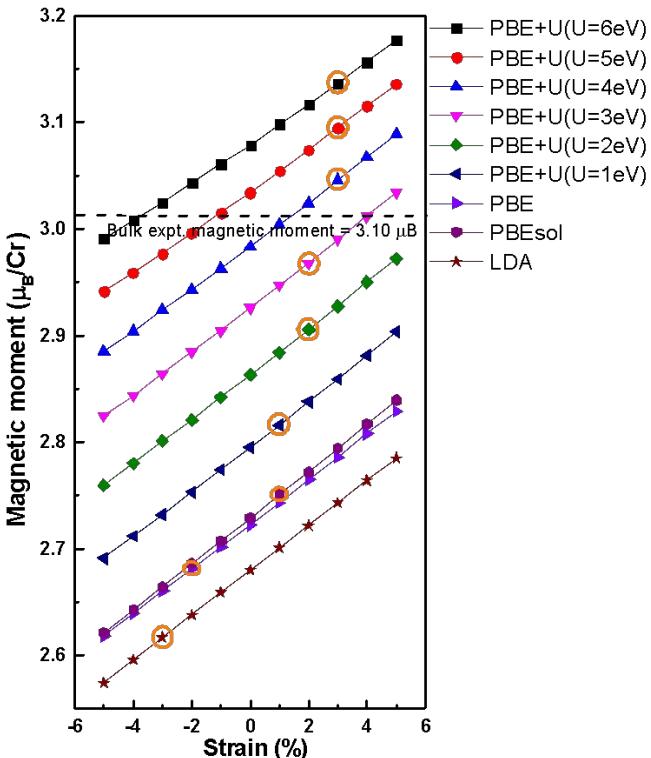
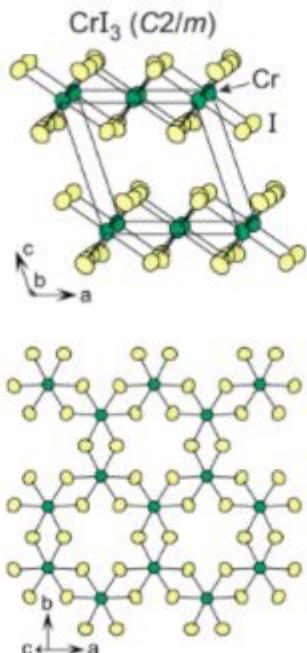
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# ONE FRUITFUL APPROXIMATION

That Can Be Very Wrong Sometimes....



## Chromium Tri-Iodide, $\text{CrI}_3$





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# STRONGLY-CORRELATED CARS

(Welcome to the Bay Area's 580)



**A Weakly-Correlated Highway**  
Cars Travel Relatively Independently



**A Strongly-Correlated Highway**  
Cars Travel Highly Dependently

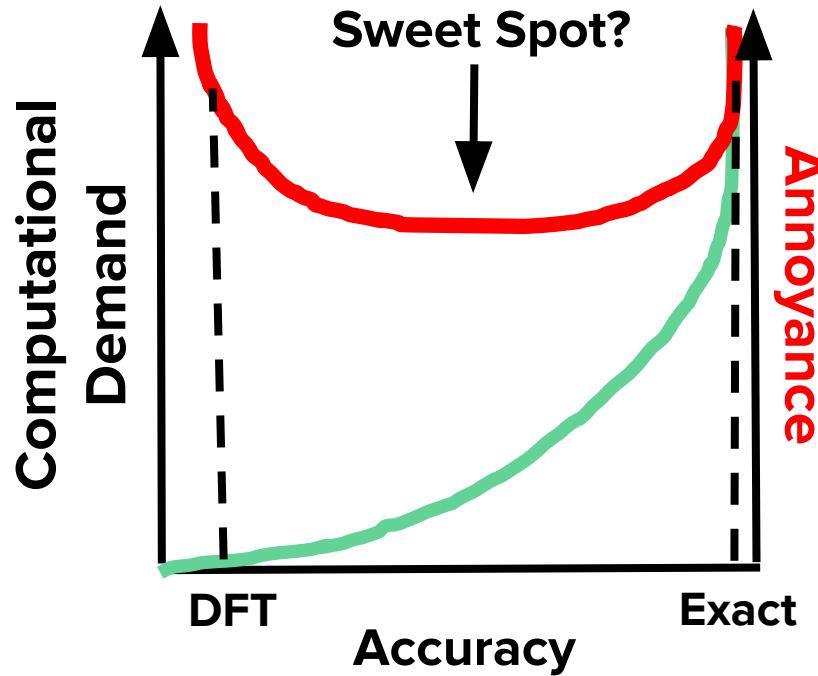
# CONSERVATION OF ANNOYANCE



There Is Always a Trade-Off Between Speed and Accuracy



Richard Friesner  
Columbia University  
Founder, Schroedinger Inc.



BUT, there is a sweet spot which motivates many of us to continue on!



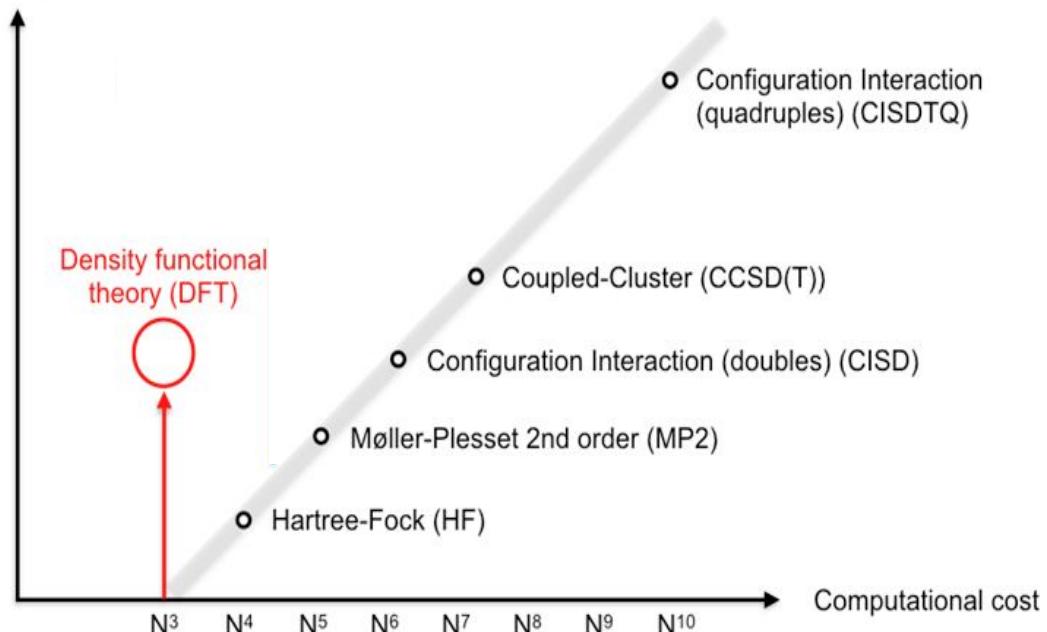
BROWN

# THE CURRENT PARADIGM

## The Hierarchy of Quantum Mechanical Methods

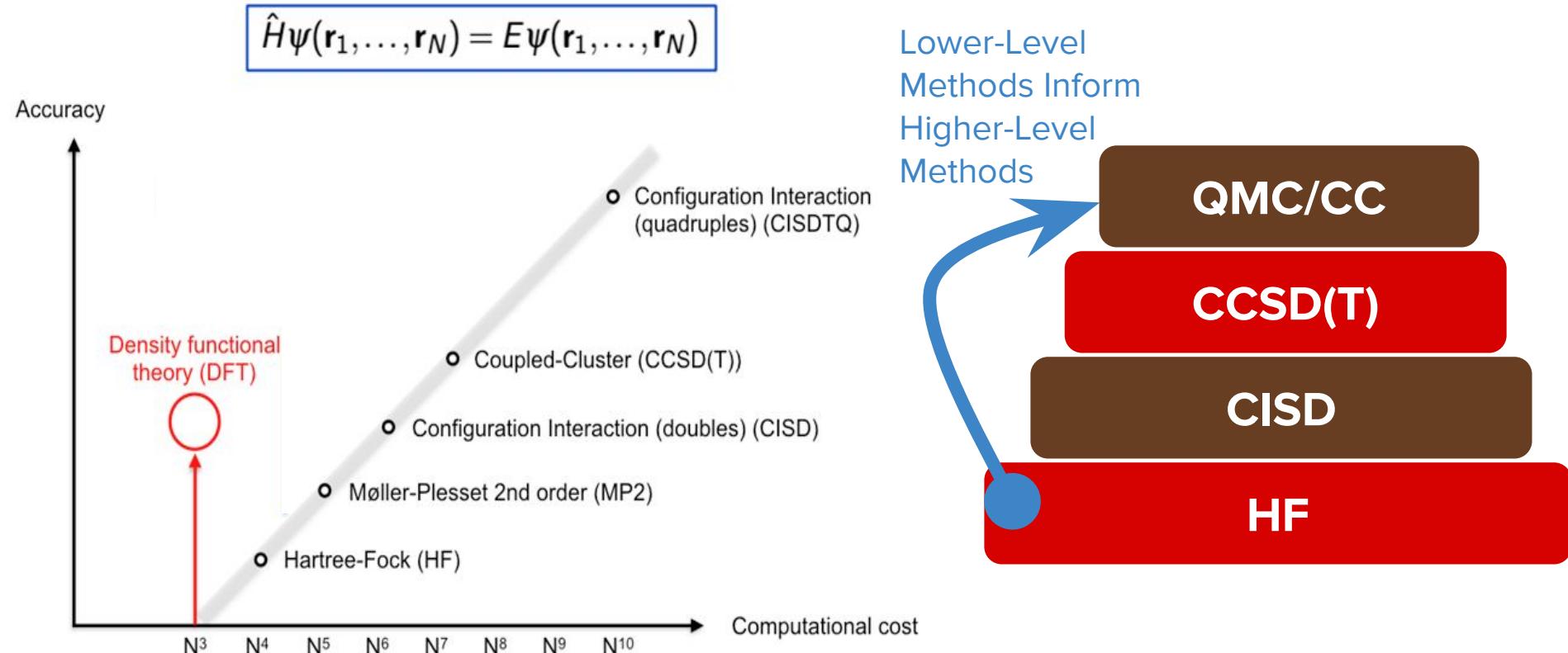
$$\hat{H}\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

Accuracy



# THE CURRENT PARADIGM

## The Hierarchy of Quantum Mechanical Methods



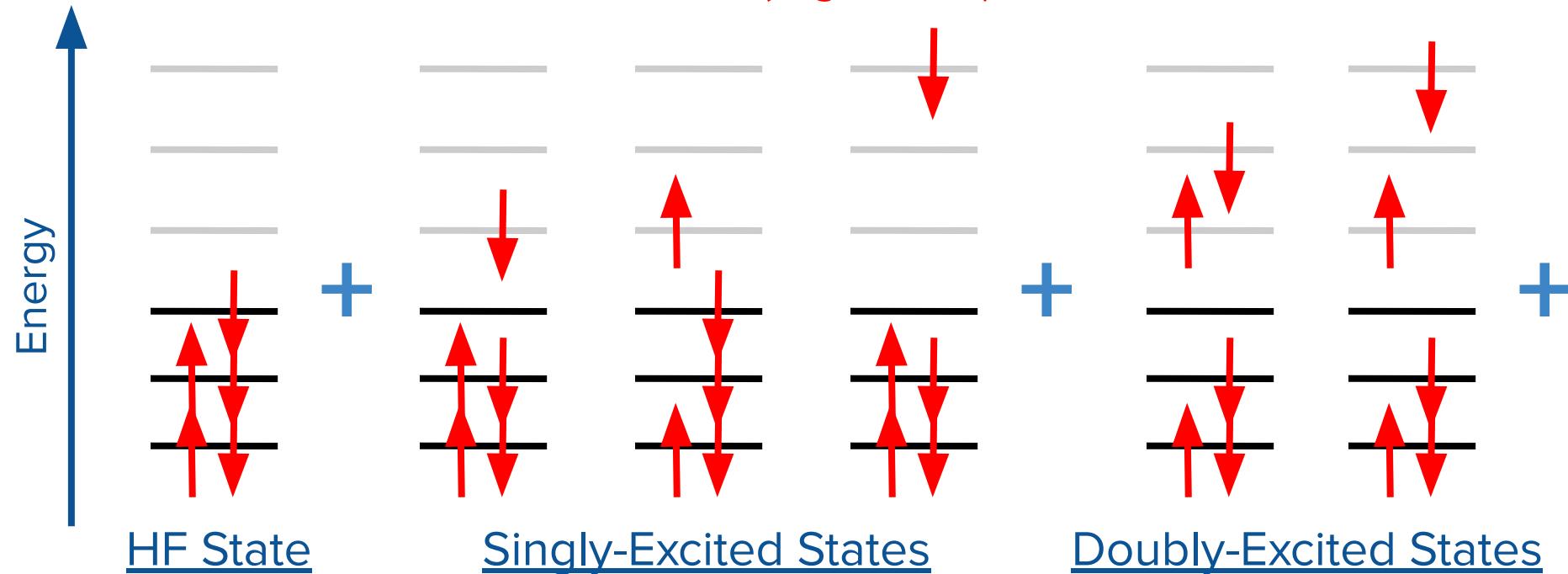


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# CONFIGURATION INTERACTION

Find the Most Important Set of States and Diagonalize

Simplest Selection of States: Just Pick Certain Combinations of  
*Excitations* (e.g., CISD)...



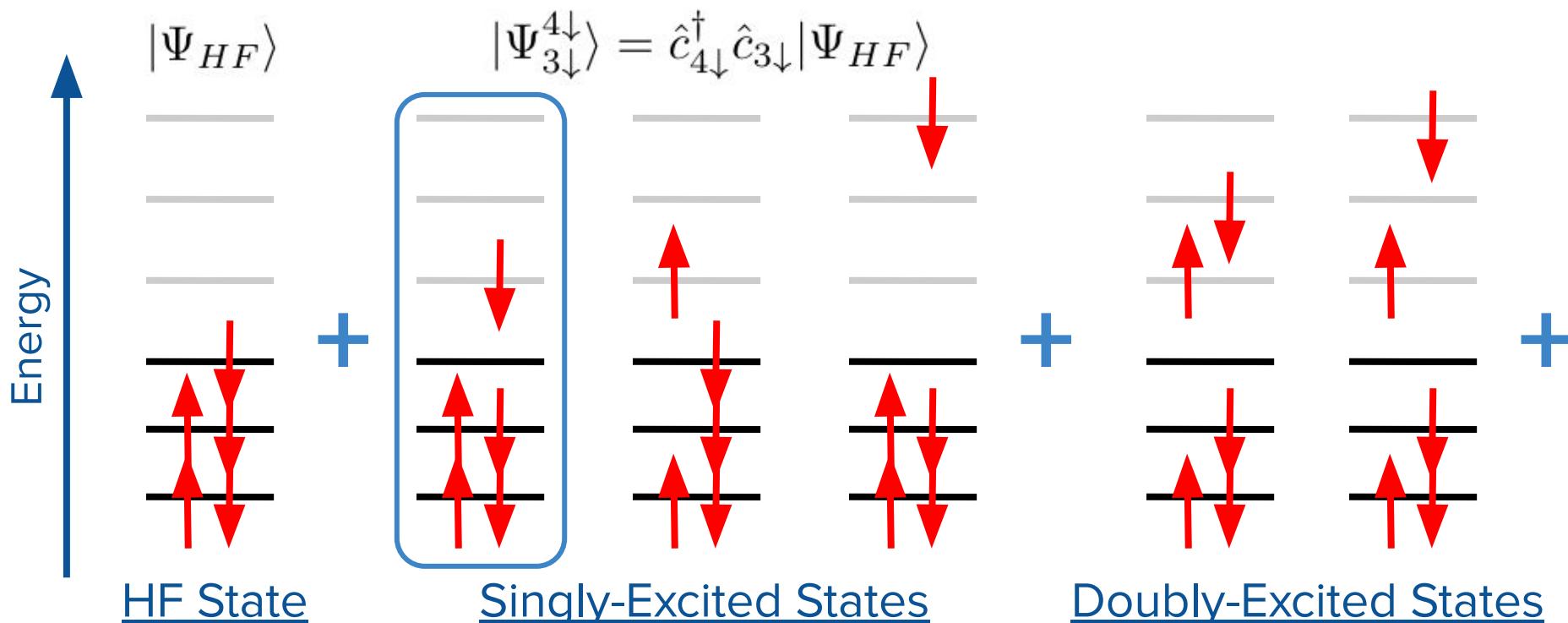


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# CONFIGURATION INTERACTION

Find the Most Important Set of States and Diagonalize

$$|\Psi_{HF}\rangle = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3\rangle$$



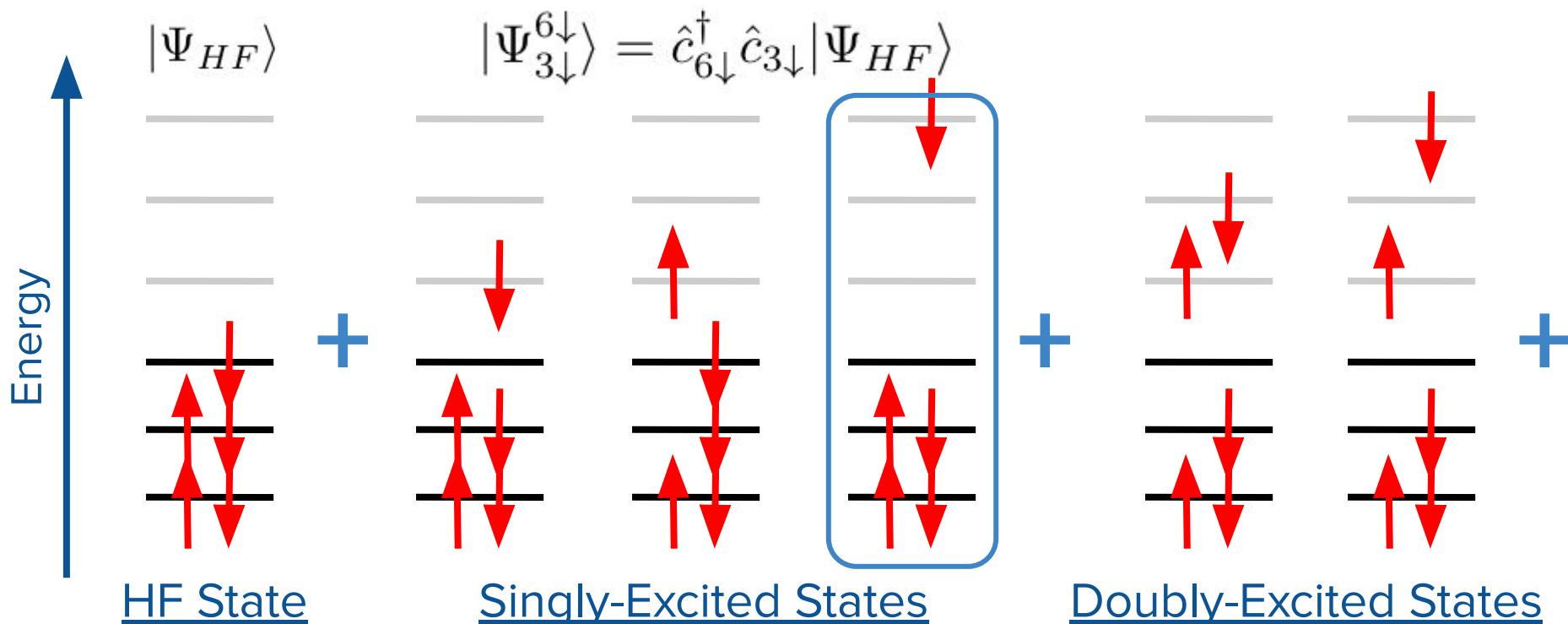


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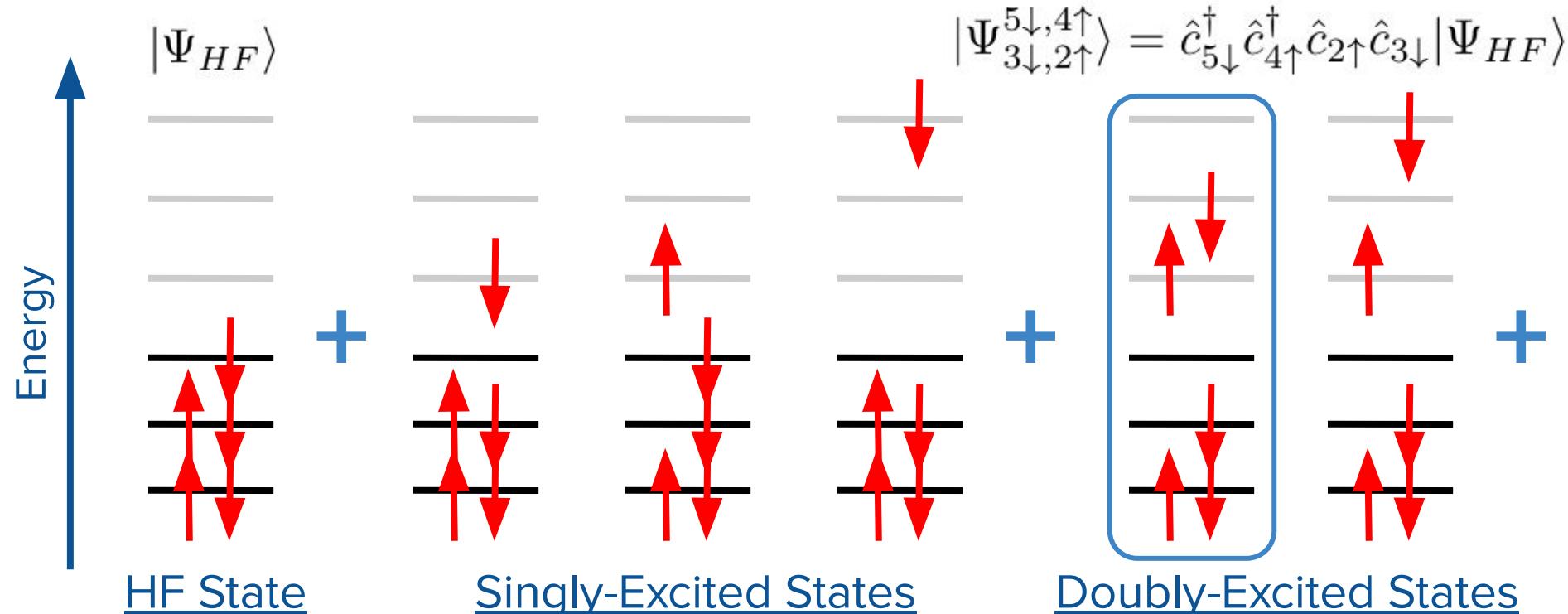


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## A Few Notes:

1. If You Consider All Excitations, You Get FULL Configuration Interaction, Which Is Just Exact Diagonalization



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$$|\Psi_{HF}\rangle = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3\rangle$$

## A Few Notes:

1. If You Consider All Excitations, You Get FULL Configuration Interaction, Which Is Just Exact Diagonalization
2. You By No Means Have To Select In the Order of Excitations → Selected CIs
3. There Are Many Other Ways of Selecting States...This Is Part of the Much Larger Selecting States Paradigm



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# COUPLED CLUSTER THEORY

Use an Exponential Ansatz to Create States

$$|\Psi\rangle = e^{\hat{T}} |\Psi_{HF}\rangle$$

Expand  
Cluster

Operator In  
Terms of  
Excitation  
Operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots$$

$$\hat{T}_1 = \sum_i \sum_a t_a^i \hat{c}_i^\dagger \hat{c}_a \quad \hat{T}_2 = \frac{1}{4} \sum_{i,j} \sum_{a,b} t_{a,b}^{i,j} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_a \hat{c}_b$$



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Use an Exponential Ansatz to Create States

$$|\Psi\rangle = e^{\hat{T}} |\Psi_{HF}\rangle$$

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Expand  
Exponential  
to Get  
Excitations

$$\begin{aligned} e^{\hat{T}} &= 1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \dots \\ &= 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \frac{1}{2} \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_2 \hat{T}_1 + \frac{1}{2} \hat{T}_2^2 + \dots \end{aligned}$$

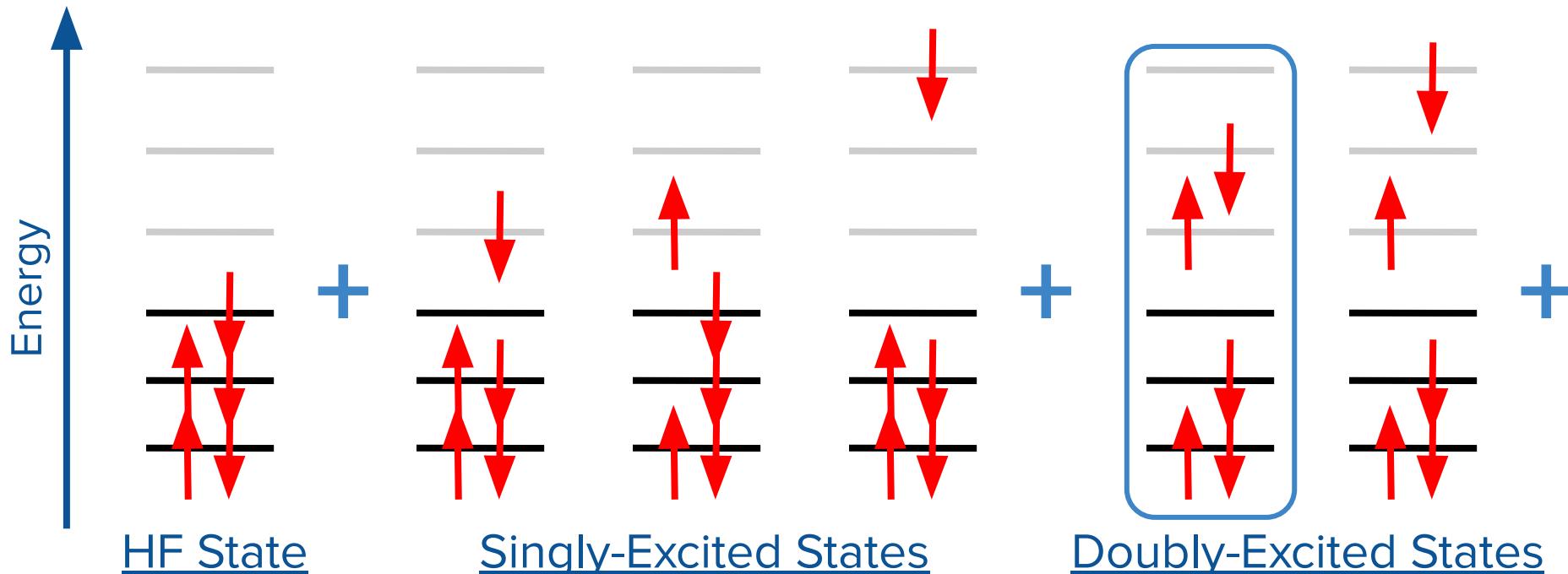


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# COUPLED CLUSTER THEORY

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$$e^{\hat{T}} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2\hat{T}_1 + \frac{1}{2}\hat{T}_2^2 + \dots$$



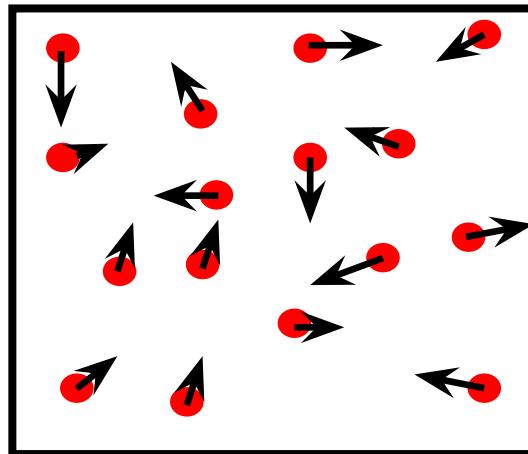
# QUANTUM MONTE CARLO (QMC)

Monte Carlo algorithms use **random numbers** to efficiently sample distributions.

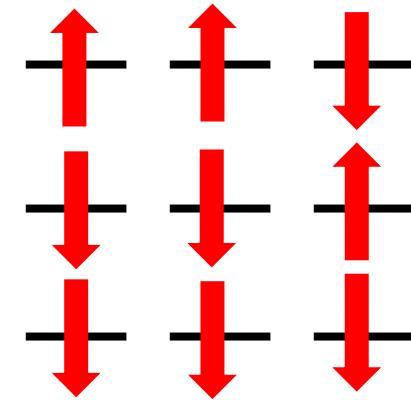


**Stanislaw Ulam**

**Distribution  
Sampled:**



**Fluids**



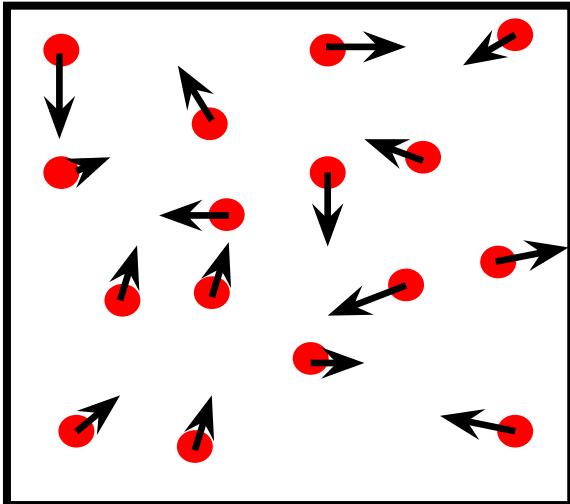
**2D Ising  
Model**

$$P(r^N) = e^{-\beta U(r^N)} / Z$$

$$P(s^N) = e^{-\beta U(s^N)} / Z$$

# QUANTUM MONTE CARLO (QMC)

Quantum Monte Carlo methods are a suite of methods that use Monte Carlo techniques to solve *quantum* problems.



Fluids:  
Sample Configurations

**Classical Systems**

$$\Psi_1 = \begin{pmatrix} 5 & -2 & 0 \\ 7 & 3 & 2 \\ 2 & -1 & 1 \end{pmatrix}$$
$$\Psi_2 = \begin{pmatrix} 6 & 3 & 2 \\ 9 & 4 & -1 \\ -2 & 8 & 4 \end{pmatrix}$$

Quantum Solids:  
Sample Wave Functions

**Quantum Systems**

# PROJECTION TECHNIQUES IN QMC

Trial Wave Function:  $|\Psi\rangle$



Apply Projection Operator

First Iteration:  $|\Psi^1\rangle$



Apply Projection Operator

Second Iteration:  $|\Psi^2\rangle$



Apply Projection Operator

Apply Projection Operator

Apply Projection Operator

$N^{th}$  Iteration:  $|\Psi^n\rangle \propto |\Psi_0\rangle$



Apply Shovel  
Projection Operator



In Quantum Monte Carlo algorithms, the ground state wave function is projected out from a trial wave function.

# DIFFUSION MONTE CARLO (REAL SPACE)

The Most Popular Form of Projection Quantum Monte Carlo

## Projection Equation

$$|\Psi_0\rangle \propto \lim_{t \rightarrow \infty} e^{-(H - E_T)t} |\Psi\rangle$$

Projection  
Operator

Trial Wave  
Function  
(Usually Mean  
Field)

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$$\lim_{t \rightarrow \infty} e^{-(H-E_T)t} |\Psi\rangle = \lim_{t \rightarrow \infty} \sum_i e^{-(E_i-E_T)t} |\Psi_i\rangle \langle \Psi_i| \Psi \rangle$$

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# DIFFUSION MONTE CARLO (REAL SPACE)

The Most Popular Form of Projection Quantum Monte Carlo

**Transformation into Position Representation**

$$|\Psi_0\rangle \propto \lim_{t \rightarrow \infty} e^{-(H-E_T)t} |\Psi\rangle$$

$$\langle \mathbf{X}_f | \Psi(t) \rangle = \int d\mathbf{X}_i \langle \mathbf{X}_f | e^{-(\hat{H}-E_T)t} | \mathbf{X}_i \rangle \langle \mathbf{X}_i | \Psi \rangle$$

# DIFFUSION MONTE CARLO (REAL SPACE)

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$$\Psi(\mathbf{X}_f, t) = \int d\mathbf{X}_i G(\mathbf{X}_f | \mathbf{X}_i; t) \Psi(\mathbf{X}_i)$$



Green's Function

# DIFFUSION MONTE CARLO (REAL SPACE)

The Most Popular Form of Projection Quantum Monte Carlo

## Short-Time Green's Function

$$f(\mathbf{X}) = \lim_{M \rightarrow \infty} \int d\mathbf{X}_1 d\mathbf{X}_2 \dots d\mathbf{X}_M \tilde{G}(\mathbf{X}|\mathbf{X}_M; \tau) \tilde{G}(\mathbf{X}_M|\mathbf{X}_{M-1}; \tau) \dots \tilde{G}(\mathbf{X}_2|\mathbf{X}_1; \tau) \Psi(\mathbf{X}_1)^2$$

$$\tilde{G}(\mathbf{X}_f|\mathbf{X}_i; \tau) \approx \frac{1}{(2\pi\tau)^{3N/2}} e^{-\frac{(\mathbf{X}_f - \mathbf{X}_i - \mathbf{v}(\mathbf{X}_i)\tau)^2}{2\tau}} e^{-\left(\frac{E_L(\mathbf{X}_f) + E_L(\mathbf{X}_i)}{2} - E_T\right)\tau}$$

# DIFFUSION MONTE CARLO (REAL SPACE)

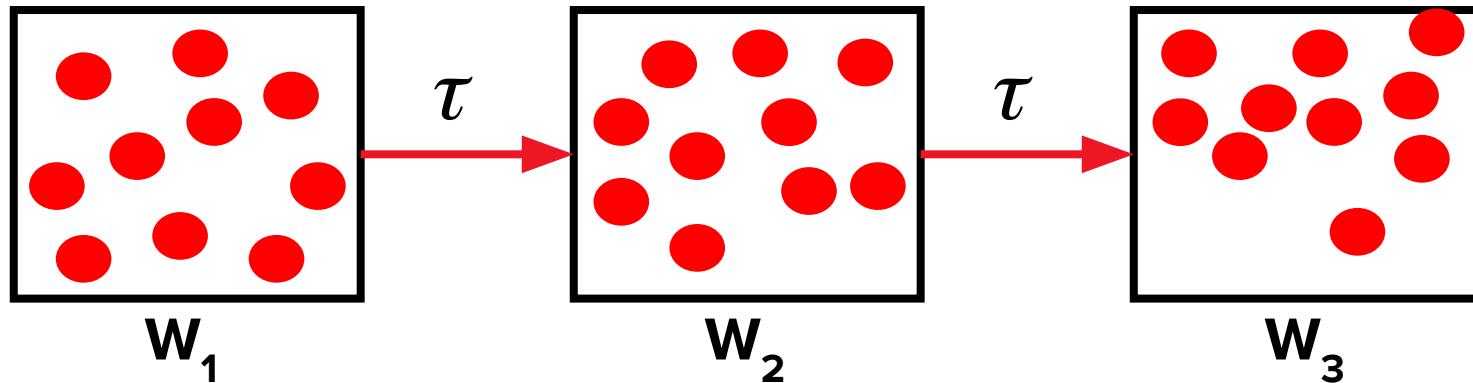
The Most Popular Form of Projection Quantum Monte Carlo

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Weight

$$e^{-\left(\frac{E_L(\mathbf{X}_f) + E_L(\mathbf{X}_i)}{2} - E_T\right)\tau}$$

**Propagator:**  
Sampled for  
Particle Moves





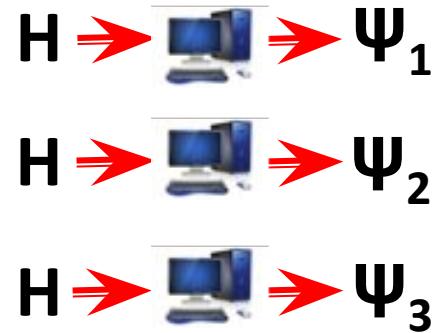
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# QUANTUM MONTE CARLO

Quantum Monte Carlo methods are **highly accurate**, yet scale **gracefully** with system size.

Method	Scaling	Accuracy
Configuration Interaction (CI)	Combinatorial	Exact, if Full CI
Coupled Cluster (CCSD(T))	$N^7$	The gold standard for small systems
Density Functional Theory (DFT)	$N^3$	Approximate mean field theory
Quantum Monte Carlo (QMC)	$N^{3*}$	Exact, barring sign problem

**Highly Parallelizable**

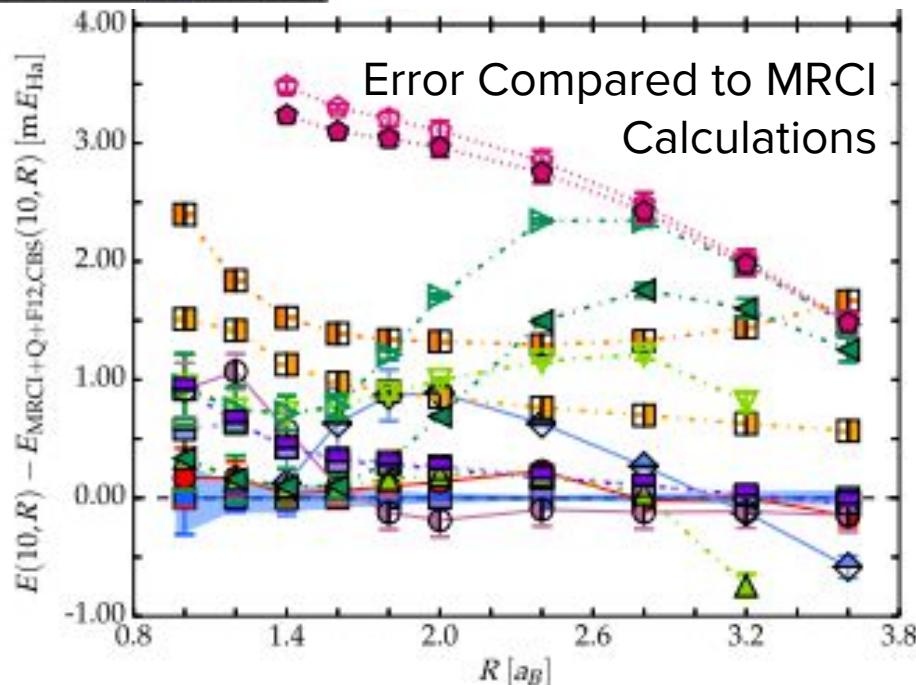
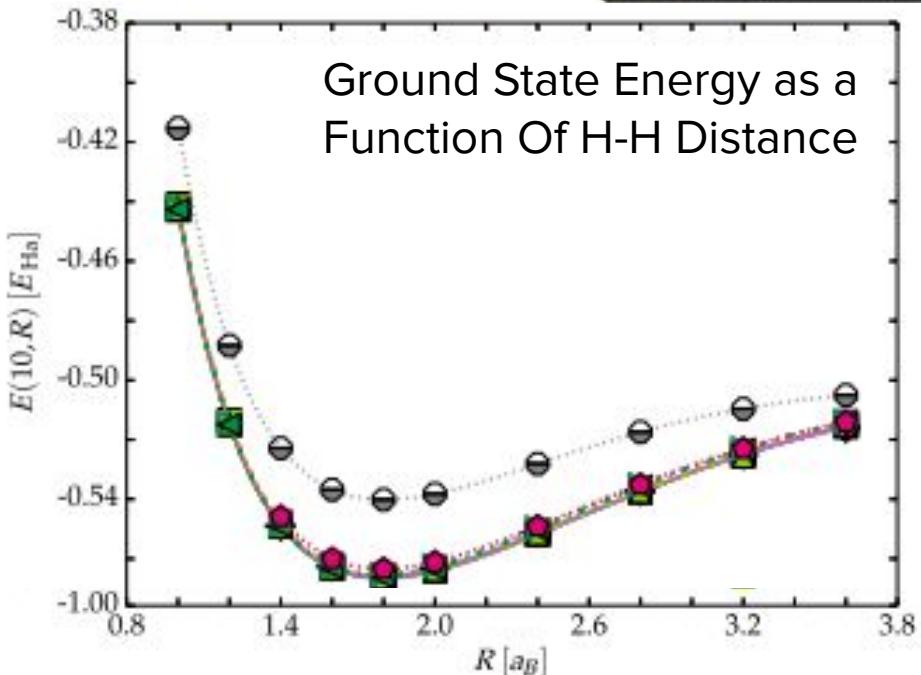
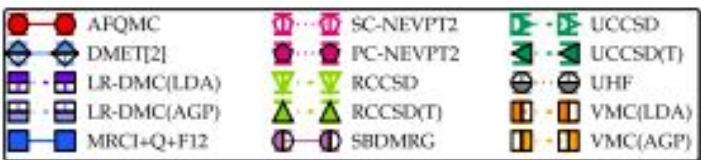




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# BACK TO HYDROGEN CHAINS

1 milliHartree  
~.027 eV ~ $4.4 \times 10^{-21}$  J



=> Accurate Physics Requires Accurate Calculations!

M. Motta et al., PRX (2017)..



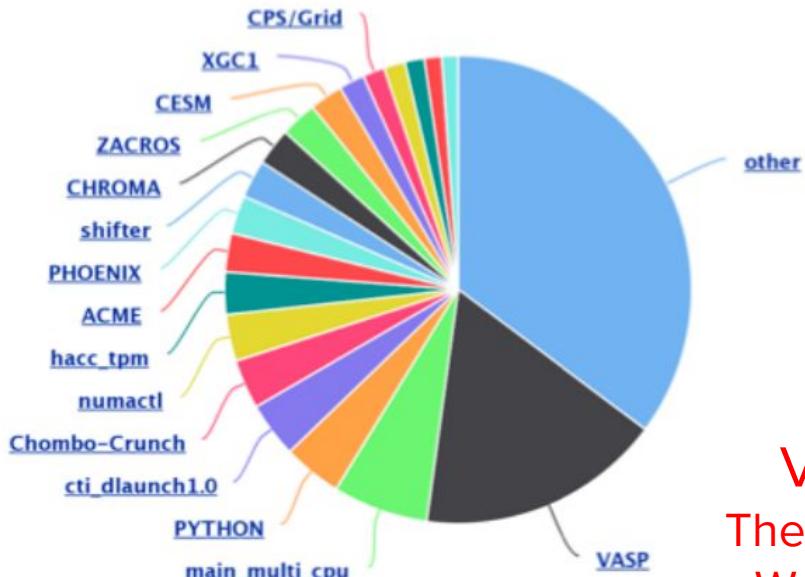
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# HOW MUCH THIS ALL COSTS

It Can Be Expensive, Gruesomely Expensive!

Cori Machine Hours Breakdown by Applications

Processes as a percentage of 100% of total machine hours (82933051 hours).



=> This Is *NOT* a  
Cheap Enterprise

VASP =  
The Quantum  
Workhorse  
(for Solids)

# IT FEELS LIKE ONE OF THOSE MOMENTS...

## When You Know You're Old



# IT FEELS LIKE ONE OF THOSE MOMENTS...



## When You Know You're Old





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# IT FEELS LIKE ONE OF THOSE MOMENTS...

When You Know You're Old



Like All of These Devices, These Quantum Mechanical Methods  
May Be On Their Way to Obsolescence (In Some Sense)



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# WHERE QUANTUM COMPUTERS COME IN

## The Reality of Quantum Chemistry/Physics

- We Can Model Many, Many Things *Pretty* Accurately, But Perhaps Not Accurately Enough to See Their True Physics
  - DFT Has Become Our Reasonably Accurate Workhorse



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- More Accurate Methods Are Very Expensive and Thus Limited to Small Systems (100s of Electrons in 100s-1000s of Orbitals)



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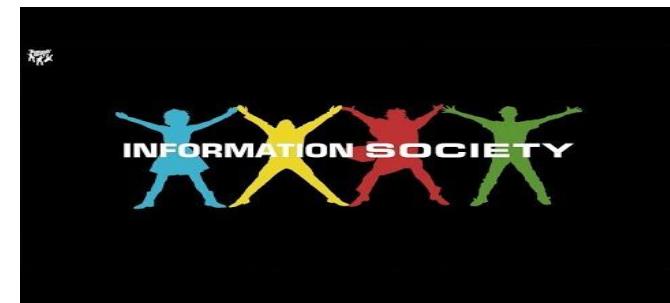
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## Quantum Computers May...

- Enable Us To Model These Many Molecules and Materials Just as Accurately, But with Exponentially Reduced Cost
- But, We Need to Develop the Software and Hardware To Do So





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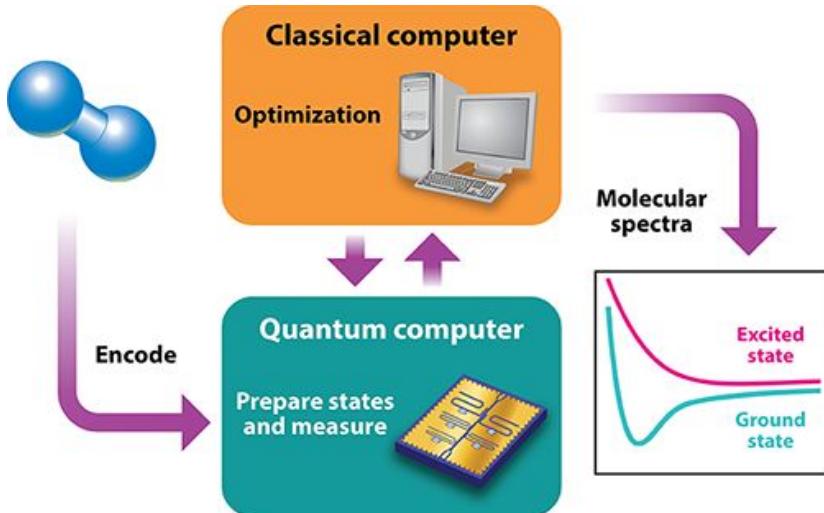
- Enable Us To Model These Many Molecules and Materials Just as Accurately, But with Exponentially Reduced Cost
- But, We Need to Develop the Software and Hardware To Do So

⇒ Promise to Scale to Larger, More Complex Systems...But We're Not There Yet

# CHEMISTRY AND MATERIALS ON QCS

PHYSICAL REVIEW X 6, 031007 (2016)

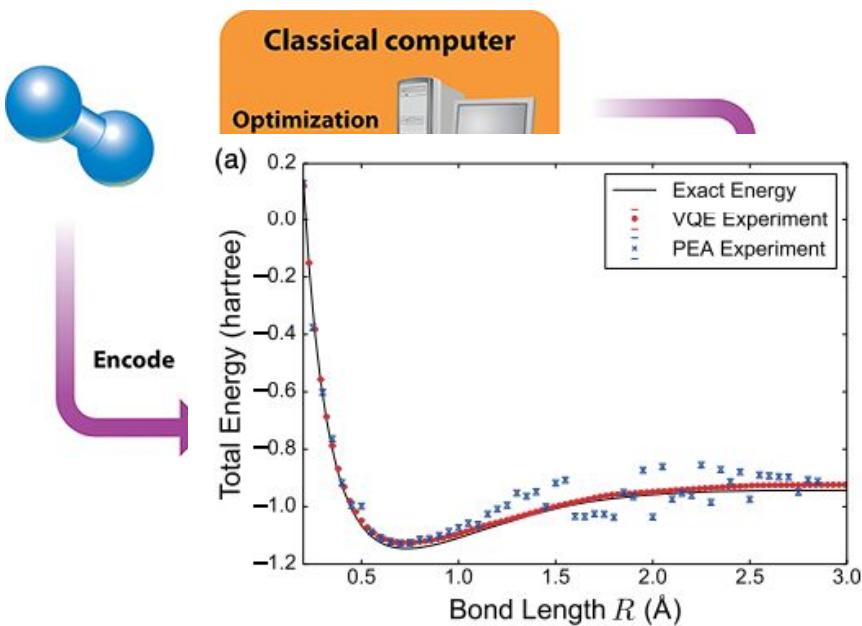
## Scalable Quantum Simulation of Molecular Energies



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PHYSICAL REVIEW X 6, 031007 (2016)

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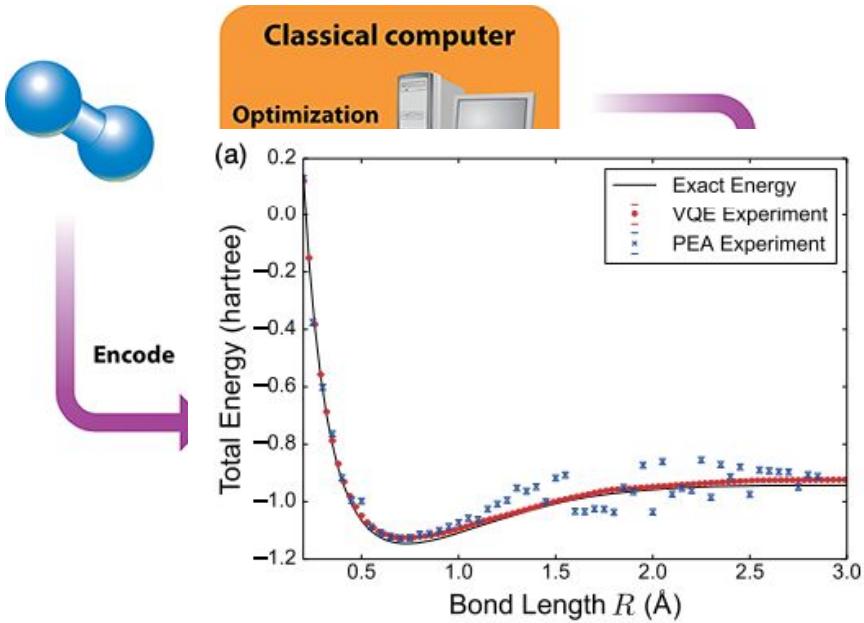


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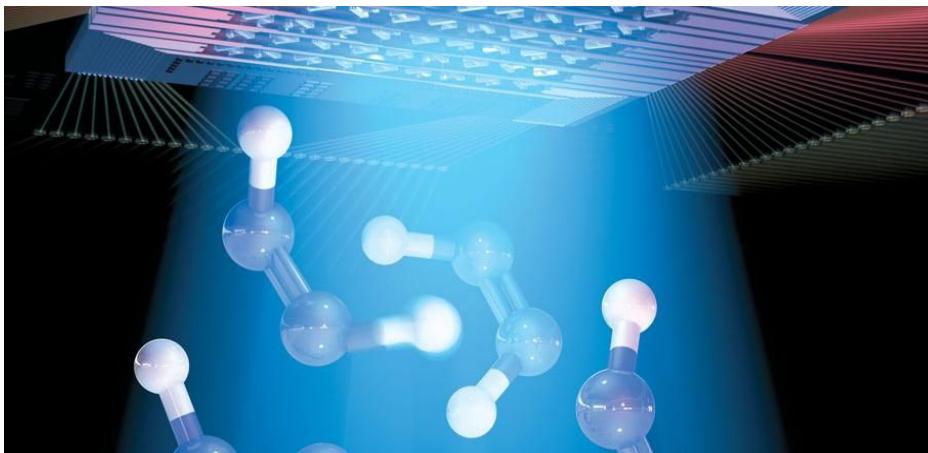
### RESEARCH ARTICLE

## Hartree-Fock on a superconducting qubit quantum computer

Google AI Quantum and Collaborators\*,†, Frank Arute, Kunal Arya, Ryan Babbush, Dave Bacon, Joseph C. Bardin, Rami Bar...

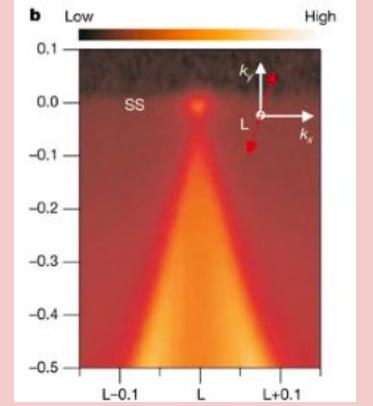
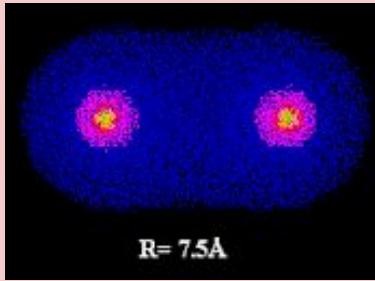
\* See all authors and affiliations

Science 28 Aug 2020;  
Vol. 369, Issue 6507, pp. 1084-1089  
DOI: 10.1126/science.abb9811



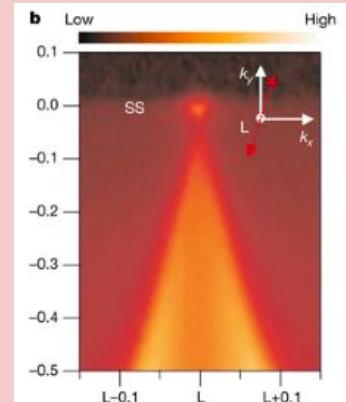
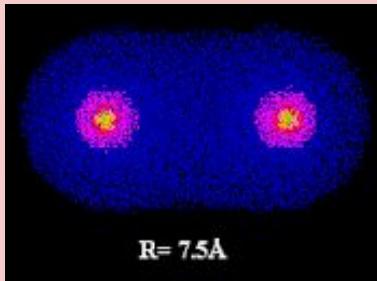
# SUMMARY

## Many-Electron Molecules and Materials

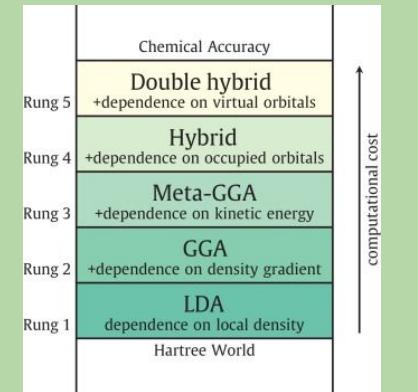
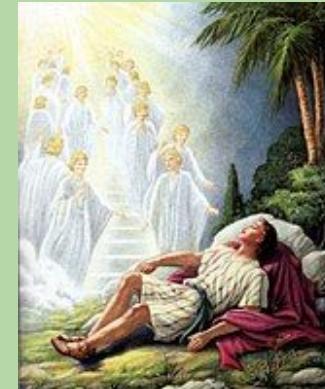


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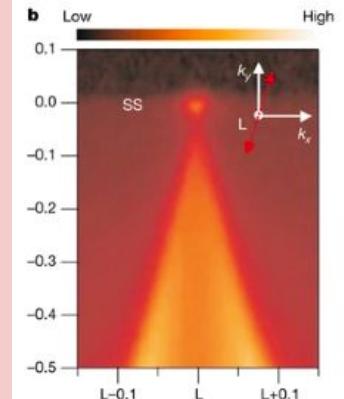
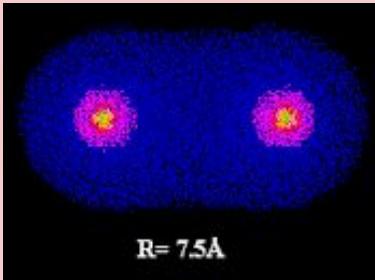


## Hierarchy of Quantum Chemical Methods

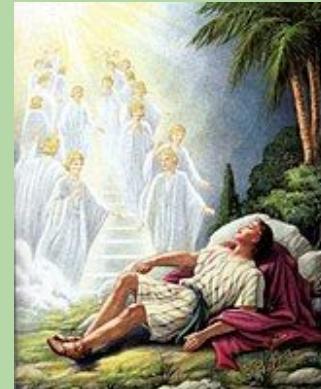


# SUMMARY

## Many-Electron Molecules and Materials



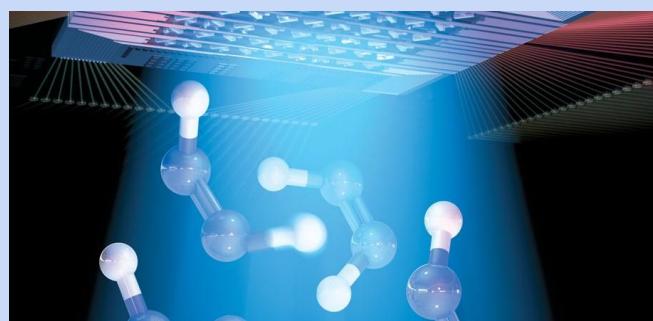
## Hierarchy of Quantum Chemical Methods



Chemical Accuracy	
Rung 5	Double hybrid +dependence on virtual orbitals
Rung 4	Hybrid +dependence on occupied orbitals
Rung 3	Meta-GGA +dependence on kinetic energy
Rung 2	GGA +dependence on density gradient
Rung 1	LDA dependence on local density Hartree World

A vertical double-headed arrow on the right side of the table is labeled "computational cost", indicating that the methods progress from low cost at the bottom to high cost at the top.

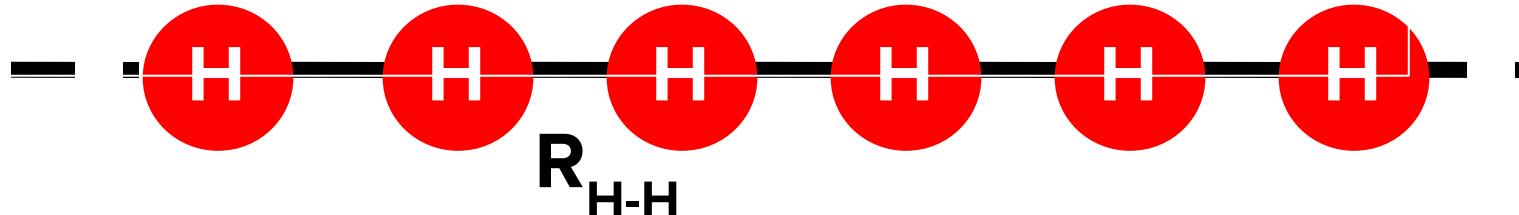
## How Quantum Computers Can Transform The Landscape (Ladder!)



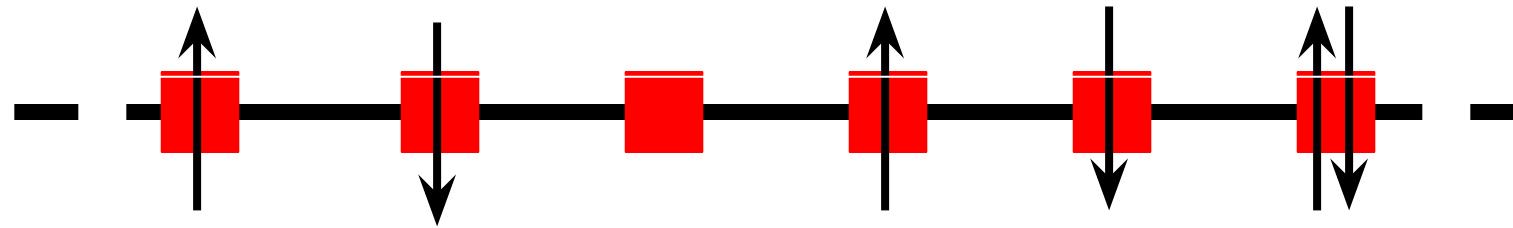
# EXCESS SLIDES

# The 1D Periodic Hydrogen Chain

## Hydrogen Chains



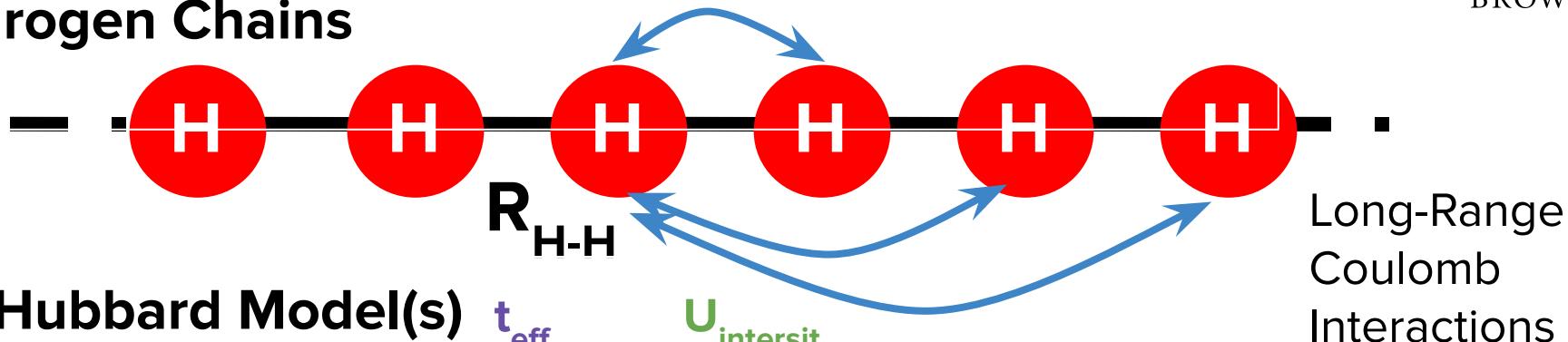
## 1D Hubbard Model(s)



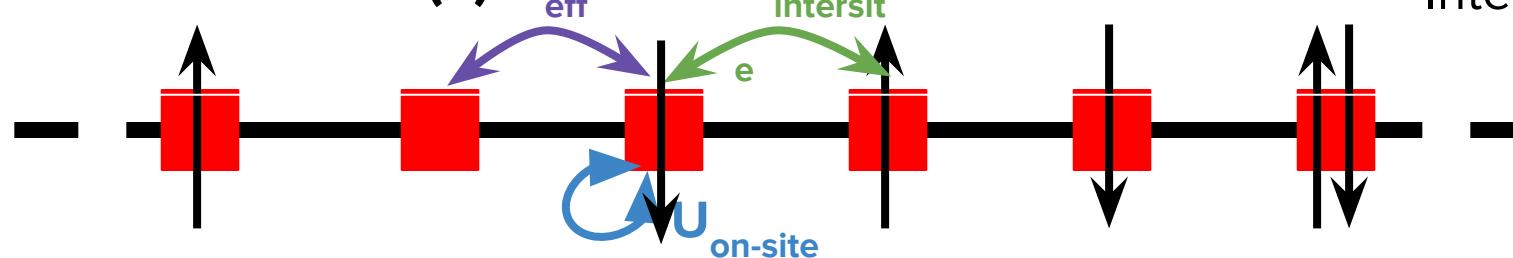
- Given its long-range Coulomb interactions, how does the  $\text{H}_{10}$  phase diagram compare to 1D Hubbard model phase diagrams?
  - 1D  $\text{H}_{10}$ : Many results by Shiba, Philips, Lieb, ...

# Comparison with 1D Hubbard Model(s)

## Hydrogen Chains

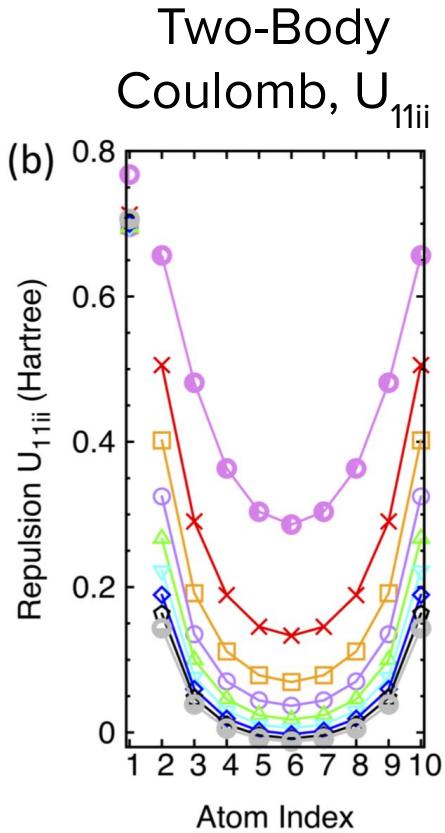
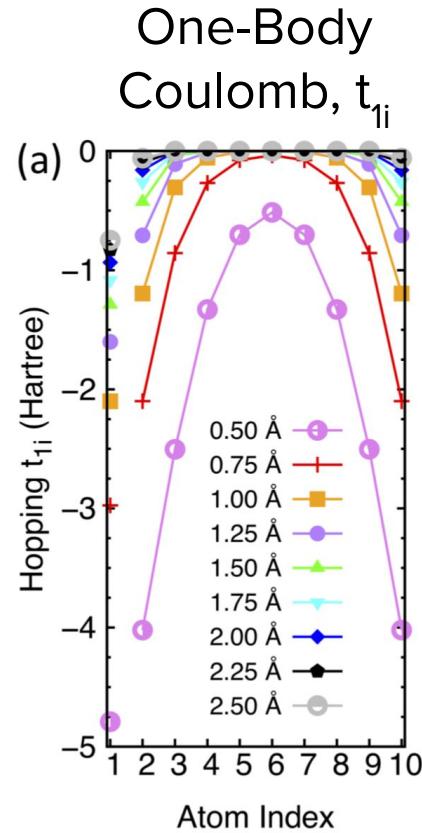


## 1D Hubbard Model(s)

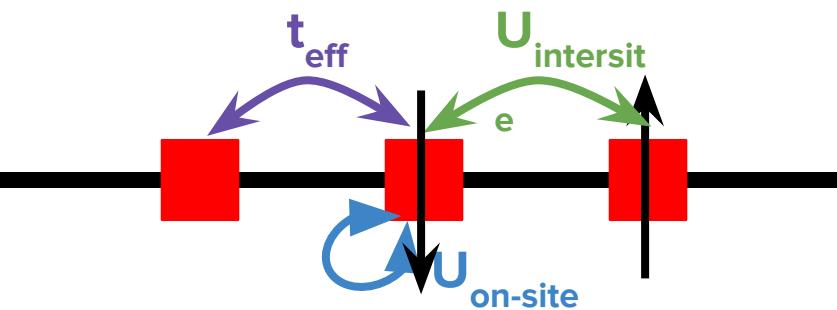


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  - 1D  $H_{10}$ : Many results by Shiba, Philips, Lieb, ...

# Comparison with 1D Hubbard Model(s)



$R_{H-H}$ (Å)	$t_{\text{eff}}$	$U_{\text{inter}}$	$\tilde{U}_{\text{inter}}$	$U_{\text{on}}$	$\tilde{U}_{\text{on}}$	$\tilde{T}_{\min}$
0.50	4.79	0.47	0.10	0.77	0.16	0.01
0.75	2.10	0.47	0.23	0.71	0.34	0.02
1.00	1.20	0.43	0.36	0.70	0.58	0.04
1.25	0.71	0.37	0.52	0.69	0.98	0.07
1.50	0.43	0.32	0.74	0.69	1.62	0.12
1.75	0.26	0.28	1.06	0.70	2.67	0.19
2.00	0.16	0.25	1.54	0.70	4.38	0.31
2.25	0.10	0.22	2.24	0.70	7.18	0.51
2.50	0.06	0.20	3.32	0.71	11.78	0.83



# GROUP ACKNOWLEDGEMENTS



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### Electronic Structure Team

- Dr. Matthew Church
- Mr. Cancan Huang
- Mr. Gopal Iyer
- Dr. Edgar Landinez
- Dr. Yuan Liu
- Mr. Tong Shen



*Rubenstein Group, Summer 2019*

### Biophysics Team

- Mr. Haobo Yang
- Mr. Gabriel M. da Silva

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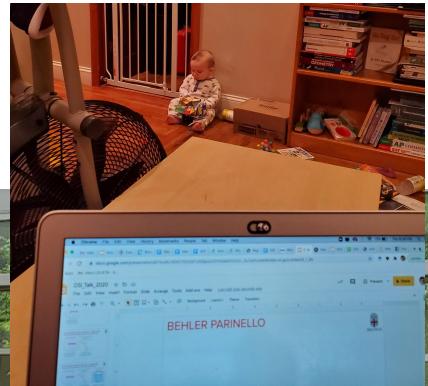
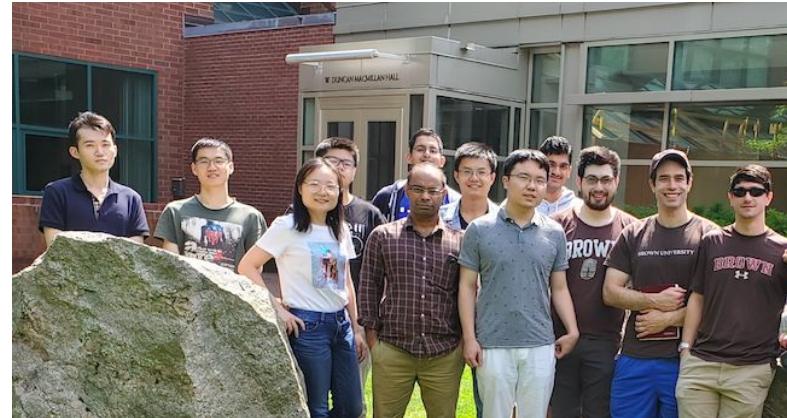


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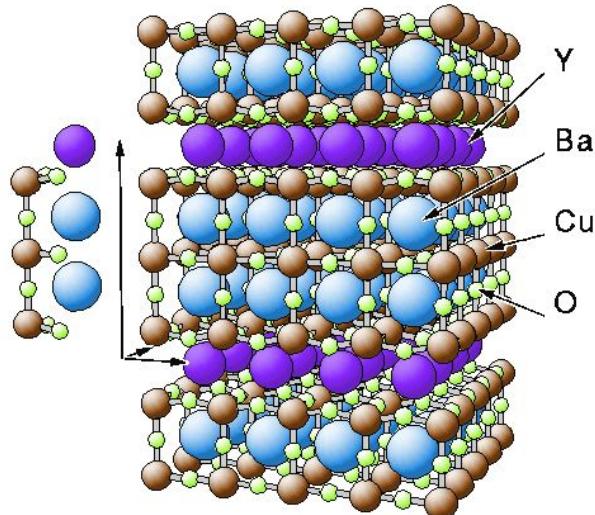
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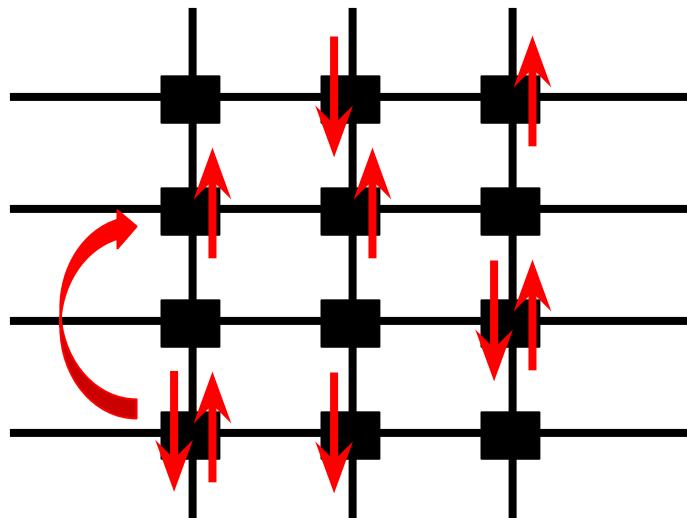
# The Hubbard Model

The Theorist's Lab Rat

$$\hat{H}_{Hubbard} = -T \sum_{\langle ij \rangle \sigma} \left( \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + H.C. \right) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$



YBaCuO (Superconductor)



Hubbard Model

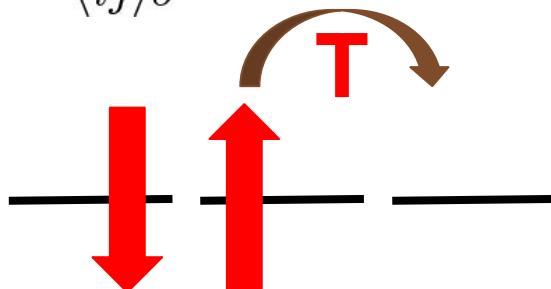
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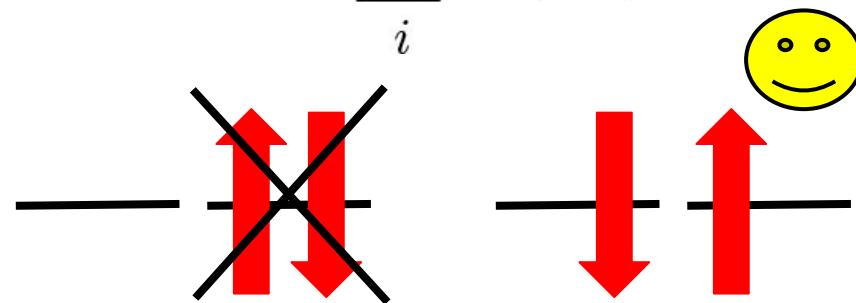
The Kinetic “Hopping” Term  
(Favors Electron Movement)

$$-T \sum_{\langle ij \rangle \sigma} \left( \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + H.C. \right)$$

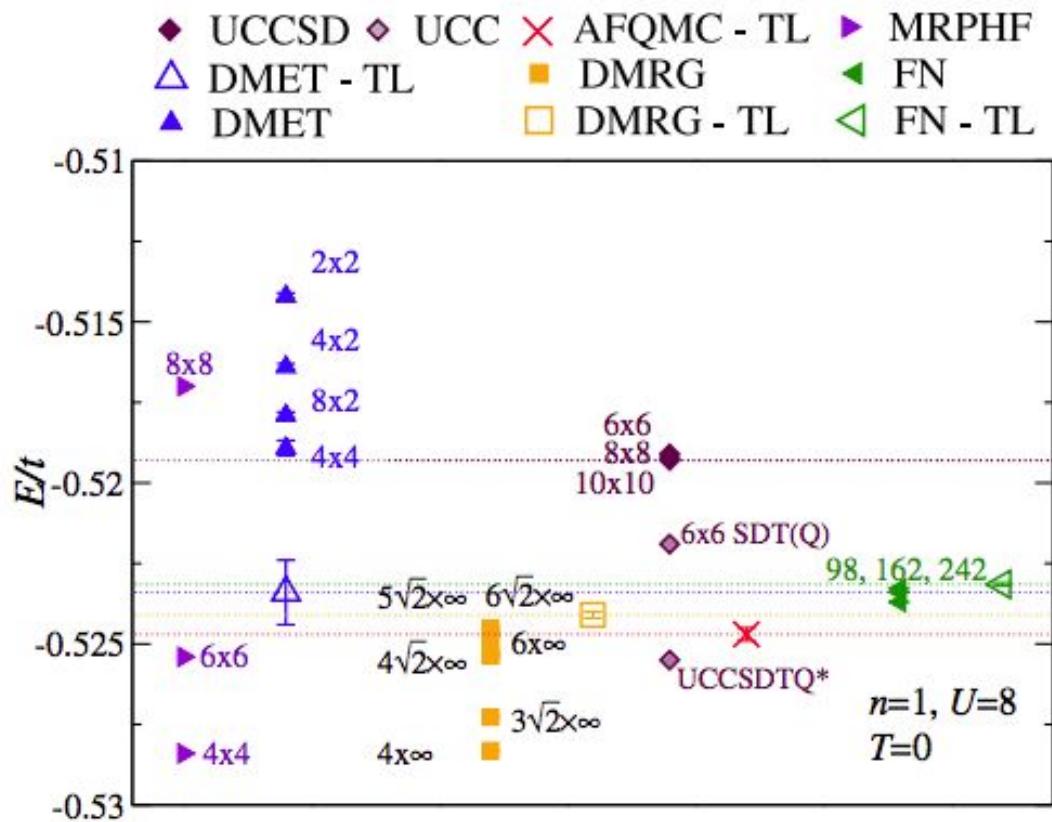


The Potential Term  
(Inhibits Double Occupancy )

$$U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$



# Hubbard Model Performance



**CC** = Coupled Cluster (The Gold Standard of Chemistry)

**DMET** = Density Matrix Embedding Theory

**DMRG** = Density Matrix Renormalization Group Theory

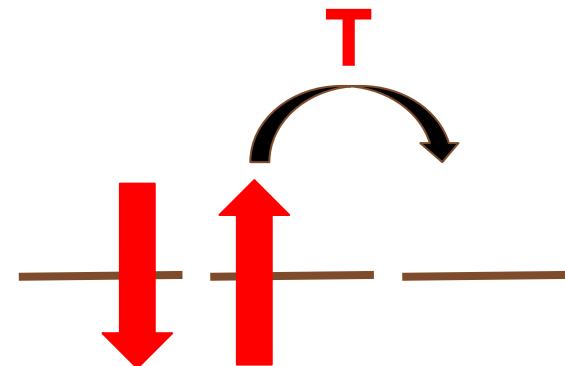
**FN** = Fixed Node Diffusion Monte Carlo

**MRPHF** = Multireference Projected Hartree Fock

# AFQMC for Real Materials

## Hubbard Hamiltonian

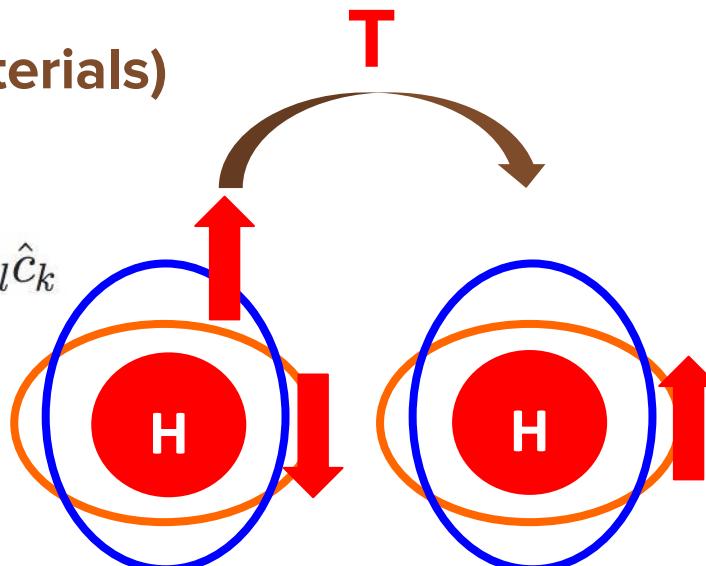
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↓  
Reality  
(aka, Chemistry, Materials)

$$\hat{H}_{Chemistry} = \sum_{ij} \left( T_{ij} \hat{c}_i^\dagger \hat{c}_j + H.C. \right) + \sum_{ijkl} V_{ijkl} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_l \hat{c}_k$$

## Coulomb Hamiltonian



# WHAT IS AFQMC?

An **exponential** projector QMC technique that samples the space of **non-orthogonal Slater determinants**.

## Taxonomy of Projector QMC Methods

<u>Method</u>	<u>Projector</u>	<u>Single-Particle Basis</u>	<u>Quantization</u>
Diffusion Monte Carlo (DMC)			
Full Configuration Interaction QMC (FCIQMC)			
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# WHAT DOES THIS MEAN?

An **exponential** projector QMC technique that samples the space of **non-orthogonal Slater determinants**.

## Second-Quantized Hamiltonians

$$\hat{H} = \sum_{\sigma} \sum_{ij}^N T_{i\sigma, j\sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \frac{1}{2} \sum_{\sigma\nu} \sum_{ijkl}^N V_{ijkl}^{\sigma\nu\sigma\nu} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\nu}^\dagger \hat{c}_{l\nu} \hat{c}_{k\sigma}$$

Can use all of the standard tools of quantum chemistry - same bases, same contractions!

Remember Second Quantization...*from Yesterday?*

$$\begin{aligned}\{\hat{c}_\alpha, \hat{c}_\beta\} &= 0 \\ \{\hat{c}_\alpha^\dagger, \hat{c}_\beta^\dagger\} &= 0 \\ \{\hat{c}_\alpha, \hat{c}_\beta^\dagger\} &= \delta_{\alpha,\beta}\end{aligned}$$

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$$T_{i\sigma,j\sigma} = \int d\vec{r} \phi_{p,\sigma}(\vec{r}) \left( -\frac{1}{2} \frac{\partial^2}{\partial \vec{r}^2} - \sum_{a=1}^{N_n} \frac{Z_a}{|\vec{r} - \vec{R}_a|} \right) \phi_{q,\sigma}(\vec{r})$$

$$V_{ijkl}^{\sigma\nu\sigma\nu} = \int d\vec{r} d\vec{r}' \phi_{i,\sigma}(\vec{r}) \phi_{j,\nu}(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \phi_{k,\sigma}(\vec{r}) \phi_{l,\nu}(\vec{r}')$$

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$$|\Psi_0\rangle = \lim_{n \rightarrow \infty} \left( e^{-\Delta\tau \hat{H}} \right)^n |\Phi_T\rangle$$

Like DMC...But in second-quantization, must be evaluated in a different way...(more later!)

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## Non-Orthogonal Slater Determinants

### Non-Orthogonal Orbitals

$$|\Psi\rangle = \prod_{i=1}^{N_\uparrow} \hat{c}_{u_i, \uparrow}^\dagger \prod_{i=1}^{N_\downarrow} \hat{c}_{v_i, \downarrow}^\dagger |\Phi\rangle$$

$$|u_i\rangle = \sum_p (U_\uparrow)_{pi} |\phi_p\rangle$$

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$$|u_i\rangle = \sum_p (U_\uparrow)_{pi} |\phi_p\rangle$$

Non-Zero Overlap!

$$\langle \Phi | \Psi \rangle = \prod_{\sigma} \det(V_{\sigma}^\dagger U_{\sigma}) \neq 0$$

# WHY DO WE NEED ANOTHER QMC?

- Being able to exploit conventional quantum chemical techniques is a **HUGE** advantage
  - Can directly import trial wave functions (HF, CASSCF, etc.) from other codes
  - Can directly import one- and two-body integrals, same PPs
  - Can potentially mix techniques

# The Zoo of GS Quantum Monte Carlo Algorithms

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# Diffusion Monte Carlo (Real Space)

The key disadvantage of Variational Monte Carlo algorithms are their use of a fixed wave function form. Diffusion Monte Carlo remedies this by projecting an initial wave function to the ground state.

## Importance Sampling

$$\Psi(\mathbf{X}_f, t) = \int d\mathbf{X}_i G(\mathbf{X}_f | \mathbf{X}_i; t) \Psi(\mathbf{X}_i)$$

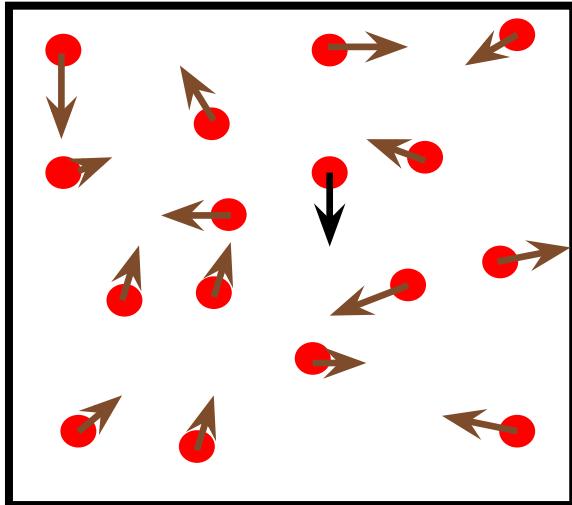
$$f(\mathbf{X}_f, t) = \int d\mathbf{X}_i \tilde{G}(\mathbf{X}_f | \mathbf{X}_i; t) \Psi(\mathbf{X}_i)^2 \quad f(\mathbf{X}, t) = \Psi(\mathbf{X}, t) \Psi(\mathbf{X})$$

$$\tilde{G}(\mathbf{X}_f | \mathbf{X}_i; t) = \Psi(\mathbf{X}_f) G(\mathbf{X}_f | \mathbf{X}_i; t) \frac{1}{\Psi(\mathbf{X}_i)}$$

# QUANTUM MONTE CARLO ALGORITHMS

# Quantum Monte Carlo

Quantum Monte Carlo methods are a suite of methods that use Monte Carlo techniques to solve *quantum* problems.



Fluids:  
Sample Configurations

**Classical Systems**

$$\Psi_1 = \begin{pmatrix} 5 & -2 & 0 \\ 7 & 3 & 2 \\ 2 & -1 & 1 \end{pmatrix}$$

$$\Psi_2 = \begin{pmatrix} 6 & 3 & 2 \\ 9 & 4 & -1 \\ -2 & 8 & 4 \end{pmatrix}$$

Quantum Systems:  
Sample Wave Functions

**Quantum Systems**

# QMC Origins

The first person to realize the potential for QMC was Malvin Kalos, a nuclear physicist by training. Berni Alder and David Ceperley brought the algorithm into the modern era.

Monte Carlo simulation of a many-fermion study

D. Ceperley, G. V. Chester, and M. H. Kalos  
Phys. Rev. B **16**, 3081 – Published 1 October 1977

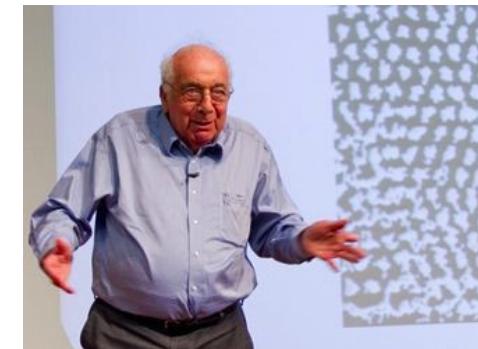


Mal

[Article](#)   [References](#)   [Citing Articles \(421\)](#)   [PDF](#)   [Export Citation](#)

Ground State of the Electron Gas by a Stochastic Method

D. M. Ceperley and B. J. Alder  
Phys. Rev. Lett. **45**, 566 – Published 18 August 1980



Berni

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# The Zoo of Quantum Monte Carlo Algorithms

Quantum Monte Carlo algorithms sample a variety of quantum quantities in an extremely wide range of bases/representations.

## Ground State\*

- Variational Monte Carlo (Both in Real and Fock Space)
- Diffusion Monte Carlo (Real Space)
- Auxiliary Field Quantum Monte Carlo, Full CI QMC (Determinant Space)
- Path Integral Ground State (Real Space)

## Finite Temperature

- Path Integral Monte Carlo (Real Space)
- Diagrammatic Monte Carlo (Diagrammatic Space)
- Density Matrix Monte Carlo (Orthogonal Determinant Space)
- Determinant Monte Carlo (Non-orthogonal Determinant Space)

\*Note that ground state variational algorithms have recently been adapted to treat excited states (Neuscamman).

# VARIATIONAL MONTE CARLO

# Variational Quantum Monte Carlo (Real Space)

Variational Monte Carlo algorithms estimate the ground state energy by sampling an approximate wave function.

## Rearranging Variational Energy

$$E_{var} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

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$$E_{var} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int d\mathbf{X} \Psi(\mathbf{X}) \hat{H} \Psi(\mathbf{X})}{\int d\mathbf{X} \Psi(\mathbf{X})^2}$$

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## Variational Theorem

$$E_{var} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0$$

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Slater Determinant



$$\begin{aligned} \Psi(\mathbf{X}) &= J(\mathbf{X}) \Phi(\mathbf{X}) \\ &= e^{f(\mathbf{X})} \Phi(\mathbf{X}) \end{aligned}$$



Jastrow

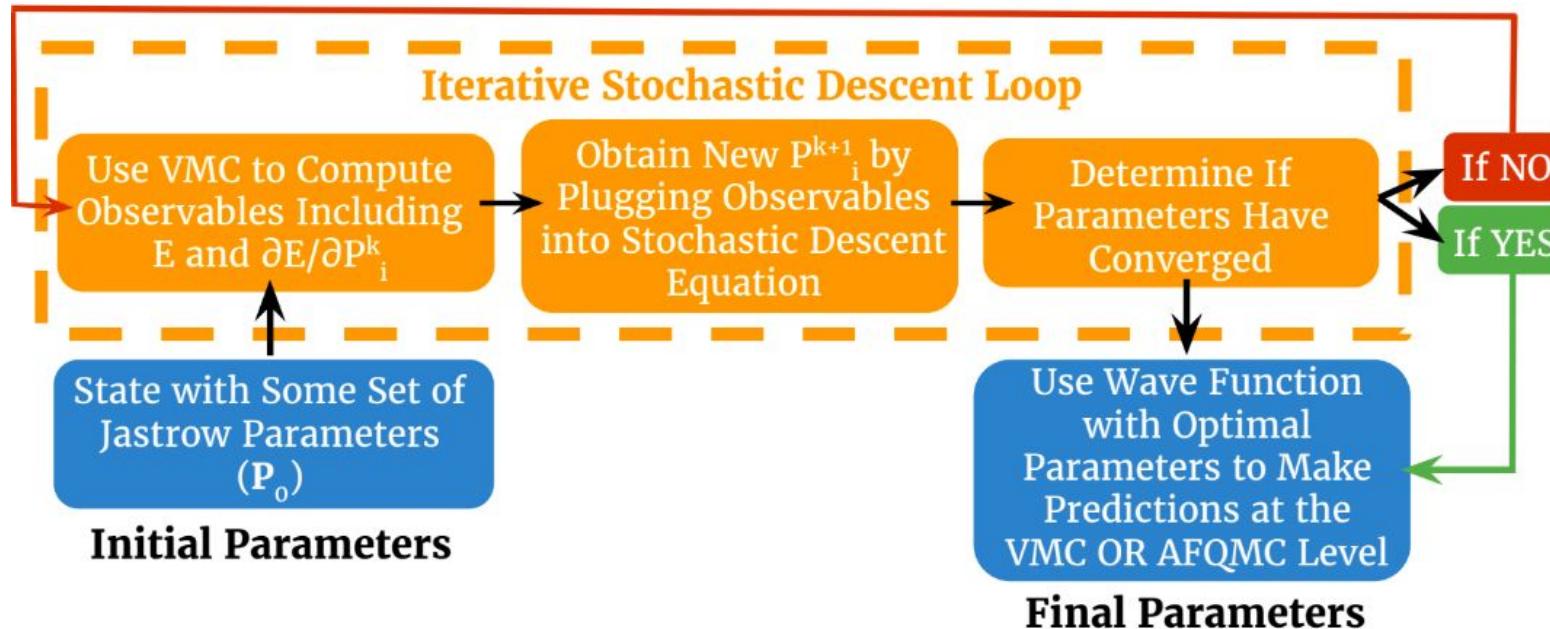
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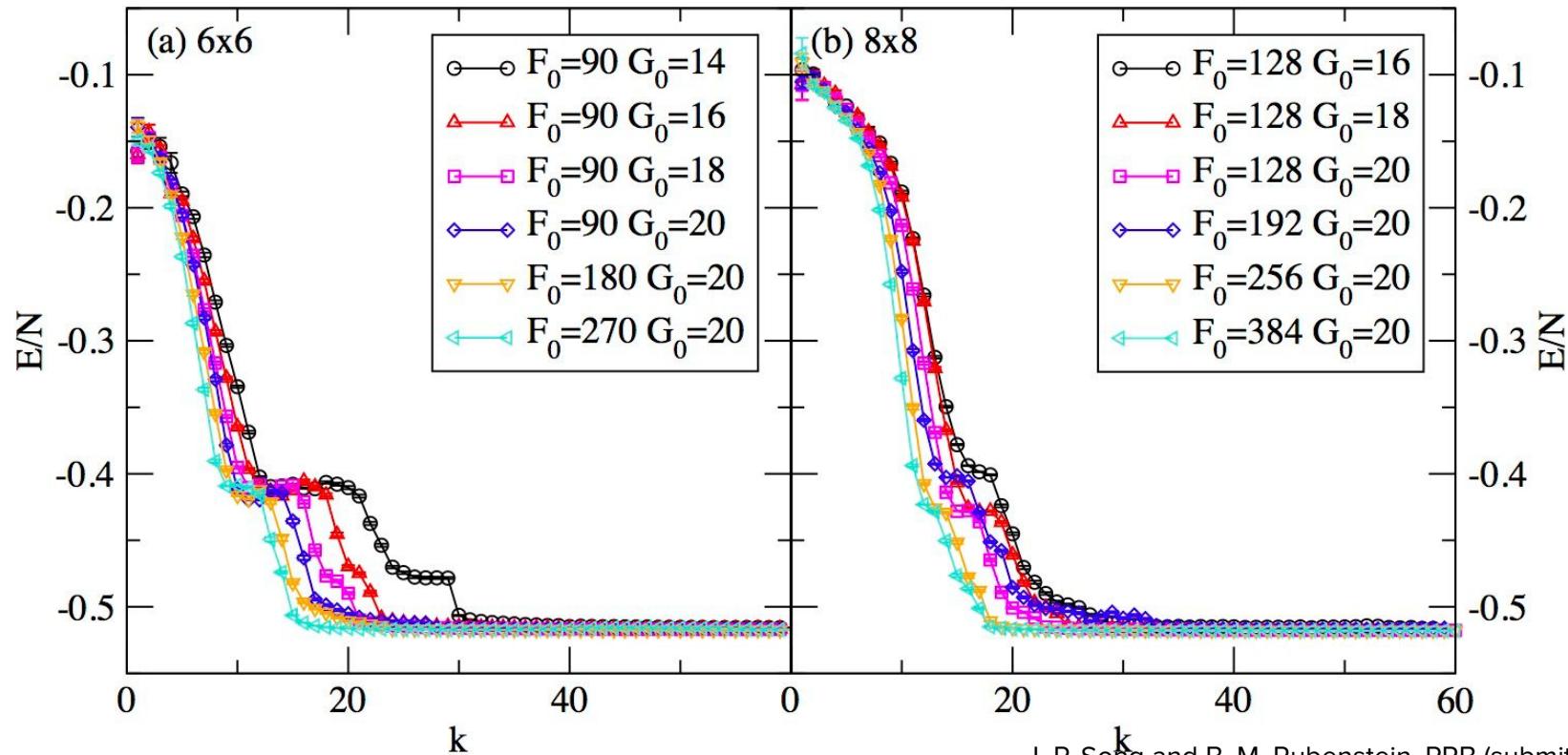
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# Variational Quantum Monte Carlo (Det Space)

Optimization of a Slater-Jastrow Wave Function  
Square Hubbard Models,  $U/t=8$ , Half-Filling



DIFFUSION  
MONTE CARLO

# Diffusion Monte Carlo (Real Space)

The key disadvantage of Variational Monte Carlo algorithms are their use of a fixed wave function form. Diffusion Monte Carlo remedies this by projecting an initial wave function to the ground state.

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## Mixed Estimator for the Energy

$$E_0 = \frac{\langle \Psi_0 | \hat{H} | \Psi \rangle}{\langle \Psi_0 | \Psi \rangle} = \frac{\int d\mathbf{X} \Psi_0(\mathbf{X}) \Psi(\mathbf{X}) E_L(\mathbf{X})}{\int d\mathbf{X} \Psi_0(\mathbf{X}) \Psi(\mathbf{X})}$$


# Projector Techniques in Quantum Monte Carlo

Trial Wave Function:  $|\Psi\rangle$



First Iteration:  $|\Psi^1\rangle$



Second Iteration:  $|\Psi^2\rangle$



$N^{th}$  Iteration:  $|\Psi^n\rangle \propto |\Psi_0\rangle$



In Quantum Monte Carlo algorithms, the ground state wave function is projected out from a trial wave function.

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## Projection Equation

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$$\begin{aligned}\lim_{t \rightarrow \infty} e^{-(H-E_T)t} |\Psi\rangle &= \lim_{t \rightarrow \infty} \sum_i e^{-(E_i-E_T)t} |\Psi_i\rangle \langle \Psi_i| \Psi \rangle \\ &= \lim_{t \rightarrow \infty} e^{-(E_0-E_T)t} |\Psi_0\rangle \langle \Psi_0| \Psi \rangle \propto |\Psi_0\rangle\end{aligned}$$

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$$\Psi(\mathbf{X}_f, t) = \int d\mathbf{X}_i G(\mathbf{X}_f | \mathbf{X}_i; t) \Psi(\mathbf{X}_i)$$



Green's Function

# Diffusion Monte Carlo (Real Space)

The key disadvantage of Variational Monte Carlo algorithms are their use of a fixed wave function form. Diffusion Monte Carlo remedies this by projecting an initial wave function to the ground state.

## Importance Sampling

$$\Psi(\mathbf{X}_f, t) = \int d\mathbf{X}_i G(\mathbf{X}_f | \mathbf{X}_i; t) \Psi(\mathbf{X}_i)$$

$$f(\mathbf{X}_f, t) = \int d\mathbf{X}_i \tilde{G}(\mathbf{X}_f | \mathbf{X}_i; t) \Psi(\mathbf{X}_i)^2 \quad f(\mathbf{X}, t) = \Psi(\mathbf{X}, t) \Psi(\mathbf{X})$$

$$\tilde{G}(\mathbf{X}_f | \mathbf{X}_i; t) = \Psi(\mathbf{X}_f) G(\mathbf{X}_f | \mathbf{X}_i; t) \frac{1}{\Psi(\mathbf{X}_i)}$$

# Diffusion Monte Carlo (Real Space)

The key disadvantage of Variational Monte Carlo algorithms are their use of a fixed wave function form. Diffusion Monte Carlo remedies this by projecting an initial wave function to the ground state.

## Short-Time Green's Function

$$f(\mathbf{X}) = \lim_{M \rightarrow \infty} \int d\mathbf{X}_1 d\mathbf{X}_2 \dots d\mathbf{X}_M \tilde{G}(\mathbf{X}|\mathbf{X}_M; \tau) \tilde{G}(\mathbf{X}_M|\mathbf{X}_{M-1}; \tau) \dots \tilde{G}(\mathbf{X}_2|\mathbf{X}_1; \tau) \Psi(\mathbf{X}_1)^2$$

$$\tilde{G}(\mathbf{X}_f|\mathbf{X}_i; \tau) \approx \frac{1}{(2\pi\tau)^{3N/2}} e^{-\frac{(\mathbf{X}_f - \mathbf{X}_i - \mathbf{v}(\mathbf{X}_i)\tau)^2}{2\tau}} e^{-\left(\frac{E_L(\mathbf{X}_f) + E_L(\mathbf{X}_i)}{2} - E_T\right)\tau}$$

# Diffusion Monte Carlo (Real Space)

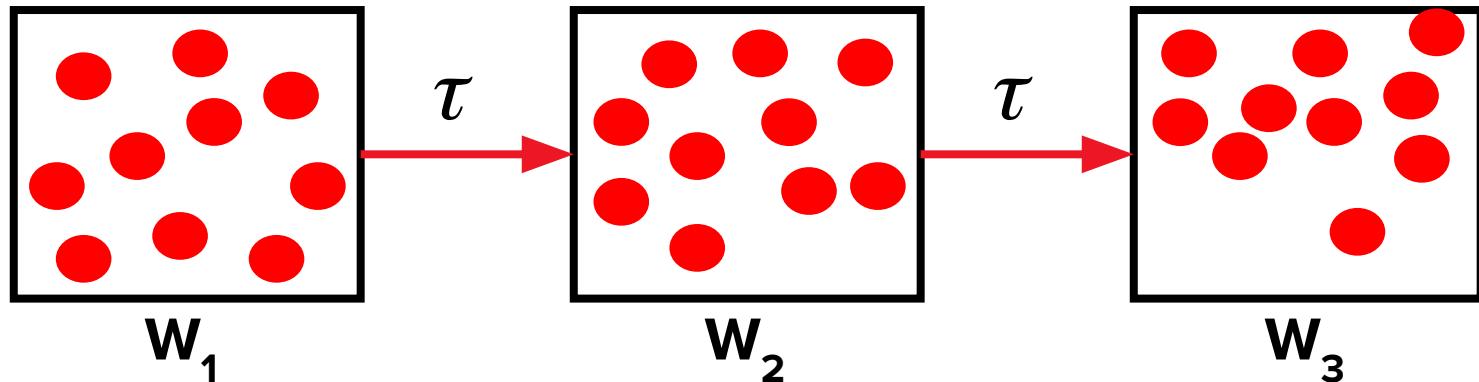
The key disadvantage of Variational Monte Carlo algorithms are their use of a fixed wave function form. Diffusion Monte Carlo remedies this by projecting an initial wave function to the ground state.

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Weight

$$e^{-\left(\frac{E_L(\mathbf{X}_f) + E_L(\mathbf{X}_i)}{2} - E_T\right)\tau}$$

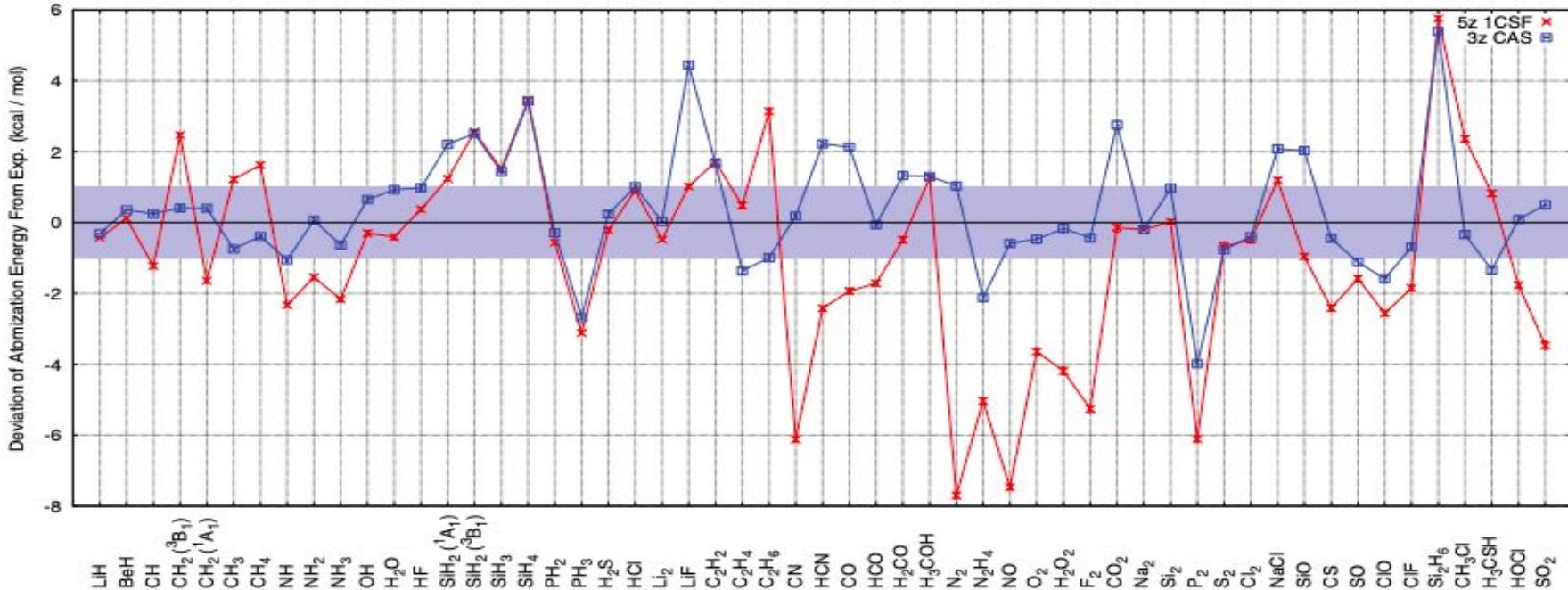
**Propagator:**  
Sampled for  
Particle Moves



# DMC For Molecules

Within Chemical Accuracy with Just a Single Determinant Trial

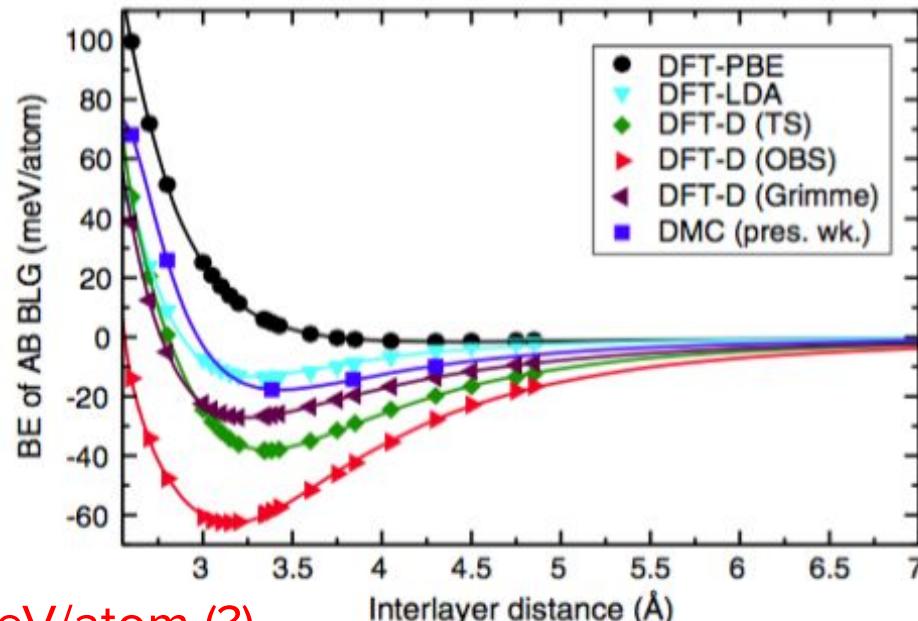
Deviation from Experimental Atomization Energies



# DFT vs. DMC (Graphene)

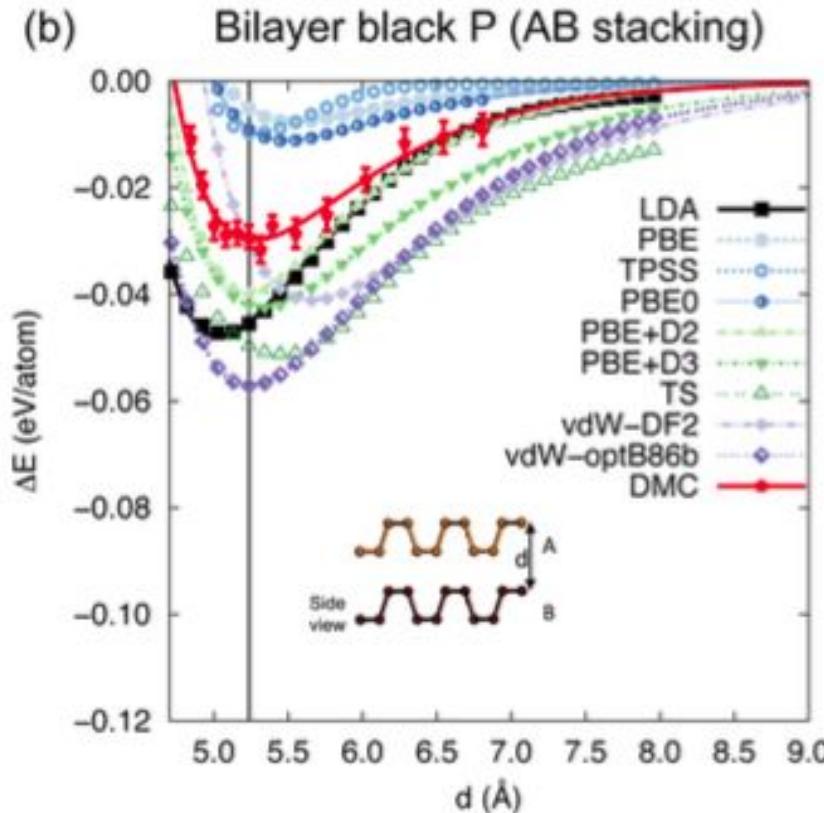
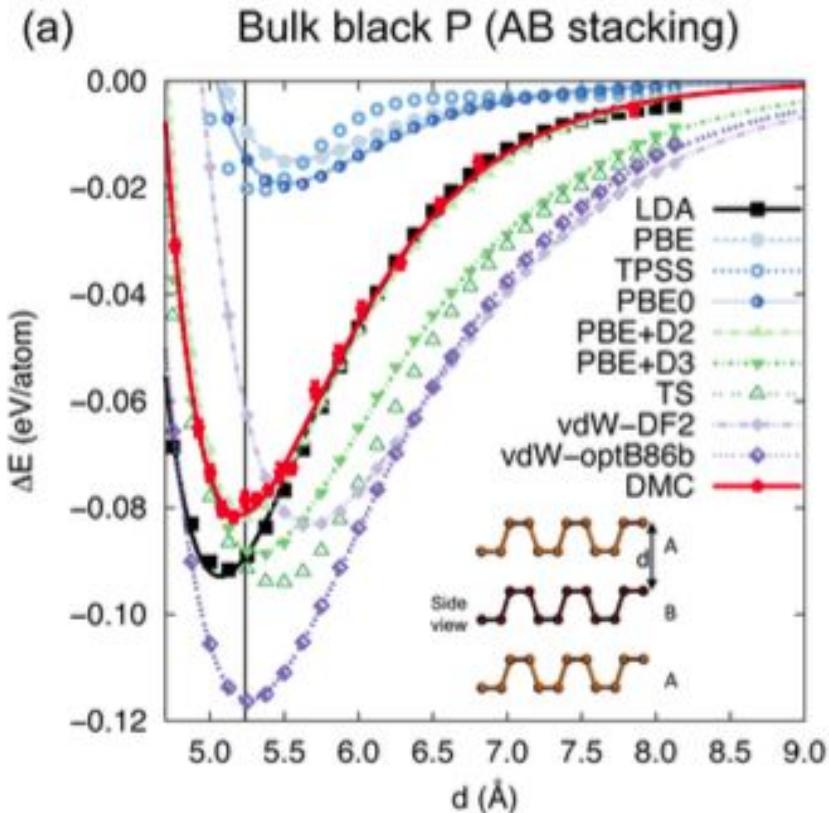
*How and With What Strength Does Bilayer Graphene Stack?*

Stacking	Method	$d$ (Å)	BE (meV/atom)
AA	vdW-DF [17]	3.35	10.4
AA	DFT-D [17]	3.25	31.1
AA	DMC (present work)	3.495	11.5(9)
AB	DFT-LCAO-OO [18]	3.1–3.2	70 (5)
AB	SAPT(DFT) [19]	3.43	42.5
AB	vdW-DF [7]	3.6	45.5
AB	vdW-DF [17]	3.35	29.3
AB	DFT-D [17]	3.25	50.6
AB	DFT-D [20]	3.32	22
AB	MBD [21]	3.37	23
AB	DMC (present work)	3.384	17.7(9)



- Experimental Binding Energy: 35 meV/atom (?)
- DMC Binding Energies Smallest, Close
- DMC Predicts AB Stacking

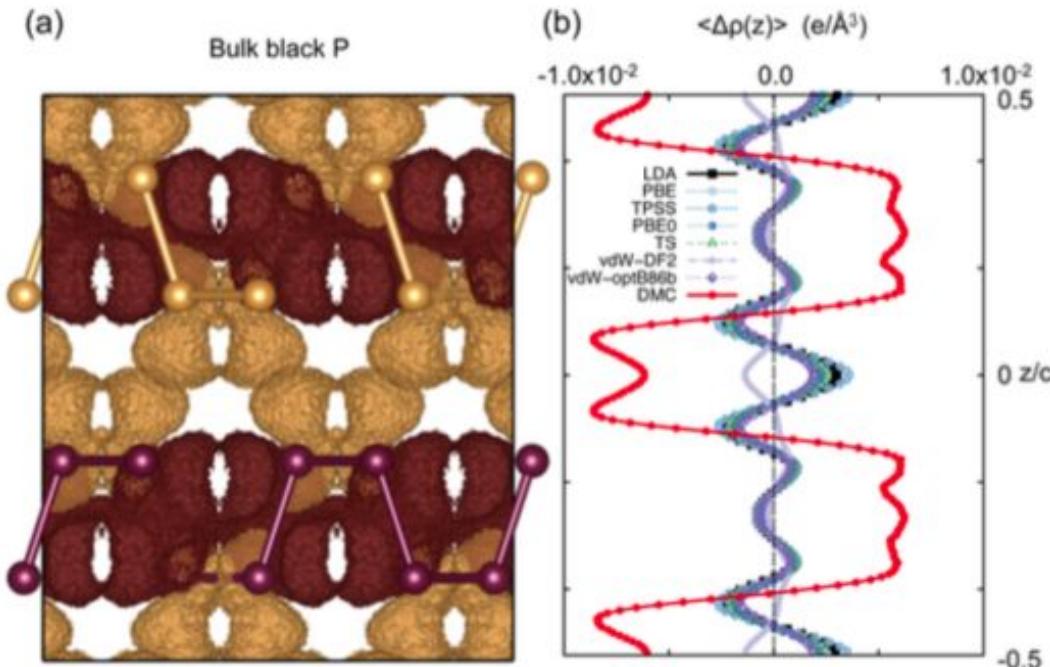
# DFT vs. DMC (Phosphorene)



# DFT vs. DMC (Phosphorene)

- Used DMC to Study Phosphorene Interlayer Interactions
- Significant Changes in Electron Densities Found With DMC, Not Seen in DFT Due to Delocaliation
- DFTs Without Dispersion Underestimated Interlayer Interactions, While Those With Dispersion Overestimated

Electron Densities Predicted By Various Methods



AUXILIARY FIELD  
QUANTUM  
MONTE CARLO

# THE FIELD THAT MAKES PEOPLE FAMOUS FOR OTHER THINGS...

## Monte Carlo calculations of coupled boson-fermion systems. I

R. Blankenbecler\*

*Laboratoire de Physique Théorique et Hautes Energies, University of Paris XI, 91405, Orsay, France*

D. J. Scalapino and R. L. Sugar

*Institute for Theoretical Physics and Department of Physics, University of California, Santa Barbara, California 93106*

(Received 15 June 1981)

## Monte Carlo Methods for the Nuclear Shell Model

C. W. Johnson, S. E. Koonin, G. H. Lang, and W. E. Ormand

*W. K. Kellogg Radiation Laboratory, California Institute of Technology, Pasadena, California 91125*

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## Quantum Monte Carlo study of the two-impurity Kondo Hamiltonian

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Doug  
Scalapino (UCSB)

High-T<sub>c</sub>  
Superconductivity

Steve  
Koonin

DOE Under-  
secretary

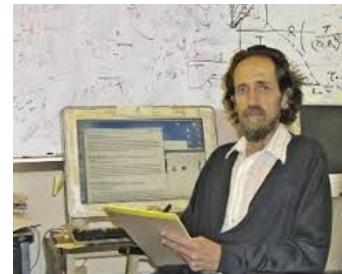


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Jorge Hirsch  
(UCSD)

h-Index!

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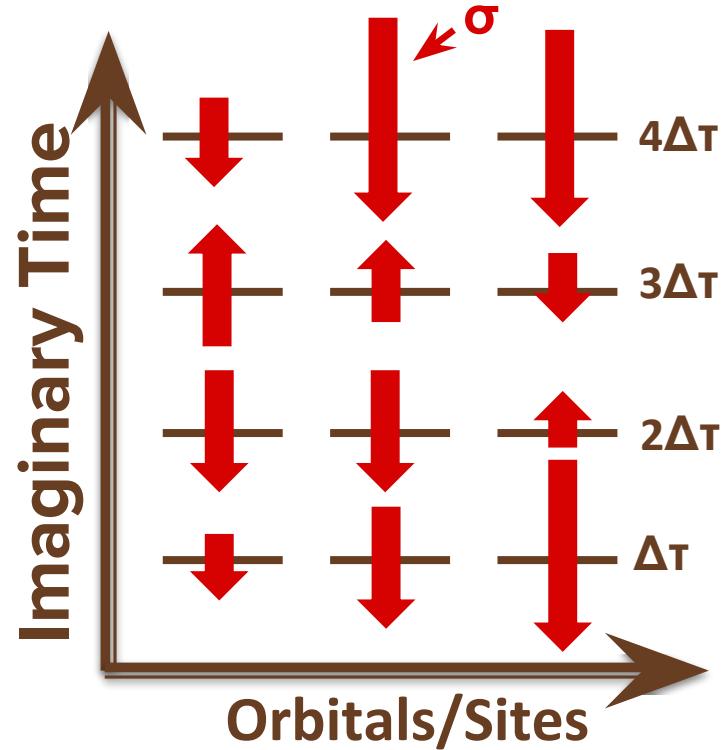
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# Auxiliary Field Quantum Monte Carlo

At a practical level, AFQMC simulations sample a Gaussian-distributed set of fields, much as in a classical MC simulation of the Ising model.



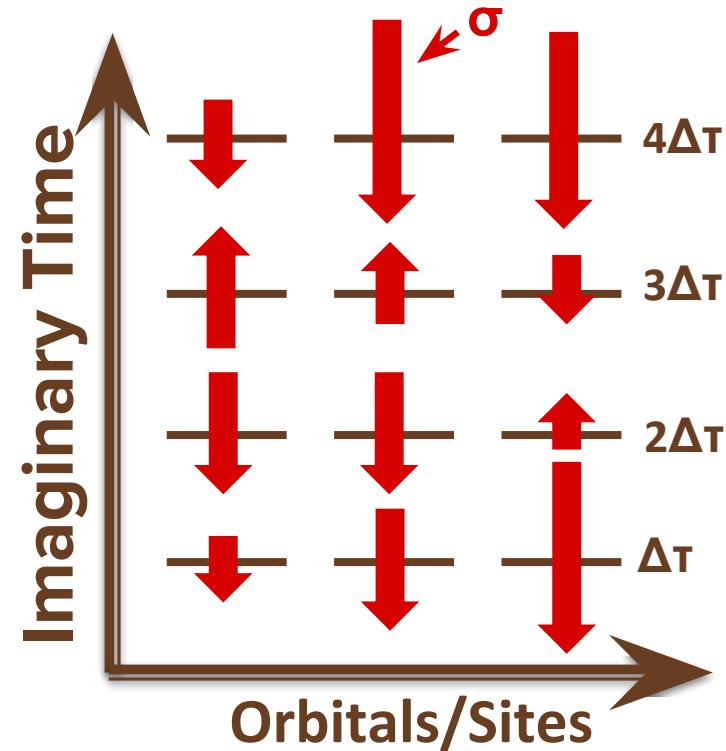
# Auxiliary Field Quantum Monte Carlo

## Ground State Projection:

The Ground State  
Wave Function

$$|\Psi_0\rangle \propto \lim_{n \rightarrow \infty} \left( e^{-\Delta\tau \hat{H}} \right)^n |\Psi_T\rangle$$

A Trial  
Wave Function (DFT)  
A Projection  
Operator



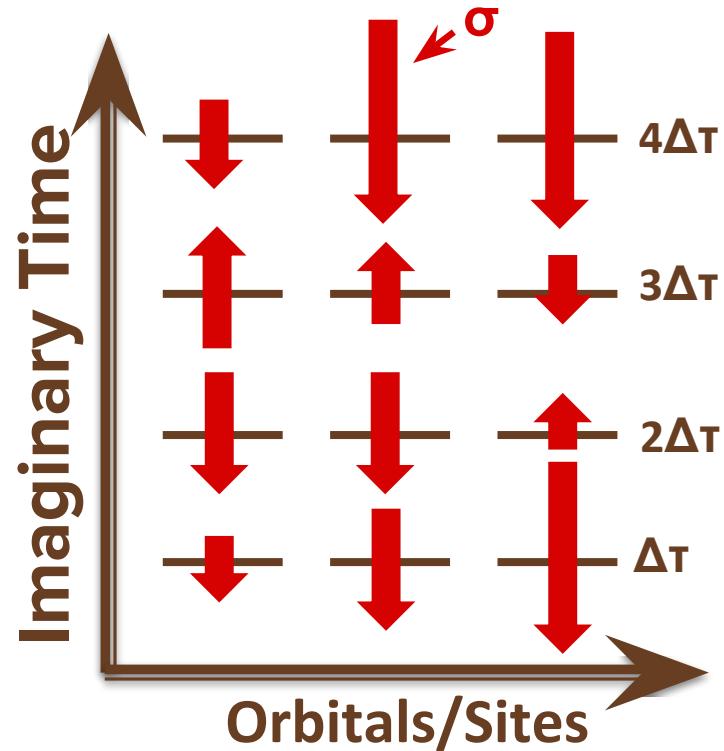
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Suzuki-Trotter Factorization:

$$e^{-\Delta\tau \hat{H}} \approx e^{-\Delta\tau \hat{K}/2} e^{-\Delta\tau \hat{V}} e^{-\Delta\tau \hat{K}/2}$$



# Auxiliary Field Quantum Monte Carlo

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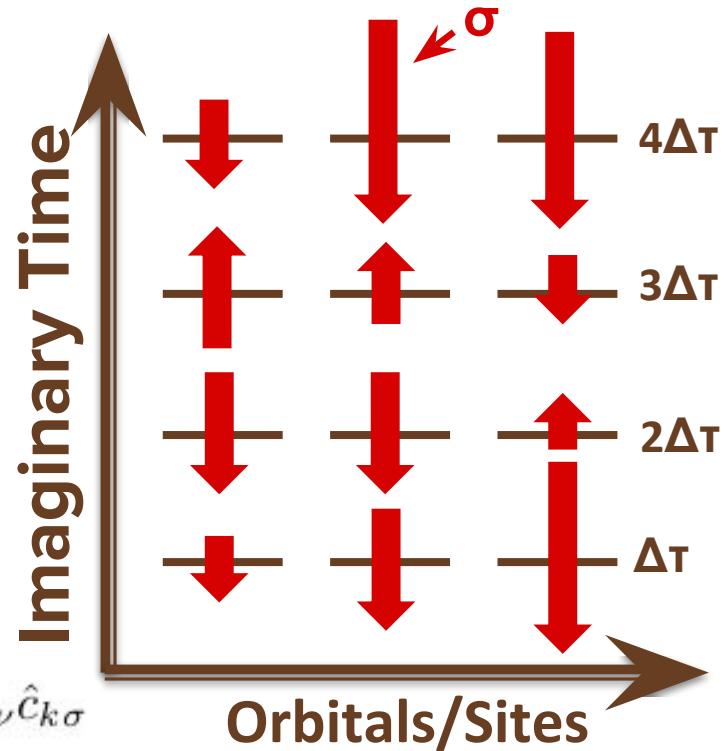
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*Ab Initio* Hamiltonian:

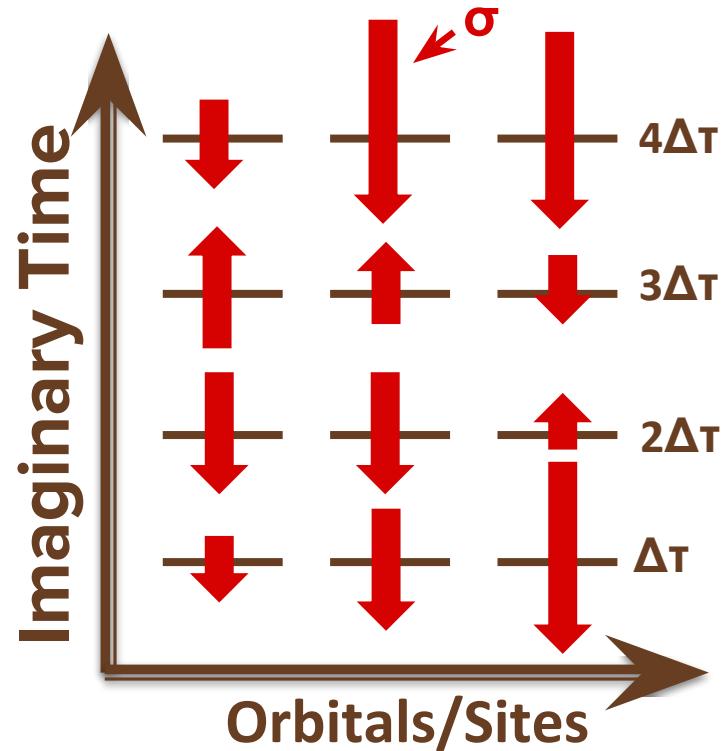
$$\hat{H} = \sum_{\sigma} \sum_{ij}^N T_{i\sigma, j\sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \frac{1}{2} \sum_{\sigma\nu} \sum_{ijkl}^N V_{ijkl}^{\sigma\nu\sigma\nu} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\nu}^\dagger \hat{c}_{l\nu} \hat{c}_{k\sigma}$$



# Auxiliary Field Quantum Monte Carlo

Writing Potential as a Square:

$$\hat{V} = \frac{1}{8} \sum_{\gamma}^{(2N)^2} \lambda_{\gamma} [(\hat{\rho}_{\gamma} + \hat{\rho}_{\gamma}^{\dagger})^2 - (\hat{\rho}_{\gamma} - \hat{\rho}_{\gamma}^{\dagger})^2] - \sum_{\alpha} \hat{\rho}_0^{\alpha}$$



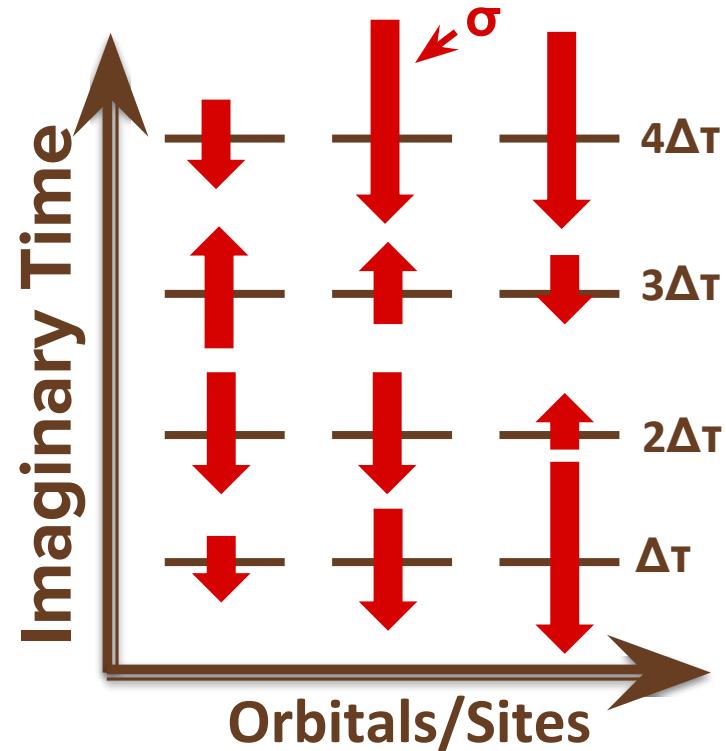
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Continuous HS Transformation:

$$e^{\Delta\tau\lambda\hat{v}^2} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\sigma e^{-\sigma^2/2} e^{\sigma\sqrt{-\lambda\Delta\tau}\hat{v}}$$



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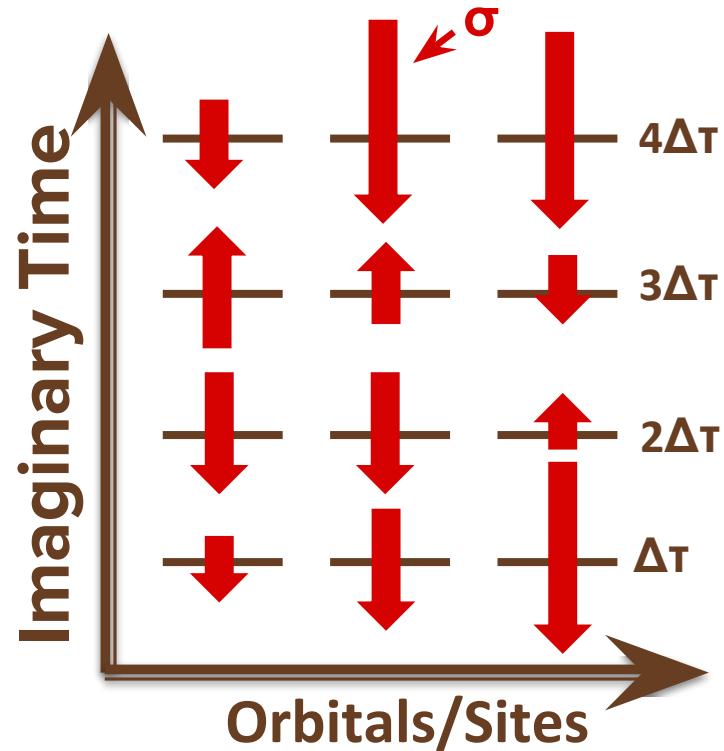
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Overall Propagator:

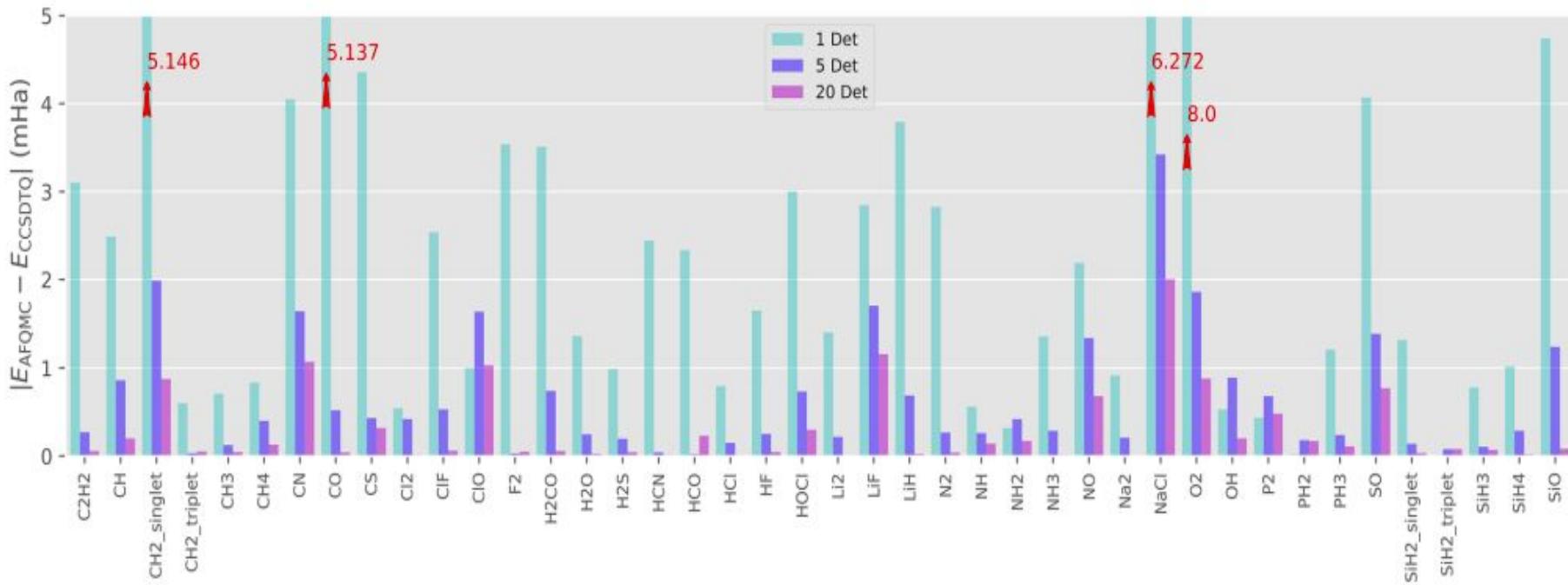
$$e^{-\Delta\tau\hat{H}} = \int_{-\infty}^{\infty} d\vec{\sigma} p(\vec{\sigma}) \hat{B}(\vec{\sigma})$$



# AFQMC For Molecules

Within Chemical Accuracy with Just a Single Determinant Trial

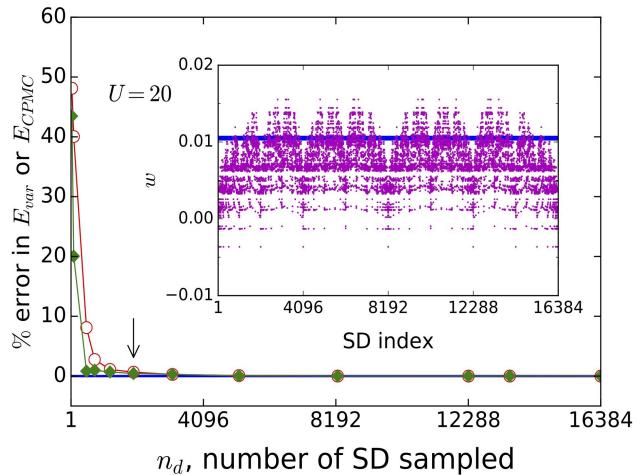
Deviation from CSDTQ Total Energies (G1 set)



# THE RUBENSTEIN GROUP @ BROWN

## Theoretical/Computational Chemistry and Physics

Focus 1: Quantum  
Statistical Mechanics

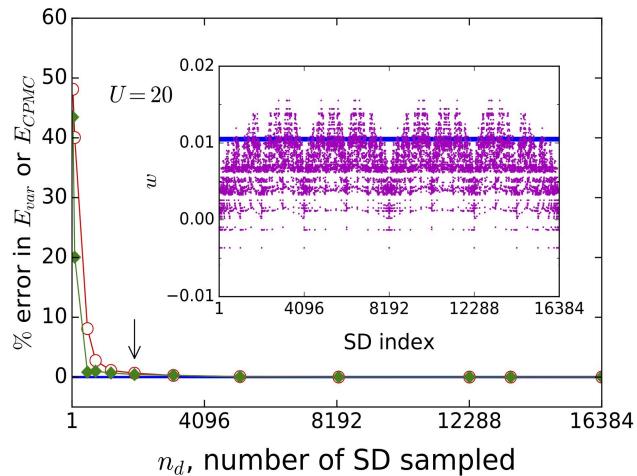


*How Can Schrodinger's  
Equation Be Solved Faster  
and More Accurately?*

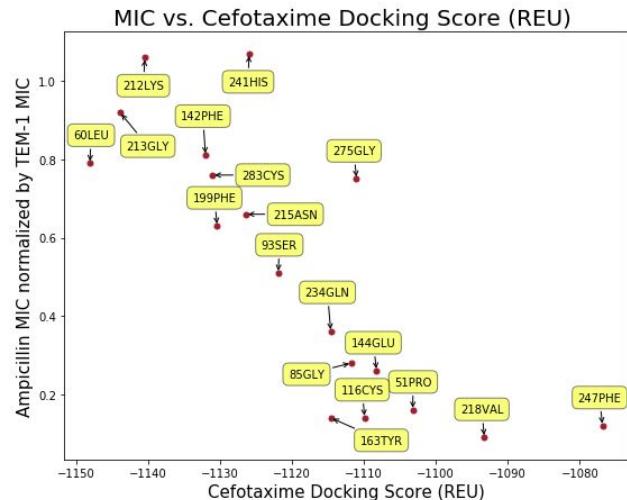
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Focus 1: Quantum  
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Focus 2: Computational  
Biophysics



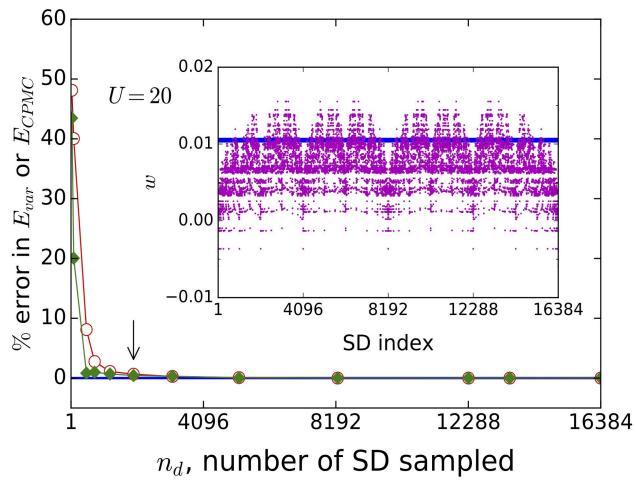
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*Can Thermodynamic  
Properties Be Used to  
Predict Organismal Fitness?*

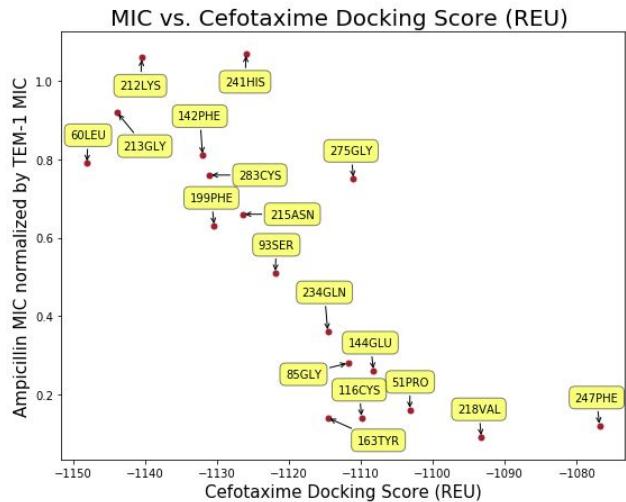
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### Focus 1: Quantum Statistical Mechanics

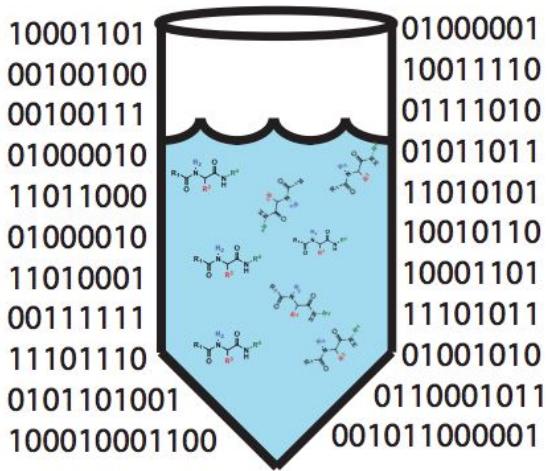


### Focus 2: Computational Biophysics



*How Can Schrodinger's Equation Be Solved **Faster** and More Accurately?*

### Focus 3: Alternative Computing



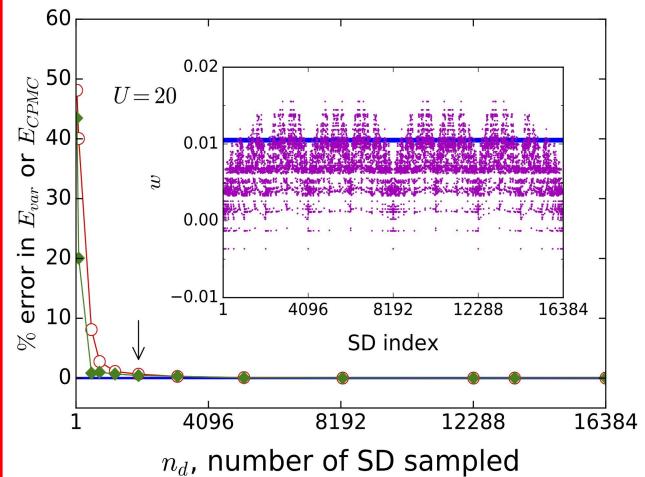
*Can Thermodynamic Properties Be Used to Predict Organismal Fitness?*

*Can Molecules/Trapped Ions Be Used to Store and Compute on Information?*

# THE RUBENSTEIN GROUP @ BROWN

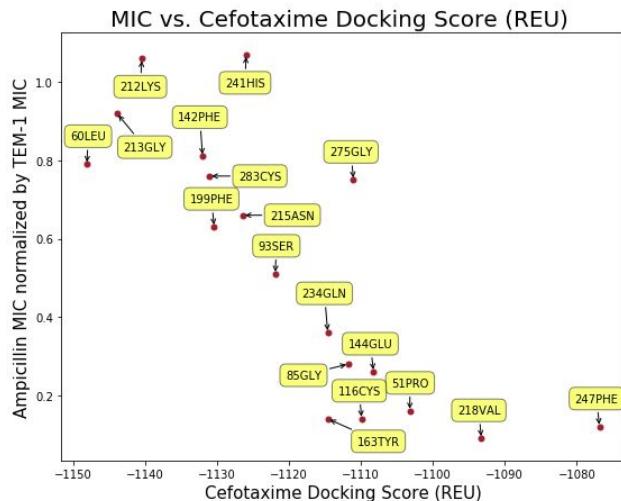
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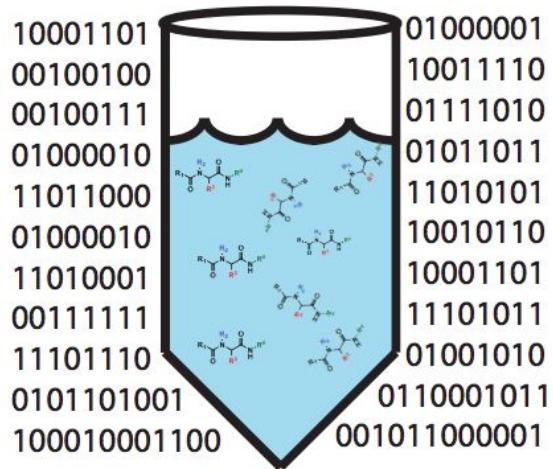
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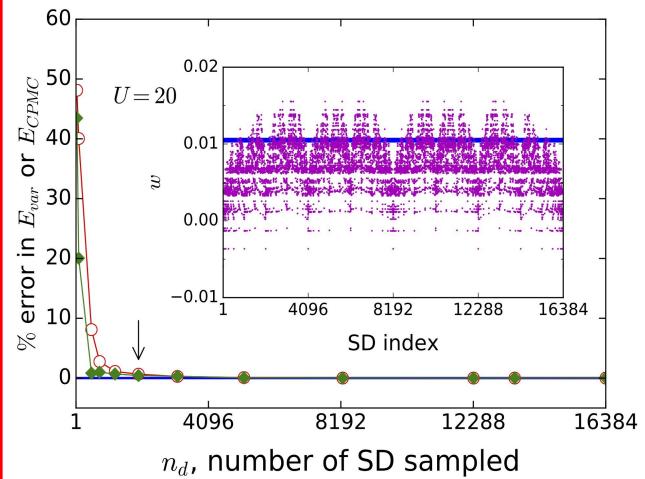


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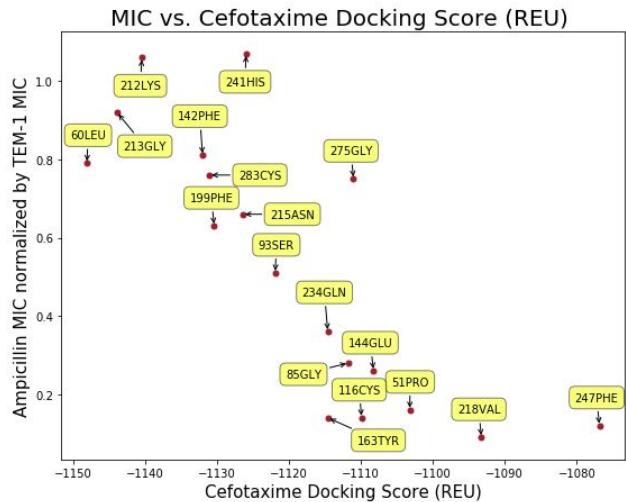
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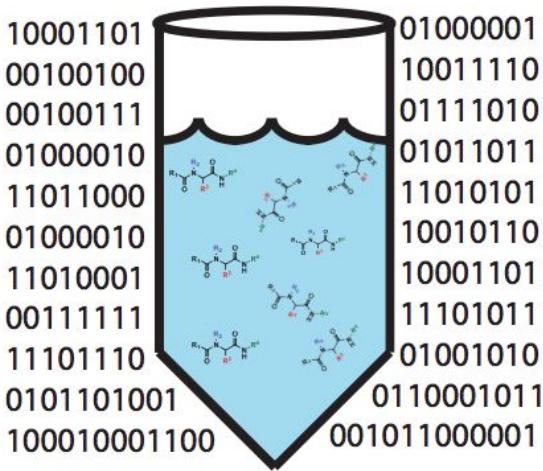
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