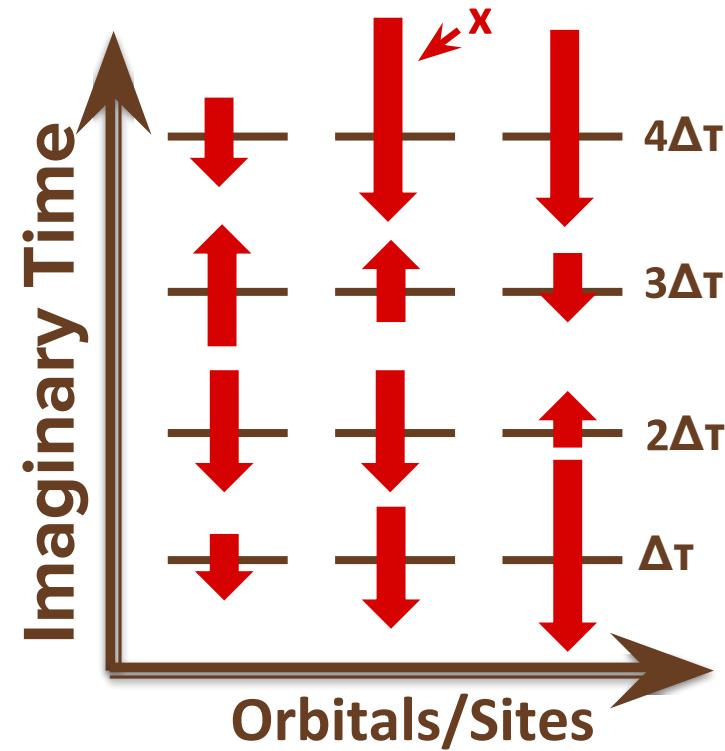


Auxiliary Field Quantum Monte Carlo 101



PROF. BRENDA RUBENSTEIN

Stochastic Methods for Electronic Structure
UPitt - August 2019 (brenda_rubenstein@brown.edu)



BROWN

TUTORIAL OUTLINE

1. INTRODUCTION: What Is AFQMC and *Why*?

2. ALGORITHM: How It Actually Works

3. EXERCISES

- PART ONE: AFQMC Propagation (Non-Interacting); Energy Evaluation
- PART TWO: Hubbard-Stratonovich Transformation; Weight

4. THE PHASE PROBLEM

5. APPLICATIONS AND OPPORTUNITIES

WHAT IS AND
WHY AFQMC?

SOME REFERENCES AND KEY PAPERS

- **USEFUL REVIEW**

- M. Motta and S. Zhang. *Ab Initio Computations of Molecular Systems by the Auxiliary-Field Quantum Monte Carlo Method*. WIREs Computational Molecular Science (2018). [Molecular Review]

- **(READABLE) ORIGINAL PAPERS**

- S. Zhang, J. Carlson, and J. Gubernatis. *Constrained Path Monte Carlo for Fermion Ground States*. Physical Review B. **55**, 7464 (1997). [Ground State Constrained Path Monte Carlo Algorithm]
- S. Zhang and H. Krakauer. *Quantum Monte Carlo Method Using Phase-Free Random Walkers with Slater Determinants*. Physical Review Letters. **90**, 136401 (2003). [Phaseless Algorithm]

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_c
Superconductivity

Steve
Koonin

DOE Under-
secretary

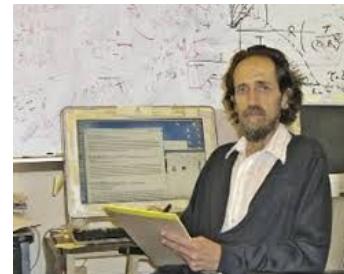


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Jorge Hirsch
(UCSD)

h-Index!

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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)			
Auxiliary Field QMC (AFQMC)			

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Full Configuration Interaction QMC (FCIQMC)	$-\tau(\hat{H} - E_T)$	ϕ_i^{orthog}	Second
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Auxiliary Field QMC (AFQMC)	$e^{-\tau(\hat{H} - E_T)}$	$\phi_i^{non-orthog}$	Second

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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Exponential Projection Operator

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

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

WHY DO WE NEED ANOTHER QMC?

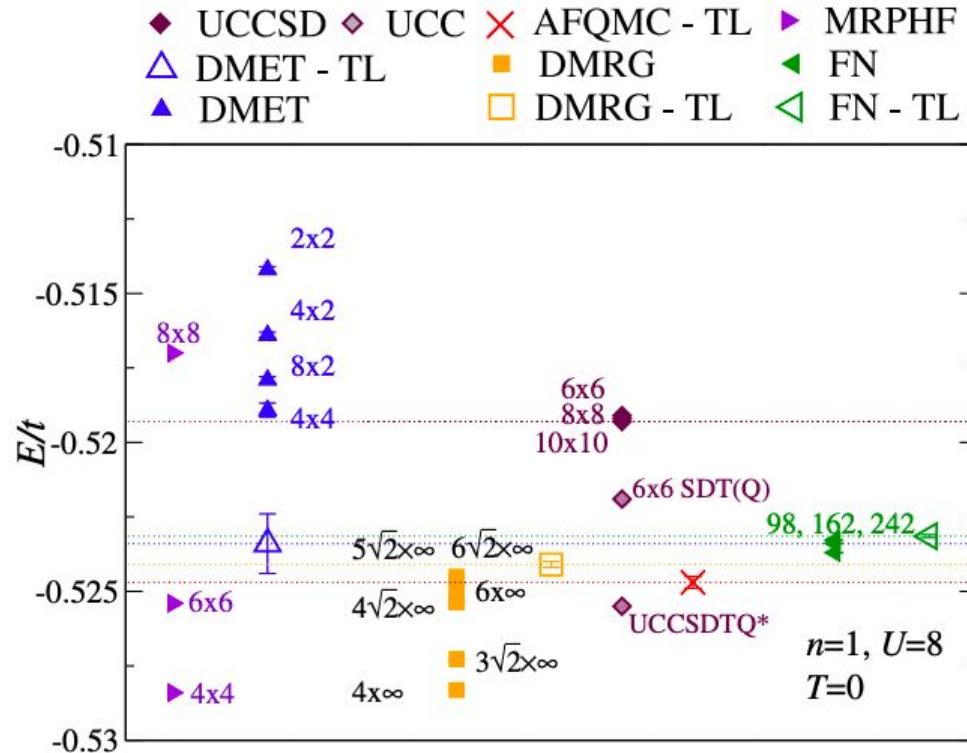
- Being able to exploit conventional quantum chemical techniques is a **HUGE** advantage
 - Can directly import trial wave functions (HF, CASSCF, etc.) from other codes
 - Can directly import one- and two-body integrals, same PPs
 - Can potentially mix techniques
- The sign problem varies in different representations
 - For several key cases (1D lattices, half-filling), no sign problem!
 - Sign constraints *thought* to be more accurate, mild

AFQMC: THE GOLD STANDARD IN PHYSICS

Half-Filled Hubbard Model in
Thermodynamic Limit

**AFQMC Is THE BENCHMARK
Against Which All Other
Methods Are Compared**

One could imagine perturbing off
of half-filling to get other
non-trivial results



THE LEAP TO CHEMISTRY

Method for Performing Monte Carlo Calculations for Systems with Fermions

D. J. Scalapino and R. L. Sugar

Phys. Rev. Lett. **46**, 519 – Published 23 February 1981

Article

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Citing Articles (132)

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Monte Carlo calculations of coupled boson-fermion systems. II

D. J. Scalapino and R. L. Sugar

Phys. Rev. B **24**, 4295 – Published 15 October 1981

Article

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1981



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Discrete Hubbard-Stratonovich transformation for fermion lattice models

J. E. Hirsch

Phys. Rev. B **28**, 4059(R) – Published 1 October 1983; Erratum Phys. Rev. B **29**, 4159 (1984)

Article

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THE LEAP TO CHEMISTRY

Two-dimensional Hubbard model: Numerical simulation study

J. E. Hirsch

Phys. Rev. B **31**, 4403 – Published 1 April 1985

Article

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THE LEAP TO CHEMISTRY

Numerical study of the two-dimensional Hubbard model

S. R. White, D. J. Scalapino, R. L. Sugar, E. Y. Loh, J. E. Gubernatis, and R. T. Scalettar
Phys. Rev. B **40**, 506 – Published 1 July 1989

Article

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THE LEAP TO CHEMISTRY

Sign problem in the numerical simulation of many-electron systems

E. Y. Loh, Jr., J. E. Gubernatis, R. T. Scalettar, S. R. White, D. J. Scalapino, and R. L. Sugar
Phys. Rev. B **41**, 9301 – Published 1 May 1990

Article

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THE LEAP TO CHEMISTRY

Constrained Path Quantum Monte Carlo Method for Fermion Ground States

Shiwei Zhang, J. Carlson, and J. E. Gubernatis
Phys. Rev. Lett. **74**, 3652 – Published 1 May 1995

Article

References

Citing Articles (85)

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THE LEAP TO CHEMISTRY

Finally Chemistry (Sort Of)!

Quantum Monte Carlo Method using Phase-Free Random Walks
with Slater Determinants

Shiwei Zhang and Henry Krakauer

Phys. Rev. Lett. **90**, 136401 – Published 4 April 2003

Article

References

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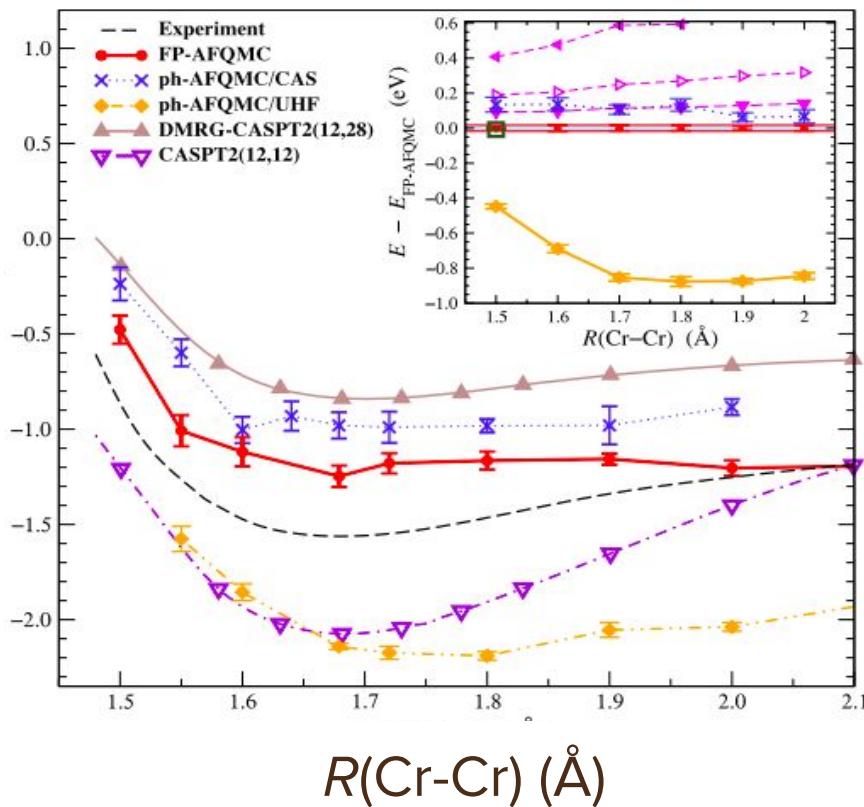
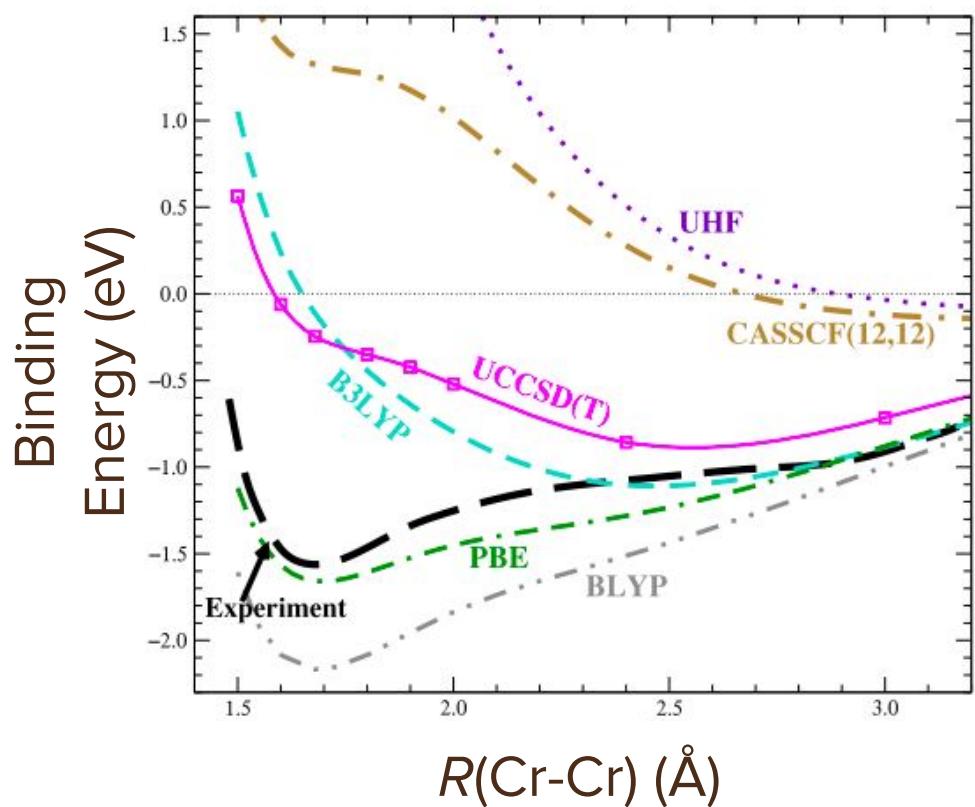
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BUT, ALSO USEFUL IN CHEMISTRY...

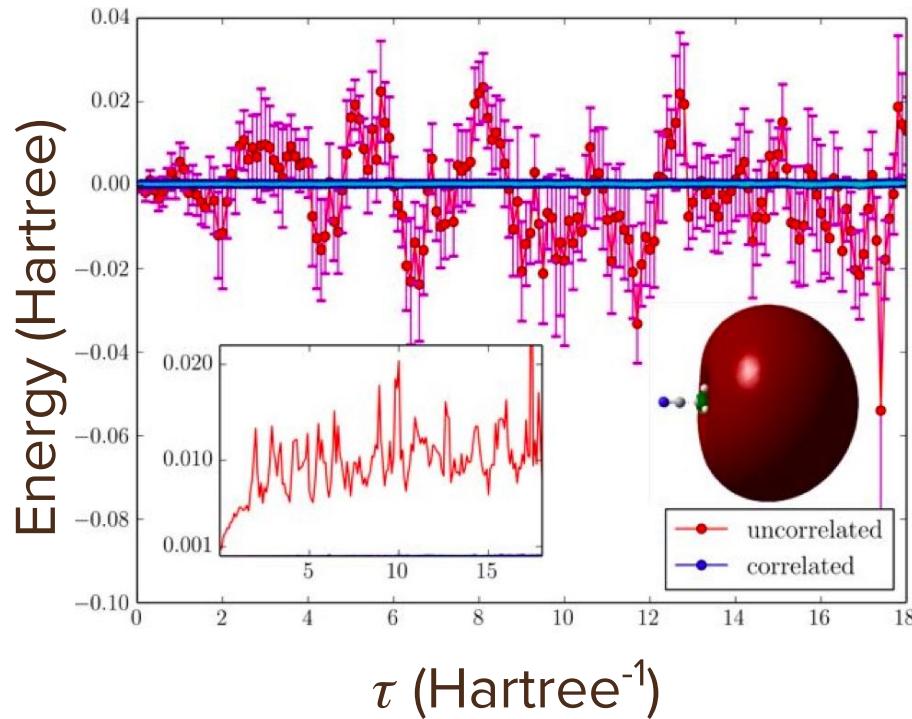
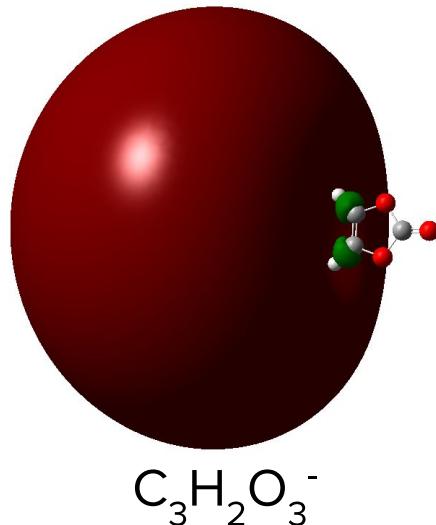
The Binding Energy of the Chromium Dimer (Historically Difficult!)



BUT, ALSO USEFUL IN CHEMISTRY...

Dipole-Bound anions bind an excess electron far from their nuclei via their dipole moments.

- **Critical Dipole Moment:** >1.625 D
- **Average Distance Between Electron and Neutral Core:** $10\text{-}100\text{s } \text{\AA}$
- **Molecular Electron Binding Energies:** $>10\text{s cm}^{-1}$



BUT, ALSO USEFUL IN CHEMISTRY...

Smaller Error Bars via AFQMC than DMC for
Significantly Less Cost...

Table 1. EBEs and Dipole Moments of Selected Species from Experiment and Self-Consistent Field [HF], Coupled Cluster [CCSD(T)], DMC, and C-AFQMC Calculations

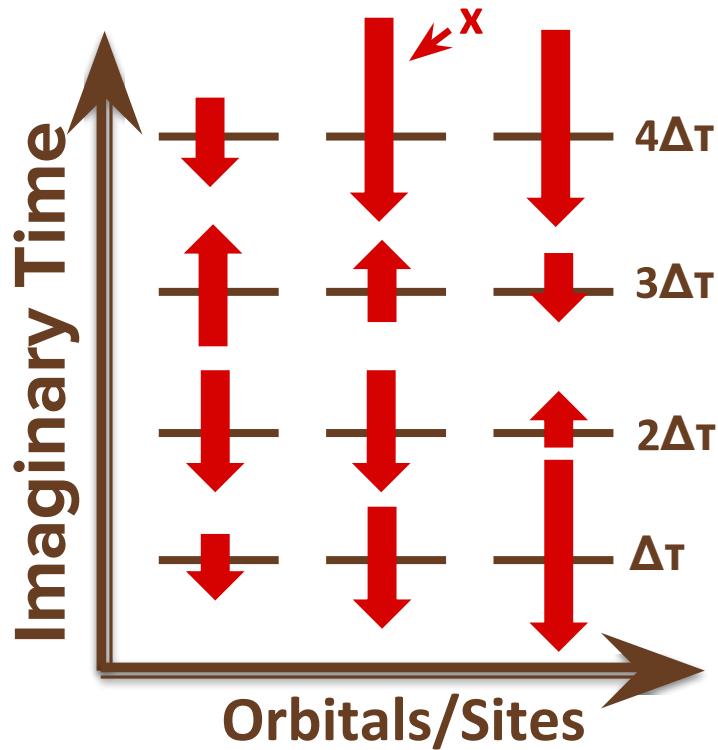
	dipole moment (D)	EBE (cm^{-1})			
		experiment	ΔSCF^a	CCSD(T) ^a	DMC ^b
SO	1.55 ⁶²	not bound	-3.84	-4.13	-308.20 ± 70.82
HCN	2.98 ⁶²	13 ⁶³	11.00	7.44	46.17 ± 45.30
CH_2CHCN	3.87 ⁶²	56–87 ^{12,64}	43.30	61.87	106.63 ± 58.12
CH_3CN	3.92 ⁶²	93–145 ^{12,64}	50.83	103.00	93.83 ± 36.21
C_3H_2	4.14 ⁶⁵	170 ± 50^{66}	54.61	162.08	151.22 ± 64.25^{d}
$\text{C}_3\text{H}_2\text{O}_3$	4.55 ⁶²	194 ± 24^{67}	103.13	163.31	213.98 ± 116.15
					C-AFQMC ^c

Note: Perhaps, More Accurate DMC Calculations Could Be Achieved...

THE MATH BEHIND
THE ALGORITHM

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.

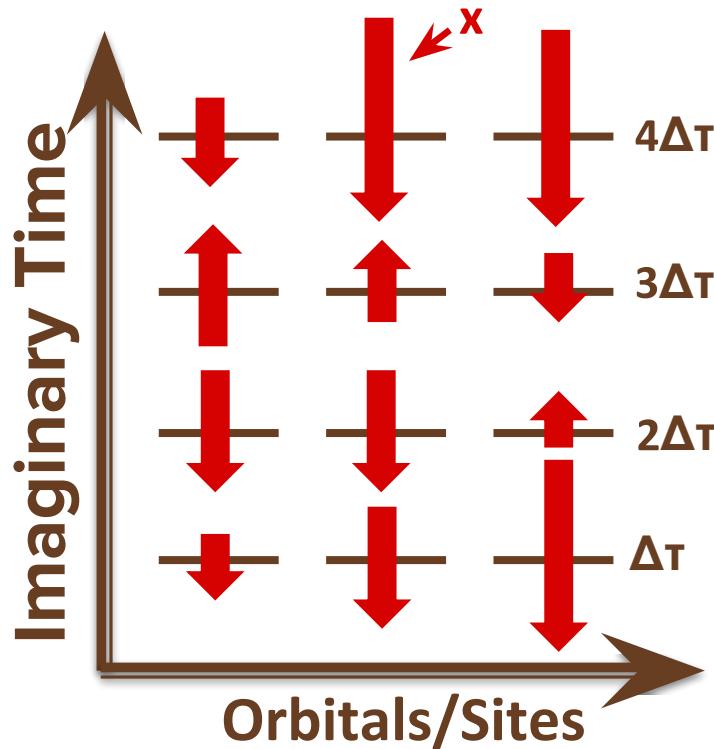


AUXILIARY FIELD QUANTUM MONTE CARLO

Ground State Projection:

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

Exact Ground
State Wave
Function



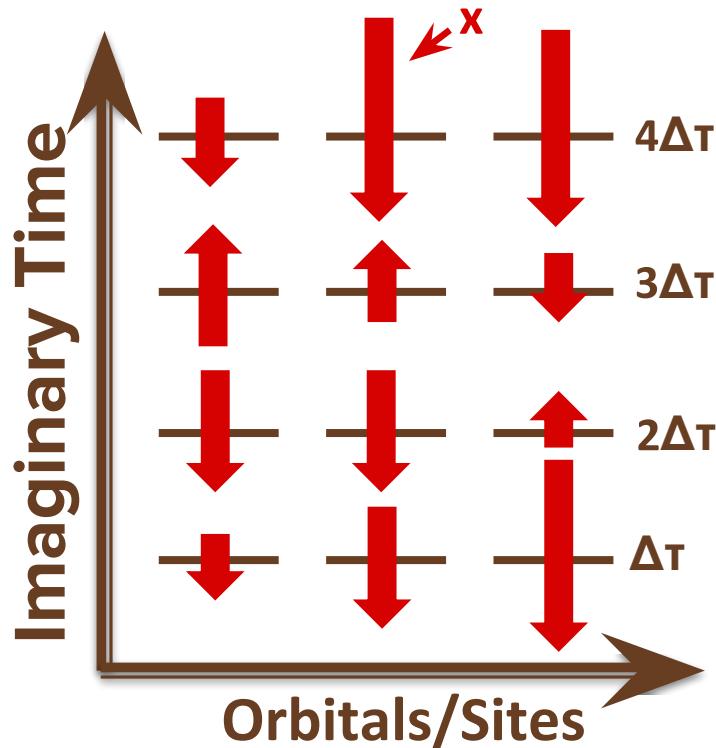
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Function

Trial Wave
Function
(HF, Non-Interacting,
DFT, CASSCF...)



AUXILIARY FIELD QUANTUM MONTE CARLO

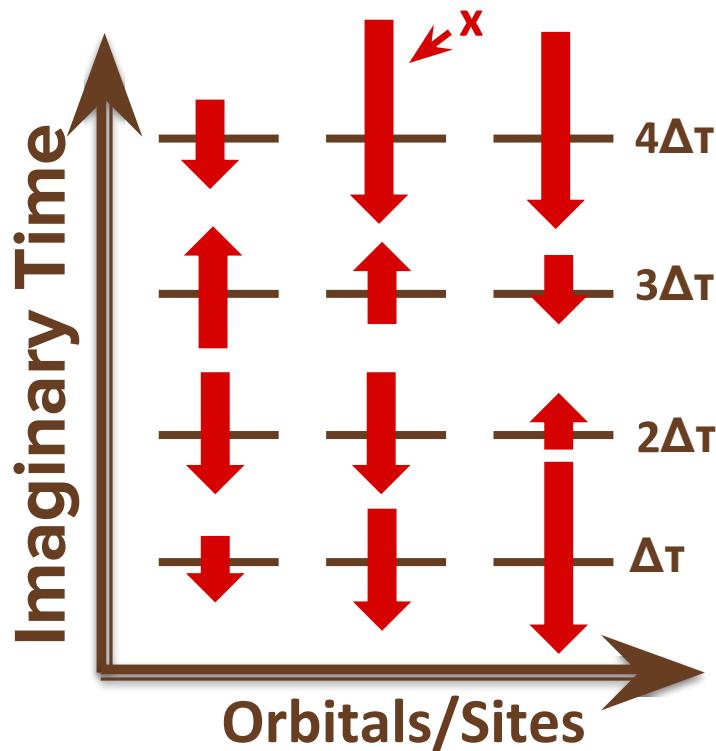
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Exact Ground
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Function

Projection
Operator

Trial Wave
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(HF, Non-Interacting,
DFT, CASSCF...)



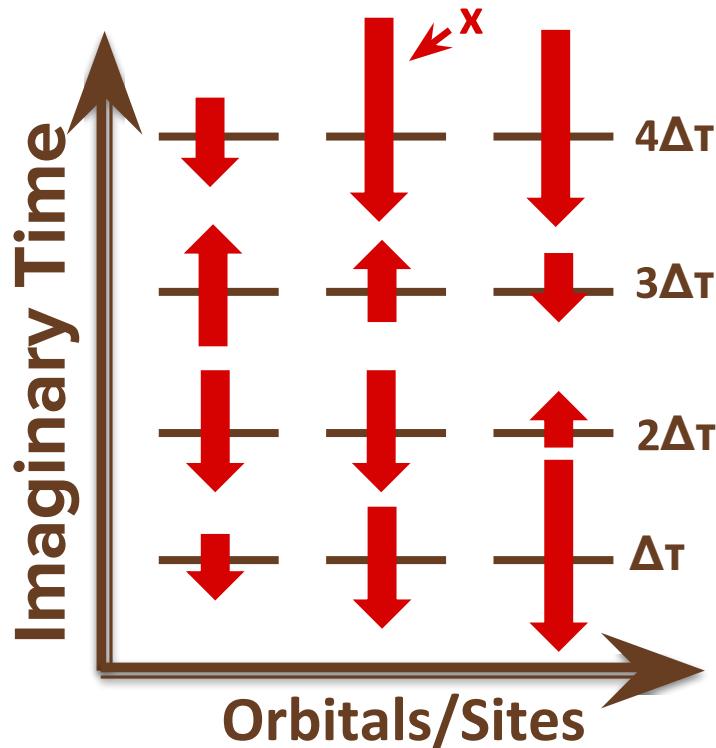
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But, This Is The Exponential of a
Two-Body Operator! (And, We Can't
Express This As a Matrix)



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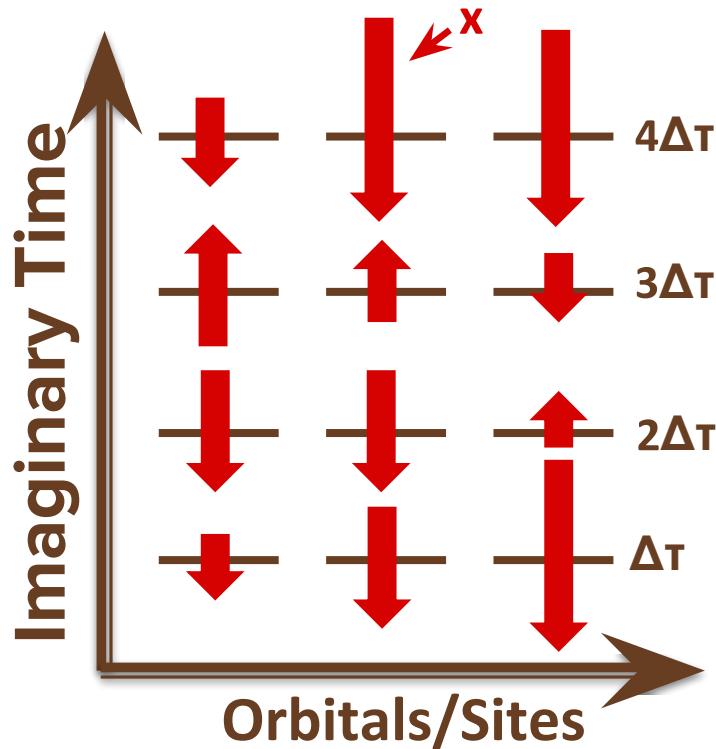
Projection
Operator

But, This Is The Exponential of a
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Express This As a Matrix)

$$|\Phi'\rangle = e^{\hat{A}} |\Phi\rangle$$

One-Body
Operator

Thouless's Theorem



AUXILIARY FIELD QUANTUM MONTE CARLO

Ground State Projection:

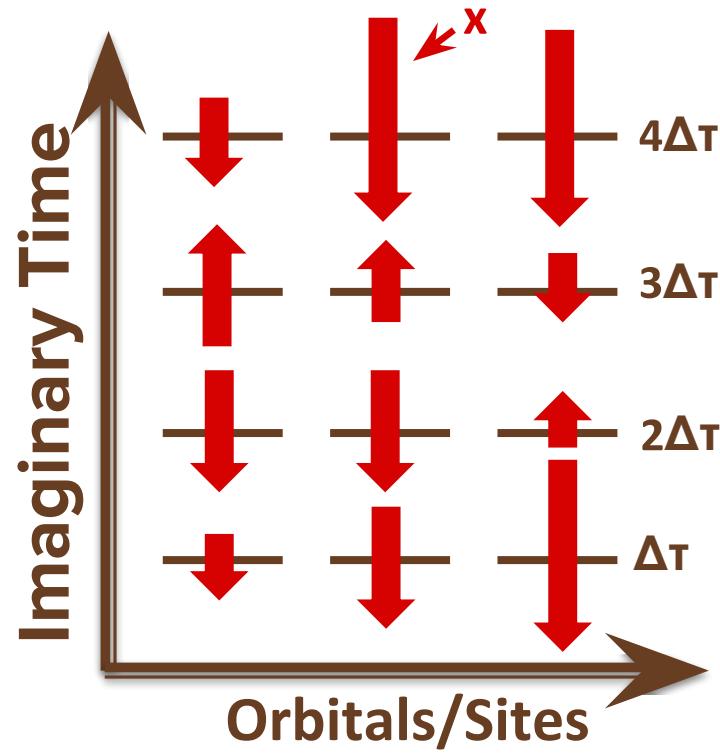
$$|\Psi_0\rangle = \lim_{n \rightarrow \infty} \left(e^{-\Delta\tau \hat{H}} \right)^n |\Psi_T\rangle$$

Suzuki-Trotter Factorization:

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

One-Body
Operators

Two-Body
Operators



AUXILIARY FIELD QUANTUM MONTE CARLO

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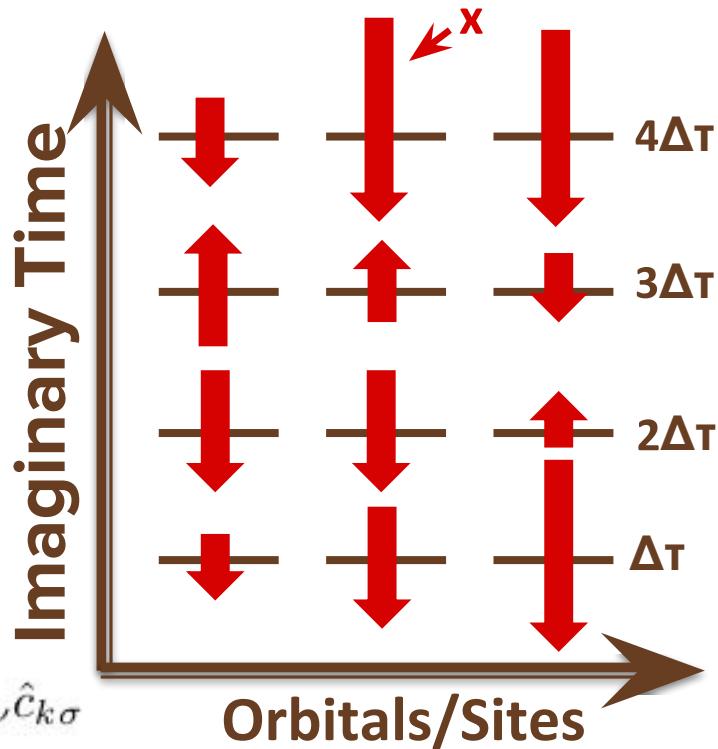
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Ab Initio Hamiltonian (Hard!):

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



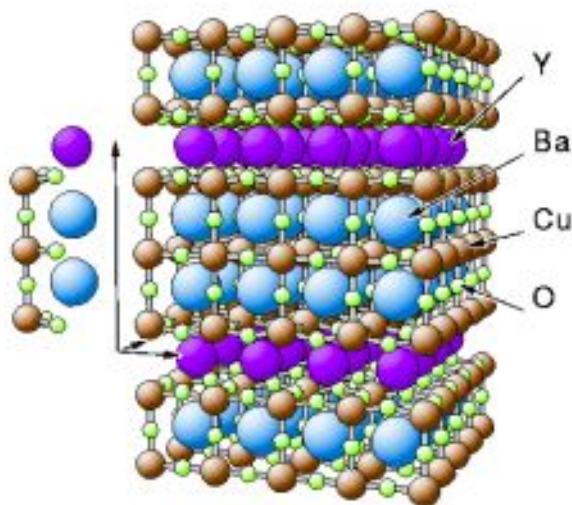
THE HUBBARD MODEL

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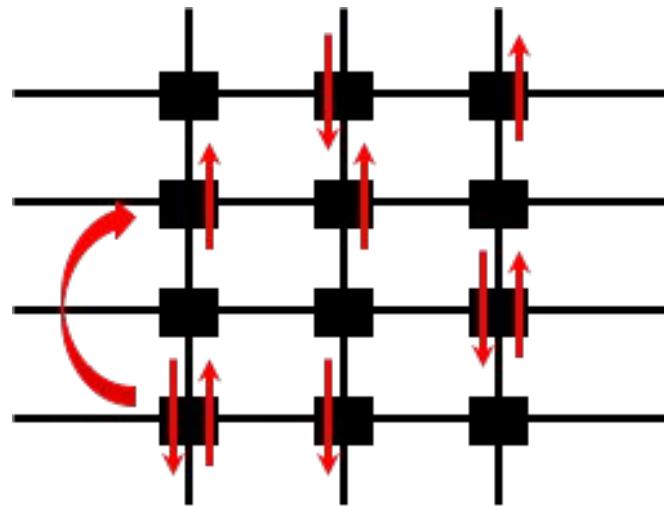
The Theorist's Lab Rat

Site Basis!

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



Map to
Single-Band
Model



YBaCuO (Superconductor)

2D Lattice Model

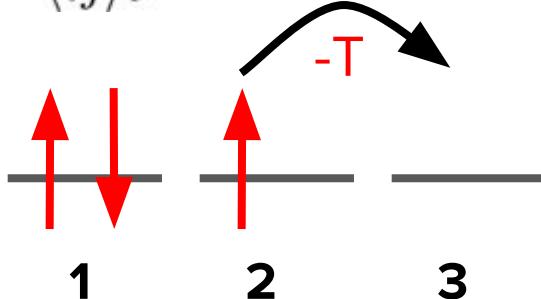
THE HUBBARD MODEL

The Theorist's Lab Rat

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Kinetic ("Hopping") Term

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



$$K_\uparrow = \begin{bmatrix} 1 & 2 & 3 \\ 1 & 0 & -T & -T \\ 2 & -T & 0 & -T \\ 3 & -T & -T & 0 \end{bmatrix}$$

With Periodic Boundary Conditions

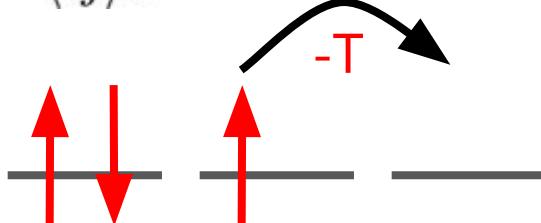
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The Theorist's Lab Rat

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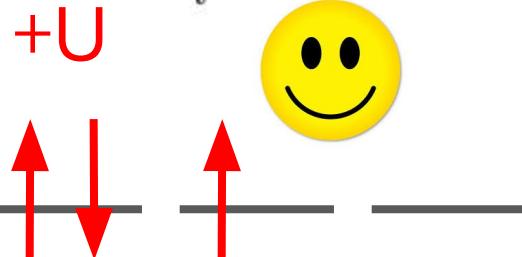
Kinetic ("Hopping") Term

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



Electron Repulsion Term

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



(BACK TO) THE MATH
BEHIND THE
ALGORITHM

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Ground State Projection:

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

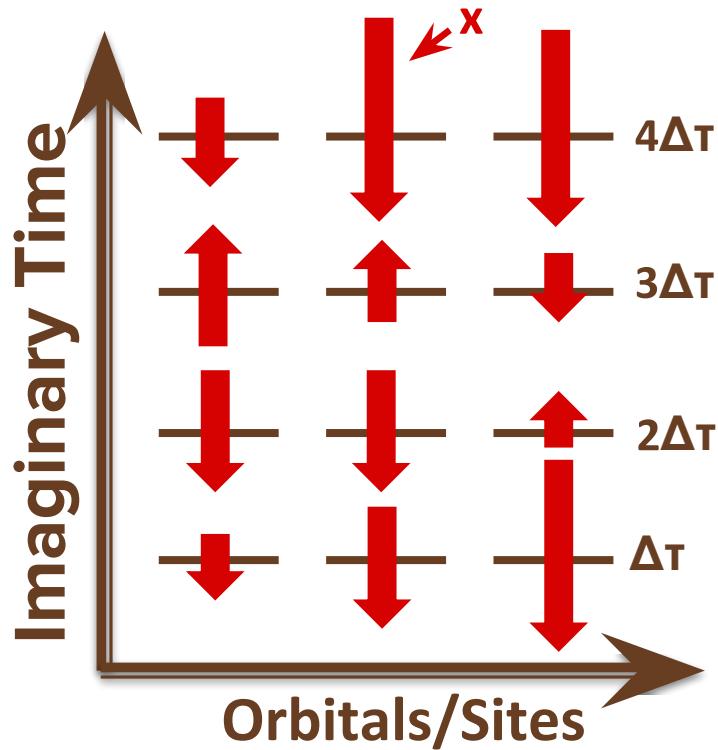
Suzuki-Trotter Factorization:

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

For Hubbard(!):

$$e^{-\Delta\tau \hat{K}} = e^{-\Delta\tau t \sum_{ij,\sigma} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma})}$$

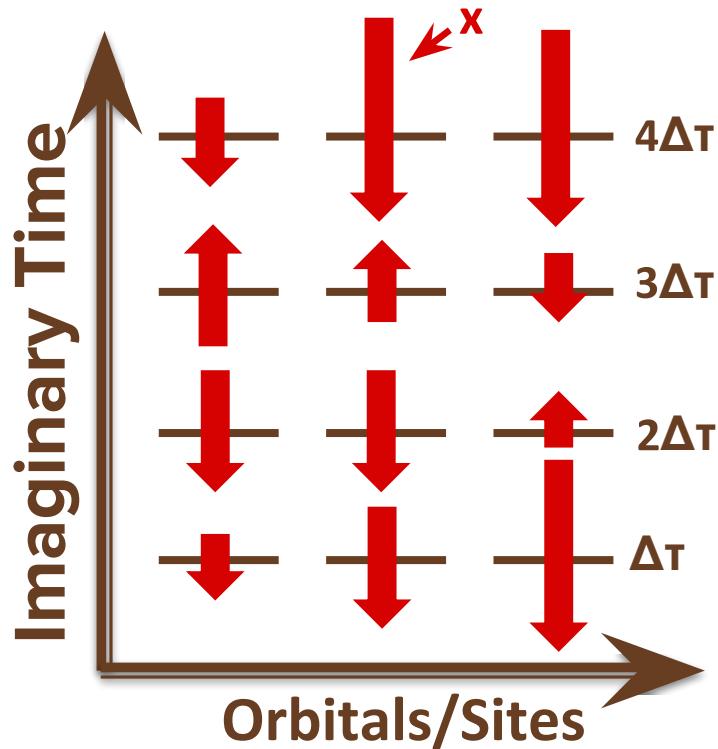
$$e^{-\Delta\tau \hat{V}} = e^{-\Delta\tau U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}$$



HUBBARD-STRATONOVICH TRANSFORM

Gaussian Integral:

$$1 = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-1/2(x \pm y)^2} dx.$$



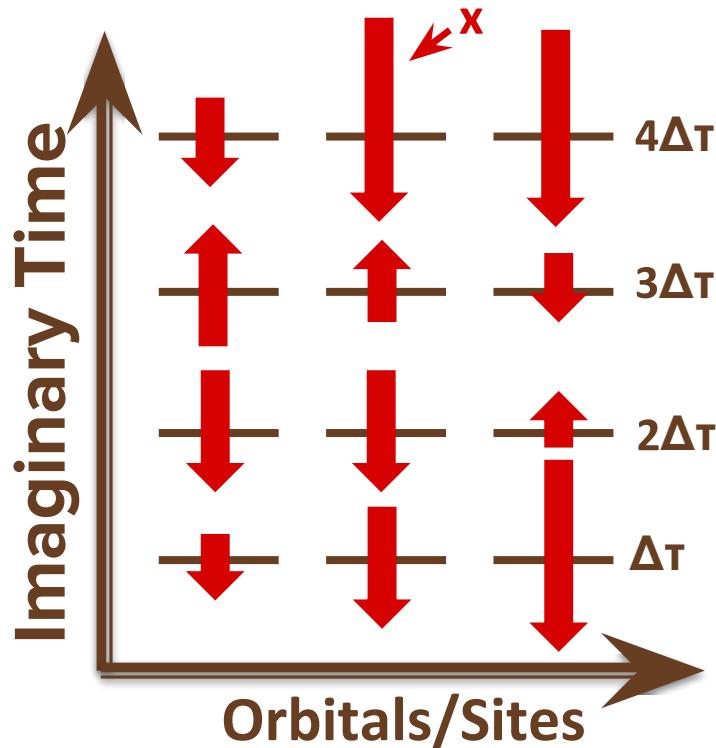
HUBBARD-STRATONOVICH TRANSFORM

Gaussian Integral:

$$1 = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-1/2(x \pm y)^2} dx.$$

Bring y-Exponential to Other Side:

$$e^{y^2/2} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-1/2(x^2 \pm 2xy)} dx.$$



HUBBARD-STRATONOVICH TRANSFORM

Gaussian Integral:

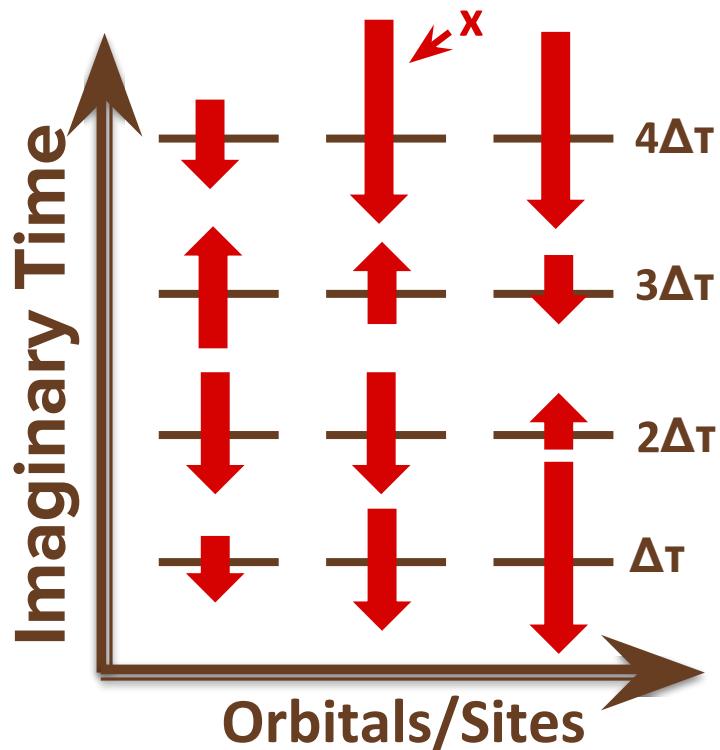
$$1 = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-1/2(x \pm y)^2} dx.$$

Bring y-Exponential to Other Side:

$$e^{y^2/2} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-1/2(x^2 \pm 2xy)} dx.$$

General Continuous Transform:

$$e^{-(\Delta\tau/2)\lambda\hat{v}^2} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{-x^2/2} e^{x\sqrt{-\Delta\tau\lambda}\hat{v}}$$



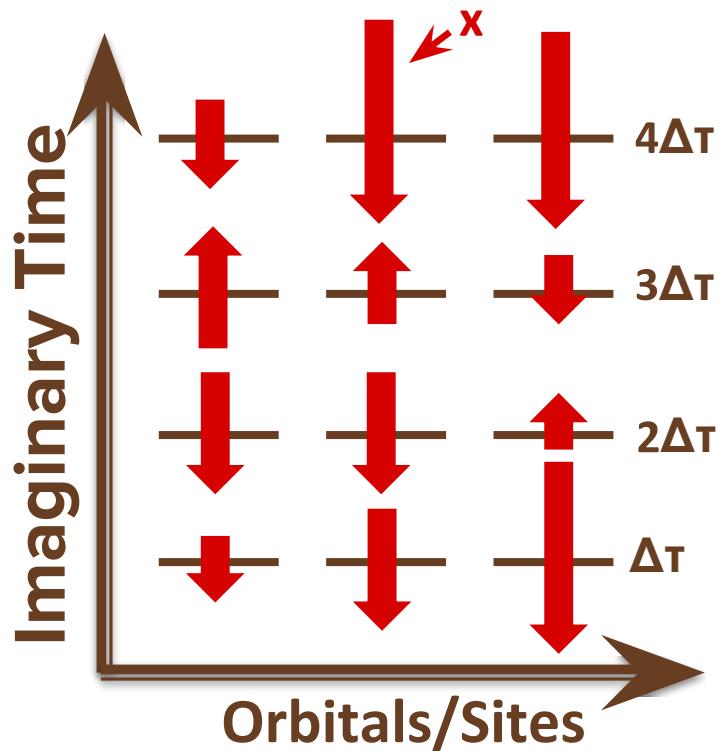
HUBBARD-STRATONOVICH TRANSFORM

General *Continuous* Transform:

$$e^{-(\Delta\tau/2)\lambda\hat{v}^2} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{-x^2/2} e^{x\sqrt{-\Delta\tau\lambda}\hat{v}}$$

Need to Rewrite As Square:

$$e^{-\Delta\tau\hat{V}} = e^{-\Delta\tau U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}$$



HUBBARD-STRATONOVICH TRANSFORM

General Continuous Transform:

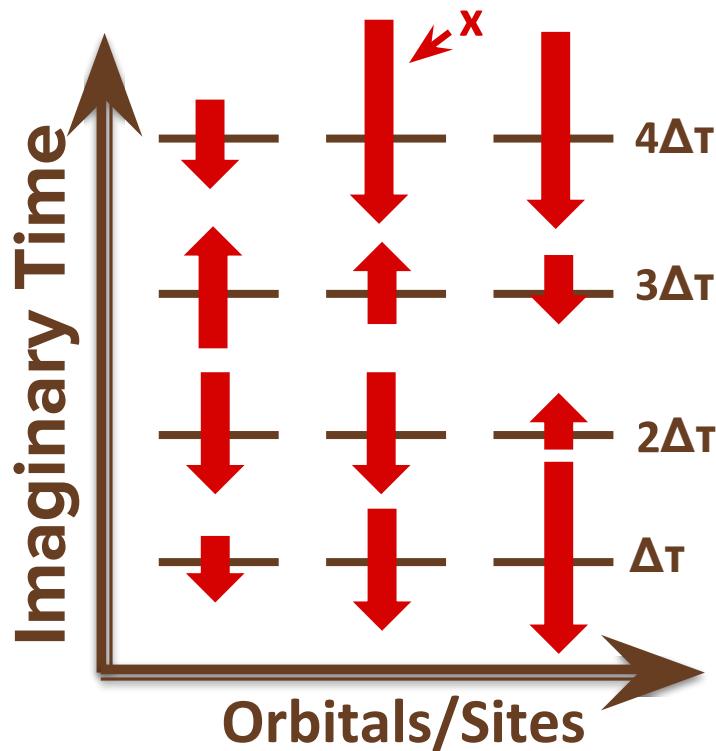
$$e^{-(\Delta\tau/2)\lambda\hat{v}^2} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{-x^2/2} e^{x\sqrt{-\Delta\tau\lambda}\hat{v}}$$

Need to Rewrite As Square:

$$e^{-\Delta\tau\hat{V}} = e^{-\Delta\tau U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}$$

$$\hat{n}_{\uparrow} \hat{n}_{\downarrow} = -\frac{(\hat{n}_{\uparrow} - \hat{n}_{\downarrow})^2}{2} + \frac{(\hat{n}_{\uparrow} + \hat{n}_{\downarrow})}{2}$$

$$e^{-\Delta\tau\hat{V}} = \prod_i e^{\Delta\tau U (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow})^2/2} e^{-\Delta\tau U (\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow})/2}$$



HUBBARD-STRATONOVICH TRANSFORM

Do HS Transform:

$$e^{-\Delta\tau \hat{V}} = \prod_i e^{\Delta\tau U(\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow})^2/2} e^{-\Delta\tau U(\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow})/2}$$

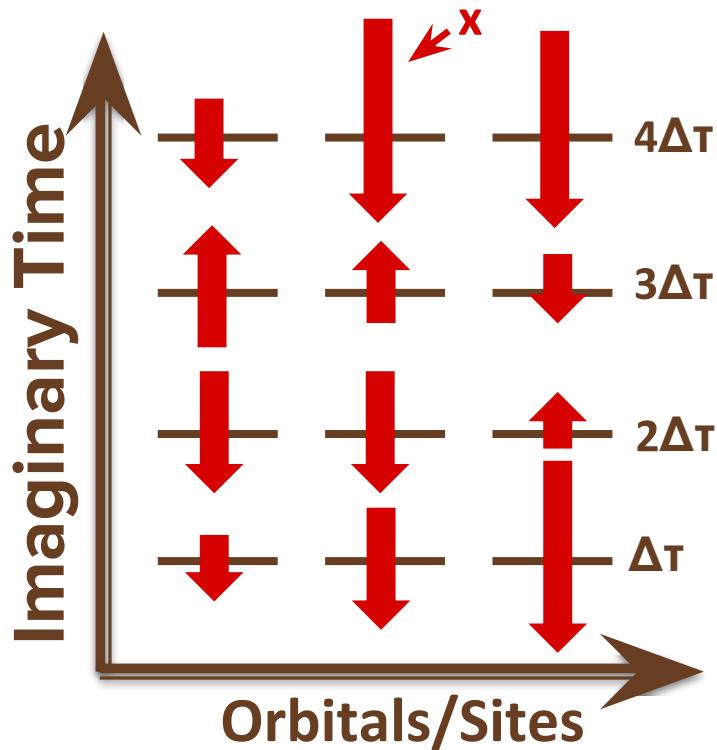
$$e^{-\Delta\tau \hat{V}} = \prod_i e^{-\Delta\tau U(\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow})/2}$$

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx_i e^{-x_i^2/2} e^{x_i \sqrt{\Delta\tau U} (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow})}$$

Just Becomes
a Matrix!

Merge:

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



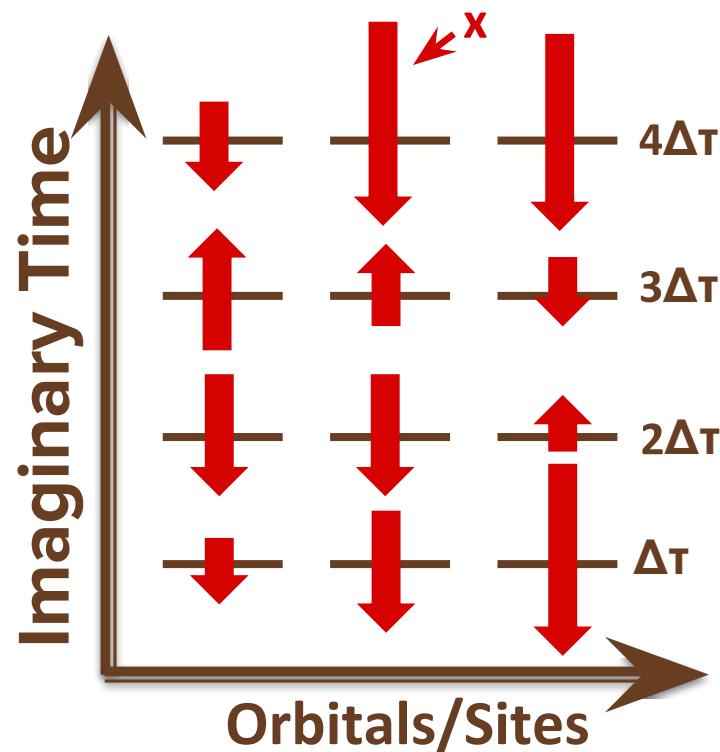
HUBBARD-STRATONOVICH TRANSFORM

What Does Transform Look Like?

$$e^{-\Delta\tau\hat{V}} = \prod_i e^{-\Delta\tau U(\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow})/2}$$
$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx_i e^{-x_i^2/2} e^{x_i \sqrt{\Delta\tau U} (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow})}$$

Up Potential Matrix

$$[e^{-\Delta\tau V}]_{\uparrow} = \begin{bmatrix} e^{-\Delta\tau U} e^{x_1 \sqrt{\Delta\tau U}} & 0 & 0 \\ 0 & e^{-\Delta\tau U} e^{x_2 \sqrt{\Delta\tau U}} & 0 \\ 0 & 0 & e^{-\Delta\tau U} e^{x_3 \sqrt{\Delta\tau U}} \end{bmatrix}$$



PART I

EXERCISES

PART I EXERCISES

- **GOAL: To Understand Propagation in the AFQMC Algorithm**

- Form the Kinetic Operator and Kinetic Propagator
- Iteratively Apply It To a Trial Wave Function
- Measure the Energy (Should Be The Same As ED)

We will take it in steps, since very different than the usual!

PART I EXERCISES

Calculating energies is more complicated than yesterday due to the non-orthogonal Slater determinants you obtain!

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

$$\begin{aligned}\langle E \rangle_{mixed} &= \frac{\langle \Psi_T | \hat{K} | \Psi \rangle}{\langle \Psi_T | \Psi \rangle} \\ &= -t \sum_{\langle ij \rangle \sigma} \frac{\langle \Psi_T | \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma} | \Psi \rangle}{\langle \Psi_T | \Psi \rangle} \\ &= -t \sum_{\langle ij \rangle \sigma} \left(\langle \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} \rangle + \langle \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma} \rangle \right)\end{aligned}$$

PART I EXERCISES

Calculating energies is more complicated than yesterday due to the non-orthogonal Slater determinants you obtain!

$$\begin{aligned}\langle \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} \rangle &= \frac{\langle \Psi_T | \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} | \Psi \rangle}{\langle \Psi_T | \Psi \rangle} \\ &= \left[\Psi^\sigma \left[(\Psi_T^\sigma)^\dagger \Psi^\sigma \right]^{-1} (\Psi_T)^\dagger \right]_{ij}\end{aligned}$$

One-Body Density Matrix

Plug This Back Into Previous Expression

PART II

EXERCISES

PART II EXERCISES

- **GOAL: To Sample the HS Transformation and Weight Results**
 - Sample the HS Transformation To Incorporate the Potential At Each Site
 - Incorporate Measuring the Potential in the Energy
 - Iterate the Full Propagator (Kinetic + Potential)
 - Incorporate Weighting (Population Control)

We will take it in steps, since very different than the usual!

PART II EXERCISES

Reminder: HS Transformation

$$e^{-\Delta\tau \hat{V}} = \prod_i e^{-\Delta\tau U(\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow})/2} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx_i e^{-x_i^2/2} e^{x_i \sqrt{\Delta\tau U} (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow})}$$

Sample x_i 's from Normal Distribution, Then Use To
Construct Potential Matrix

$$[e^{-\Delta\tau V}]_{\uparrow} = \begin{bmatrix} e^{-\Delta\tau U} e^{x_1 \sqrt{\Delta\tau U}} & 0 & 0 \\ 0 & e^{-\Delta\tau U} e^{x_2 \sqrt{\Delta\tau U}} & 0 \\ 0 & 0 & e^{-\Delta\tau U} e^{x_3 \sqrt{\Delta\tau U}} \end{bmatrix}$$

$$[e^{-\Delta\tau V}]_{\downarrow} = \begin{bmatrix} e^{-\Delta\tau U} e^{-x_1 \sqrt{\Delta\tau U}} & 0 & 0 \\ 0 & e^{-\Delta\tau U} e^{-x_2 \sqrt{\Delta\tau U}} & 0 \\ 0 & 0 & e^{-\Delta\tau U} e^{-x_3 \sqrt{\Delta\tau U}} \end{bmatrix}$$

PART II EXERCISES

One needs to use Wick's Theorem to Evaluate the Potential Portion in Terms of Density Matrices

Expectation Value of Two-Body Term

$$U\langle \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\uparrow} \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\downarrow} \rangle = U\langle \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\uparrow} \rangle \langle \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\downarrow} \rangle$$

Density Matrices

$$\begin{aligned}\langle \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} \rangle &= \frac{\langle \Psi_T | \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} | \Psi \rangle}{\langle \Psi_T | \Psi \rangle} \\ &= \left[\Psi^\sigma \left[(\Psi_T^\sigma)^\dagger \Psi^\sigma \right]^{-1} (\Psi_T)^\dagger \right]_{ii}\end{aligned}$$

PART II EXERCISES

Weighting

Propagation

$$|\Psi_k^{n+1}\rangle = \hat{B}(\vec{x}_k^{n+1})|\Psi_k^n\rangle \quad w_k^{n+1} e^{i\theta_k^{n+1}} = \frac{\langle \Psi_T | \Psi_k^{n+1} \rangle}{\langle \Psi_T | \Psi_k^n \rangle} w_k^n e^{i\theta_k^n}$$

Overlaps

$$\langle \Psi_T | \Psi_k^{n+1} \rangle = \prod_{\sigma} \det(\Psi_T^\dagger \Psi_{k,\sigma}^{n+1})$$

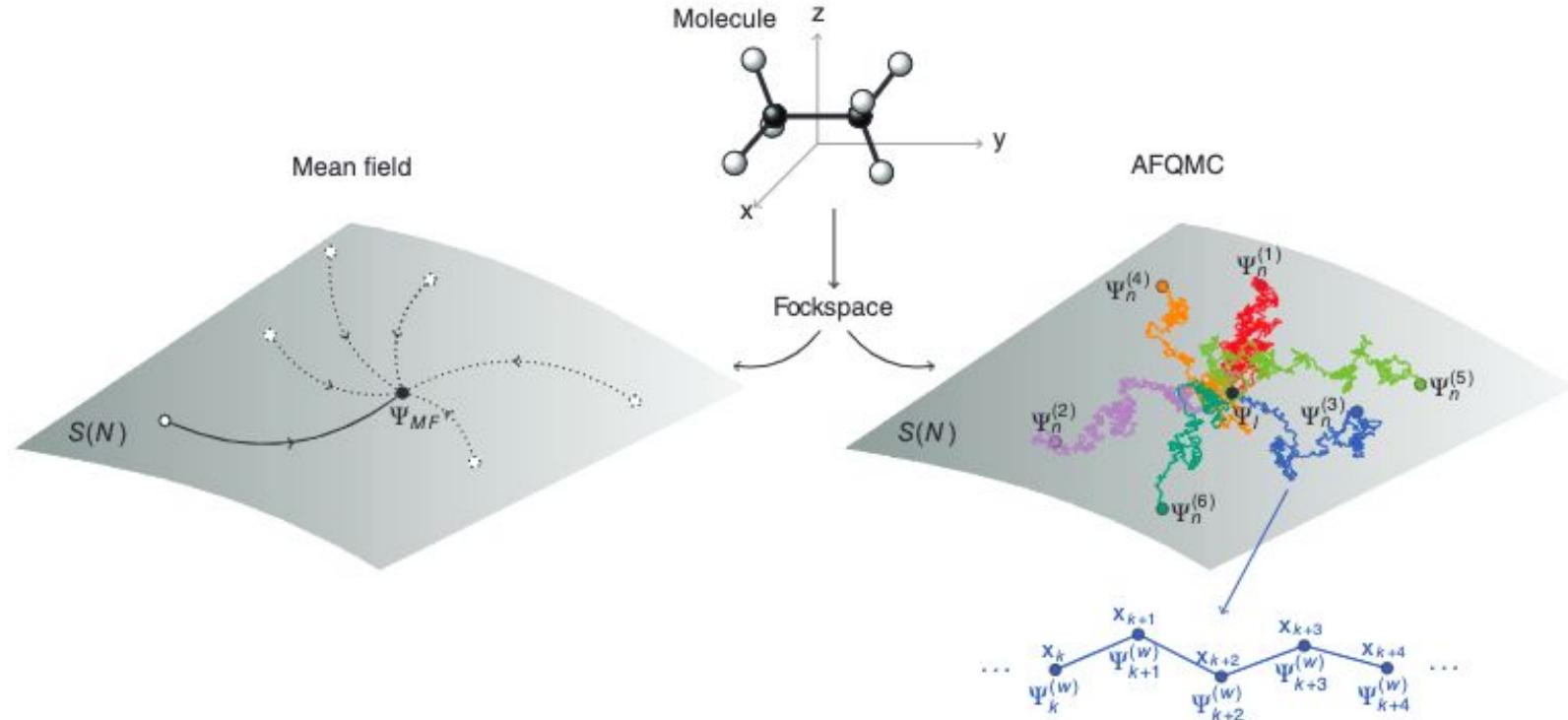
Full Mixed Estimator of the Energy

$$\langle E_{mixed} \rangle \approx \frac{\sum_k w_k e^{i\theta_k} E_{loc}(\Psi_k)}{\sum_k w_k e^{i\theta_k}}$$

For Each
Determinant

PART II EXERCISES

Walk Through Slater Determinant Space



THE SIGN AND PHASE PROBLEMS

THE PHASE PROBLEM

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

THE PHASE PROBLEM

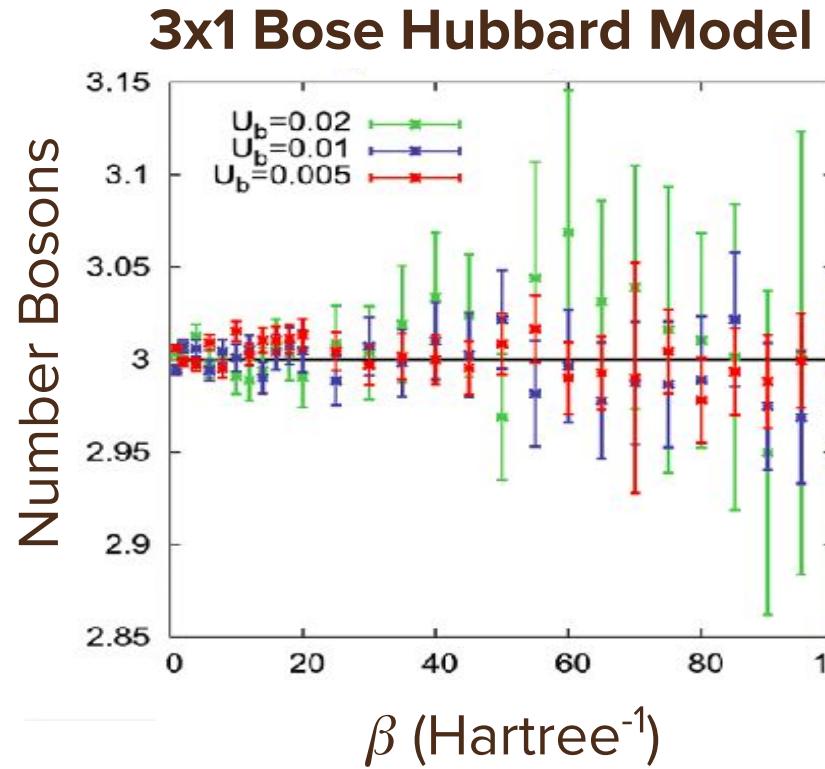
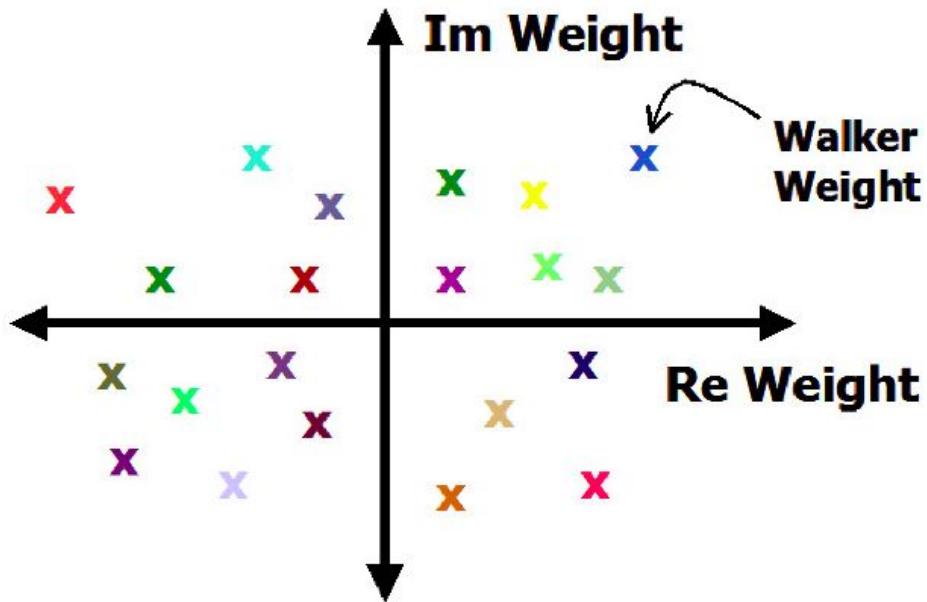
$\lambda > 0$
Fine!

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

THE PHASE PROBLEM

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

$\lambda > 0$
Fine...



B. Rubenstein, PRB (2012).

THE PHASELESS APPROXIMATION

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

$\lambda > 0$
Fine...

Propagation

$$|\Psi_k^{n+1}\rangle = \hat{B}(\vec{x}_k^{n+1})|\Psi_k^n\rangle \quad w_k^{n+1} e^{i\theta_k^{n+1}} = \frac{\langle\Psi_T|\Psi_k^{n+1}\rangle}{\langle\Psi_T|\Psi_k^n\rangle} w_k^n e^{i\theta_k^n}$$

Phaseless Approximation

$$\Delta\theta \equiv \operatorname{Im} \ln \left(\frac{\langle\Psi_T|\Psi_k^{n+1}\rangle}{\langle\Psi_T|\Psi_k^n\rangle} \right) \quad w_k^{n+1} \leftarrow \begin{cases} \cos(\Delta\theta) \left| \frac{\langle\Psi_T|\Psi_k^{n+1}\rangle}{\langle\Psi_T|\Psi_k^n\rangle} \right| w_k^n, & |\Delta\theta| < \pi/2 \\ 0, & \text{otherwise} \end{cases}$$

THE PHASELESS APPROXIMATION

Phaseless Approximation

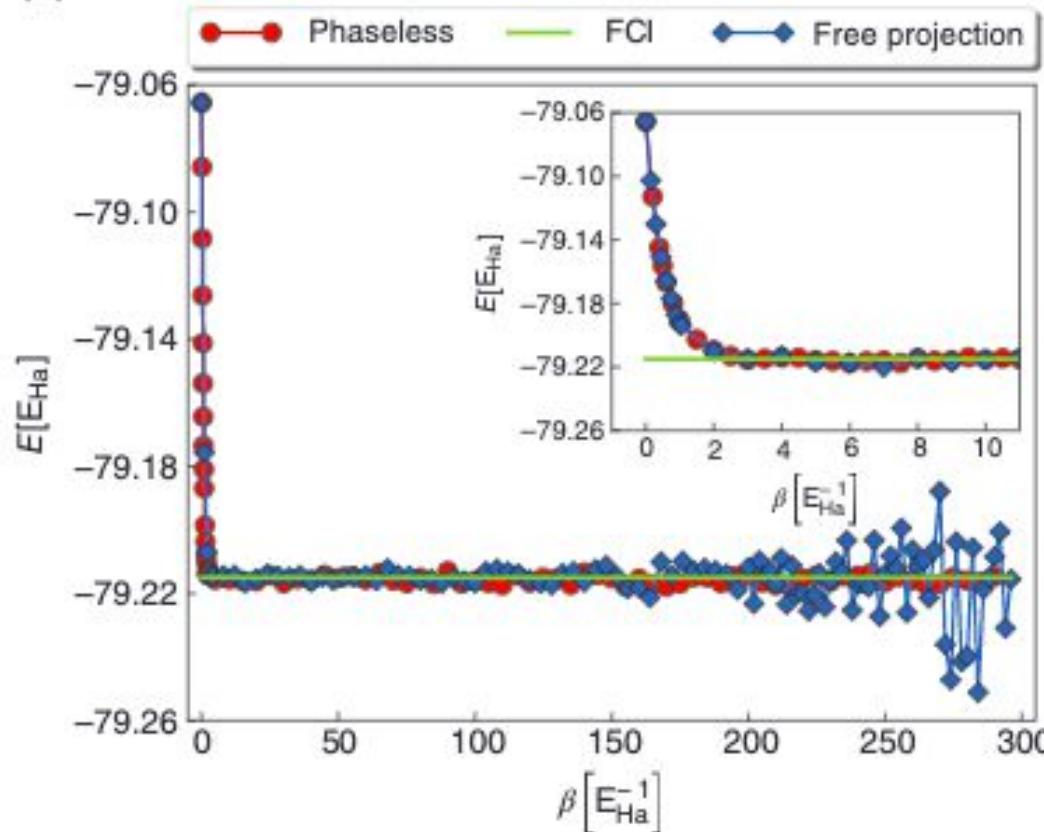
$$\Delta\theta \equiv \text{Im} \ln \left(\frac{\langle \Psi_T | \Psi_k^{n+1} \rangle}{\langle \Psi_T | \Psi_k^n \rangle} \right) w_k^{n+1} \leftarrow \begin{cases} \cos(\Delta\theta) \left| \frac{\langle \Psi_T | \Psi_k^{n+1} \rangle}{\langle \Psi_T | \Psi_k^n \rangle} \right| w_k^n, & |\Delta\theta| < \pi/2 \\ 0, & \text{otherwise} \end{cases}$$

BUT, This Would Normally Be a **HUGE** Approximation!

So, We Decrease The Magnitude of the Exponent By:

- Doing a Mean Field Background Subtraction
 - Sample Fluctuations Beyond Mean Field Theory
- Importance Sampling Based Upon Trial Wave Function

THE PHASELESS APPROXIMATION



H2O (cc-pvdz)

Typically, Phaseless
Error Is On The Scale
of MilliHartrees

(Which Is Kind of
Amazing!)

BUT, WHAT ABOUT
CHEMISTRY?

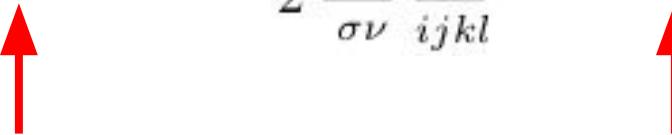
AUXILIARY FIELD QUANTUM MONTE CARLO

Ab Initio Hamiltonian (Hard!):

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

AUXILIARY FIELD QUANTUM MONTE CARLO

Ab Initio Hamiltonian (Hard!):

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


Kinetic Piece May Be
Written Similarly
(Just a Matrix, But
Off-Diagonal)

But, This Piece Must Be
Broken Up Into
Squares...Harder Than
Before!

AUXILIARY FIELD QUANTUM MONTE CARLO

Ab Initio Hamiltonian (Hard!):

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

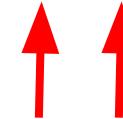
Diagonalization:

$$\mathbf{V}_{\alpha\beta} = \mathbf{V}_{(i,l),(k,j)} = V_{ijkl}$$



Supermatrix

$$\mathbf{V}_{\alpha\beta} = \sum_{\gamma} R_{\alpha,\gamma} \lambda_{\gamma} R_{\beta\gamma}^*$$



Eigenvectors Eigenvalues

AUXILIARY FIELD QUANTUM MONTE CARLO

Ab Initio Hamiltonian (Hard!):

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

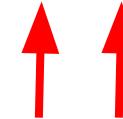
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Eigenvectors Eigenvalues

AUXILIARY FIELD QUANTUM MONTE CARLO

Ab Initio Hamiltonian (Hard!):

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

Writing Potential as a Square:

$$\begin{aligned}\hat{V} &= \sum_{ijkl} V_{ijkl} \hat{c}_i^\dagger \hat{c}_l \hat{c}_j^\dagger \hat{c}_k - \sum_{ijkl} V_{ijkl} \hat{c}_i^\dagger \hat{c}_k \delta_{jl} \\ &= \sum_{\gamma} \lambda_{\gamma} \left(\sum_{il} R_{(i,l)\gamma} \hat{c}_i^\dagger \hat{c}_l \right) \left(\sum_{jk} R_{(k,j)\gamma}^* \hat{c}_j^\dagger \hat{c}_k \right) - \sum_{ik} \left(\sum_j V_{ijkj} \right)\end{aligned}$$

AUXILIARY FIELD QUANTUM MONTE CARLO

Writing Potential as a Square:

$$\begin{aligned}\hat{V} &= \sum_{ijkl} V_{ijkl} \hat{c}_i^\dagger \hat{c}_l \hat{c}_j^\dagger \hat{c}_k - \sum_{ijkl} V_{ijkl} \hat{c}_i^\dagger \hat{c}_k \delta_{jl} \\ &= \sum_{\gamma} \lambda_{\gamma} \left(\sum_{il} R_{(i,l)\gamma} \hat{c}_i^\dagger \hat{c}_l \right) \left(\sum_{jk} R_{(k,j)\gamma}^* \hat{c}_j^\dagger \hat{c}_k \right) - \sum_{ik} \left(\sum_j V_{ijkj} \right)\end{aligned}$$

Rename Operators:

$$\begin{aligned}\hat{V} &= \frac{1}{8} \sum_{\gamma}^{(2N)^2} \lambda_{\gamma} [(\hat{\rho}_{\gamma} + \hat{\rho}_{\gamma}^\dagger)^2 - (\hat{\rho}_{\gamma} - \hat{\rho}_{\gamma}^\dagger)^2] - \sum_{\alpha} \hat{\rho}_0^{\alpha} \\ \hat{\rho}_{\gamma} &\equiv \sum_{il} R_{(i,l)\gamma} \hat{c}_i^\dagger \hat{c}_l \\ \hat{\rho}_0 &\equiv - \sum_{ik} \left[\sum_j (V_{ijkj} + V_{jijk})/2 \right] \hat{c}_i^\dagger \hat{c}_k\end{aligned}$$

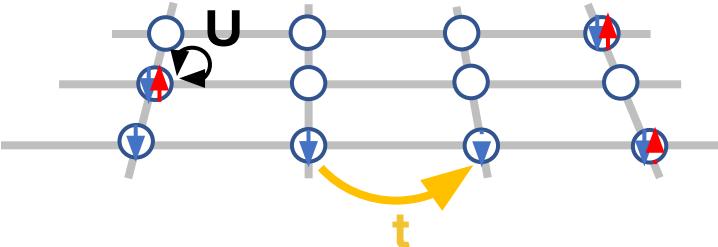
RECENT APPLICATIONS

SINGLE-BAND VS. MULTI-BAND MODELS

Single-Band Models and Materials

Hubbard Model

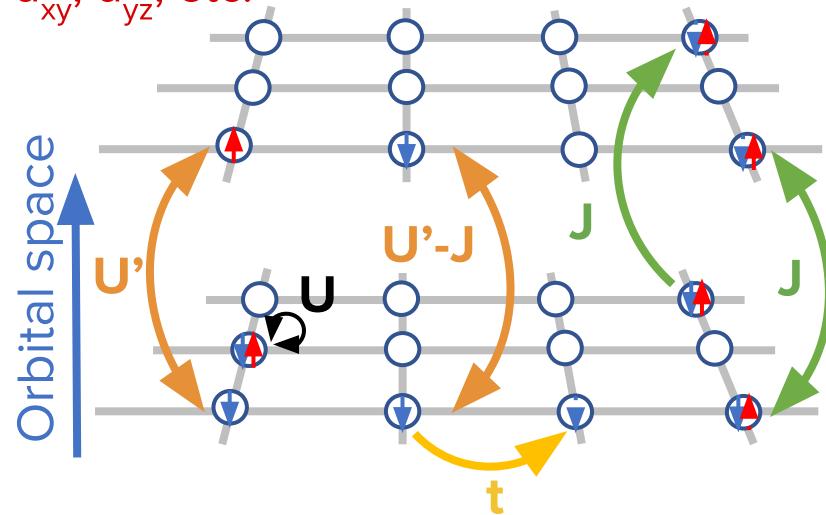
$$\hat{H}_{Single} = -t \sum_{\langle i,j \rangle \sigma} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma}) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$



Example Materials: The Cuprates, Organic Superconductors

Multi-Band Models and Materials

E.g., d_{xy} , d_{yz} , etc.



Example Materials: The Iron Pnictides and Chalcogenides, Ruthenates

THE HUBBARD-KANAMORI MODEL

One-Body Operators:

$$\hat{H} = \sum_{i \neq j, \sigma, mm'} t_{ij}^{mm'} \hat{c}_{im\sigma}^\dagger \hat{c}_{jm'\sigma} - \mu \sum_{im\sigma} \hat{n}_{im\sigma}$$

Intraorbital Repulsion:

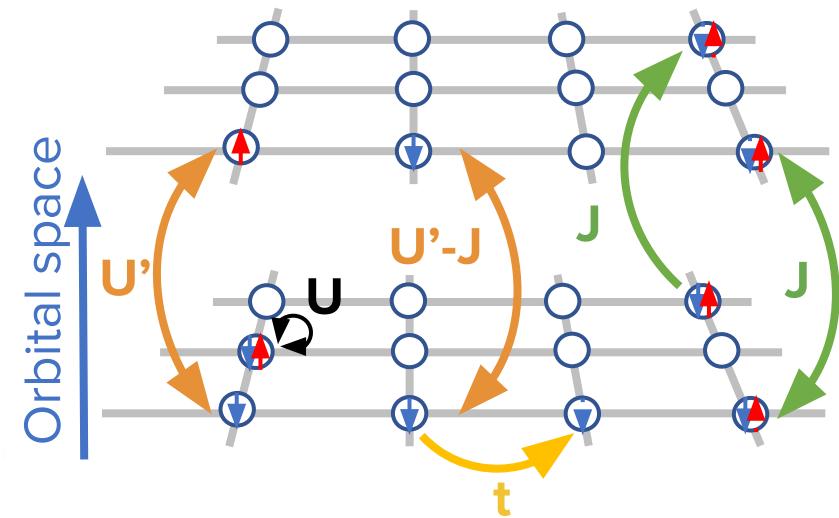
$$+ U \sum_m \hat{n}_{m\uparrow} \hat{n}_{m\downarrow}$$

Interorbital Repulsion:

$$+ U' \sum_{m \neq m'} \hat{n}_{m\uparrow} \hat{n}_{m'\downarrow} + (U' - J) \sum_{m > m', \sigma} \hat{n}_{m\sigma} \hat{n}_{m'\sigma}$$

Pair-Hopping and Exchange
Operators:

$$+ J \sum_{m \neq m'} \left(\hat{c}_{m\uparrow}^\dagger \hat{c}_{m'\uparrow}^\dagger \hat{c}_{m'\downarrow} \hat{c}_{m\downarrow} + \hat{c}_{m\uparrow}^\dagger \hat{c}_{m'\uparrow}^\dagger \hat{c}_{m\downarrow}^\dagger \hat{c}_{m'\downarrow} \right)$$



2-Band Case Depicted, But Many Bands Possible

AFQMC FOR THE HK MODEL

$$\hat{H}_J = \sum_{i < j} J^{ij} (\hat{c}_{i\uparrow}^\dagger \hat{c}_{j\downarrow}^\dagger \hat{c}_{i\downarrow} \hat{c}_{j\uparrow} + \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\downarrow}^\dagger \hat{c}_{j\downarrow} \hat{c}_{j\uparrow} + H.c.)$$

$$\hat{\rho}_{ij} \equiv \sum_{\sigma} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma})$$

$$\hat{\rho}_{ij}^2 = \sum_{\sigma\sigma'} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma})(\hat{c}_{i\sigma'}^\dagger \hat{c}_{j\sigma'} + \hat{c}_{j\sigma'}^\dagger \hat{c}_{i\sigma'})$$

Discrete Transform

$$\hat{H}_J = \sum_{i < j} \frac{J^{ij}}{2} \hat{\rho}_{ij}^2 - \sum_{i < j, \sigma} \frac{J^{ij}}{2} (\hat{n}_{i\sigma} + \hat{n}_{j\sigma}) + \sum_{i < j, \sigma} J^{ij} \hat{n}_{i\sigma} \hat{n}_{j\sigma}$$

Continuous Transform

THE HUBBARD-KANAMORI MODEL

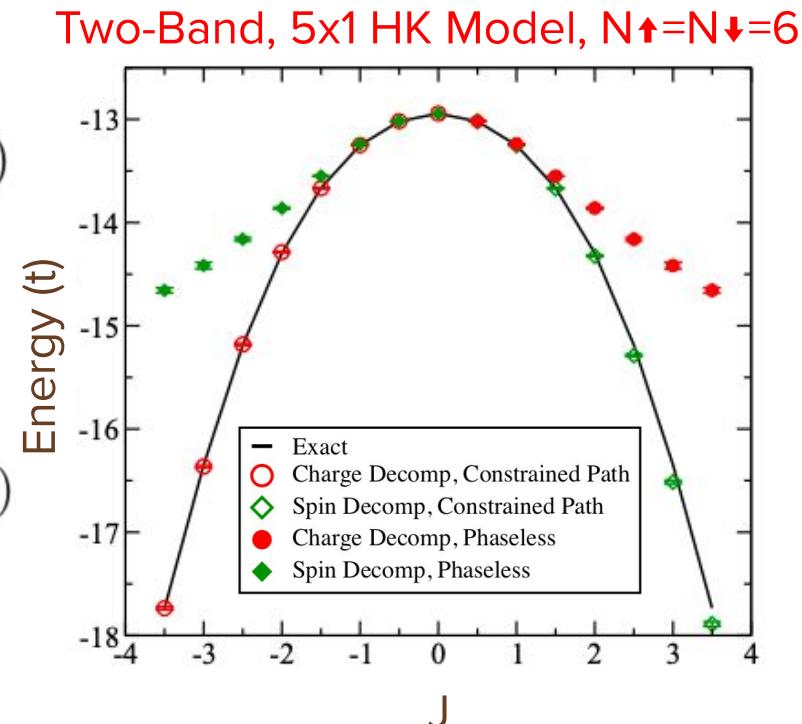
We have developed a novel ground state framework for treating the HK model that we are extending to finite temperature.

Phase-Free Transforms

$$\hat{H}_J = \sum_{i < j} J^{ij} (\hat{c}_{i\uparrow}^\dagger \hat{c}_{j\downarrow}^\dagger \hat{c}_{i\downarrow} \hat{c}_{j\uparrow} + \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\downarrow}^\dagger \hat{c}_{j\downarrow} \hat{c}_{j\uparrow} + H.c.)$$

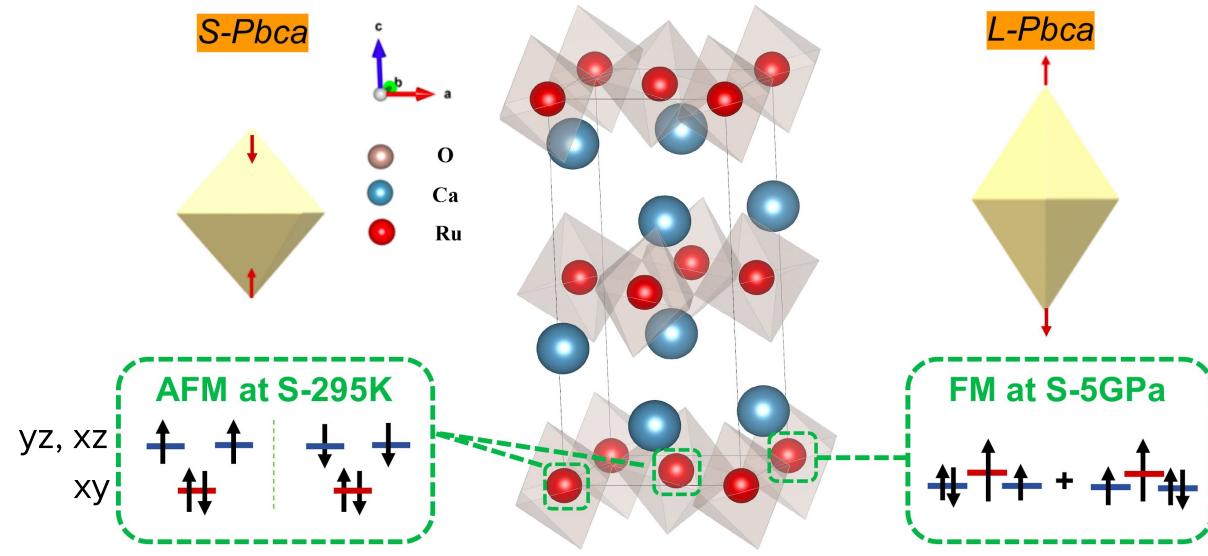
$$\hat{\rho}_{ij} = \sum_{\sigma} \delta_{\sigma} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma})$$

$$\hat{\rho}_{ij}^2 = \sum_{\sigma\sigma'} \delta_{\sigma}\delta_{\sigma'} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma})(\hat{c}_{i\sigma'}^\dagger \hat{c}_{j\sigma'} + \hat{c}_{j\sigma'}^\dagger \hat{c}_{i\sigma'})$$



GOING BEYOND BENCHMARKS: Ca_2RuO_4

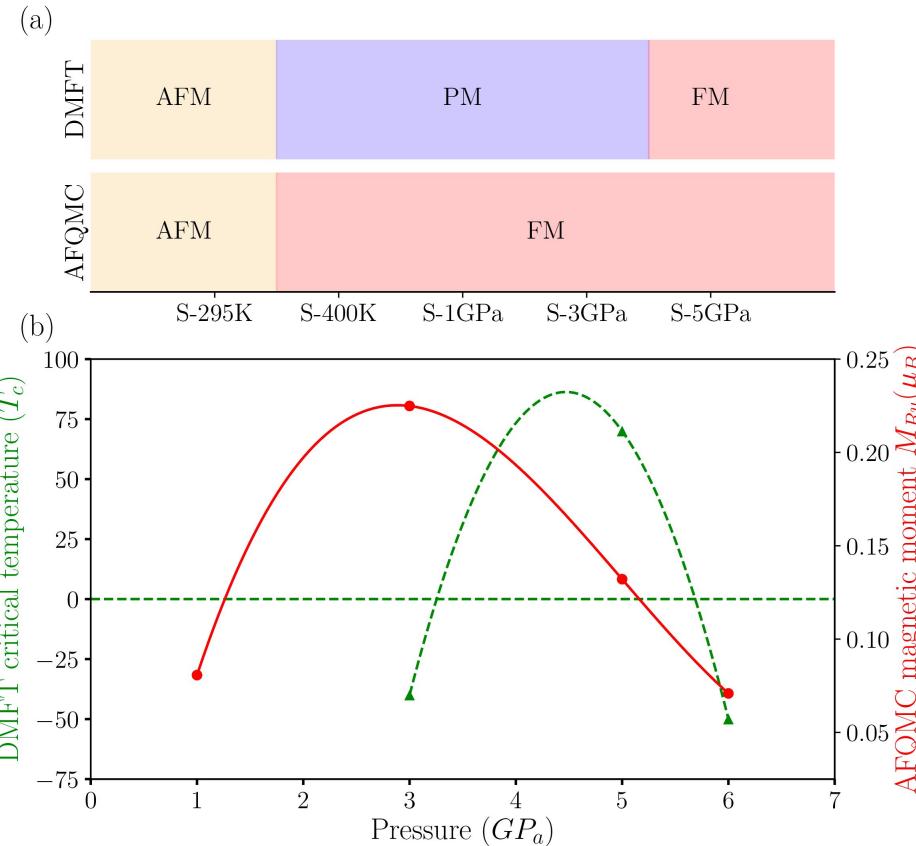
- Ca_2RuO_4 is a layered perovskite isostructural with the cuprates
- Possesses a number of interesting metal/insulator, magnetic, and superconducting phase transitions
- Low Temperature (<300 K), Low Pressure (< 0.5 GPa): Antiferromagnetic Insulator with S-Pbca structure
- High Temperature, High Pressure: Ferromagnetic Metal with L-Pbca structure



Low T, Low P —————→ High T, High P
Can AFQMC (and DMFT) predict these transitions?

FULL Ca_2RuO_4 PHASE DIAGRAM

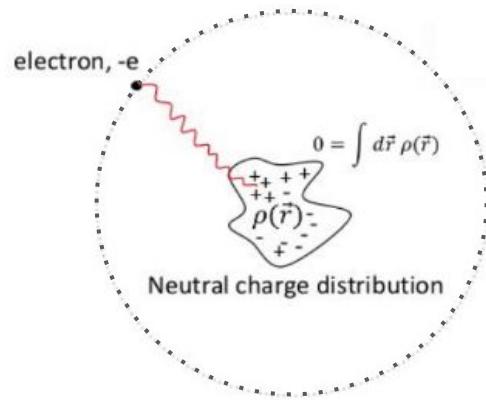
- AFQMC and DMFT agree for S-295K and S-5GPA, but disagree at other pressures/temperatures
- Disagreement may stem from the presence of a mixed state at intermediate pressures observed experimentally
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DIPOLE-BOUNDED ANIONS

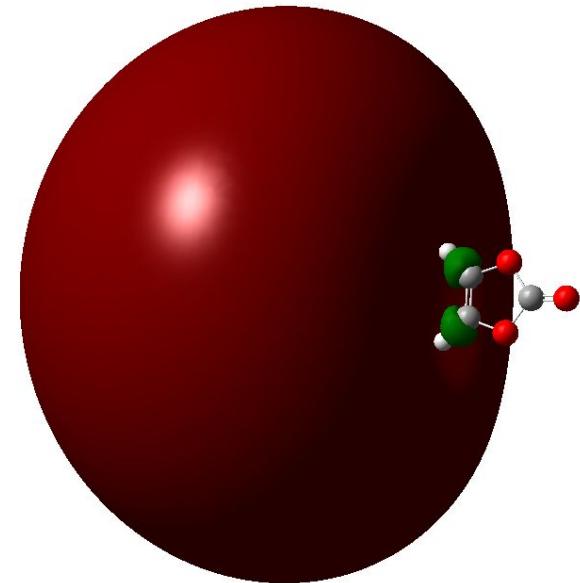
Dipole-Bound anions bind an excess electron far from their nuclei via their dipole moments.

Multipole-Bound Anions



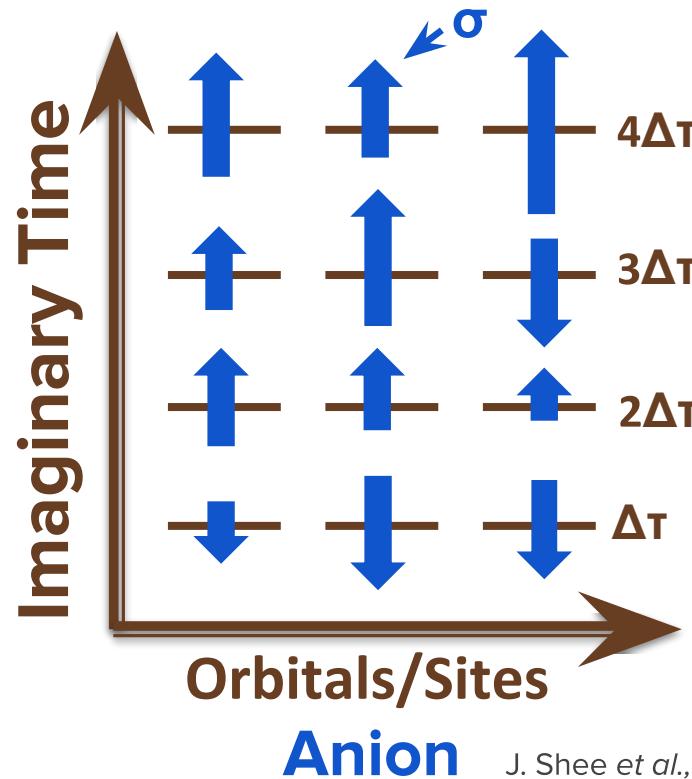
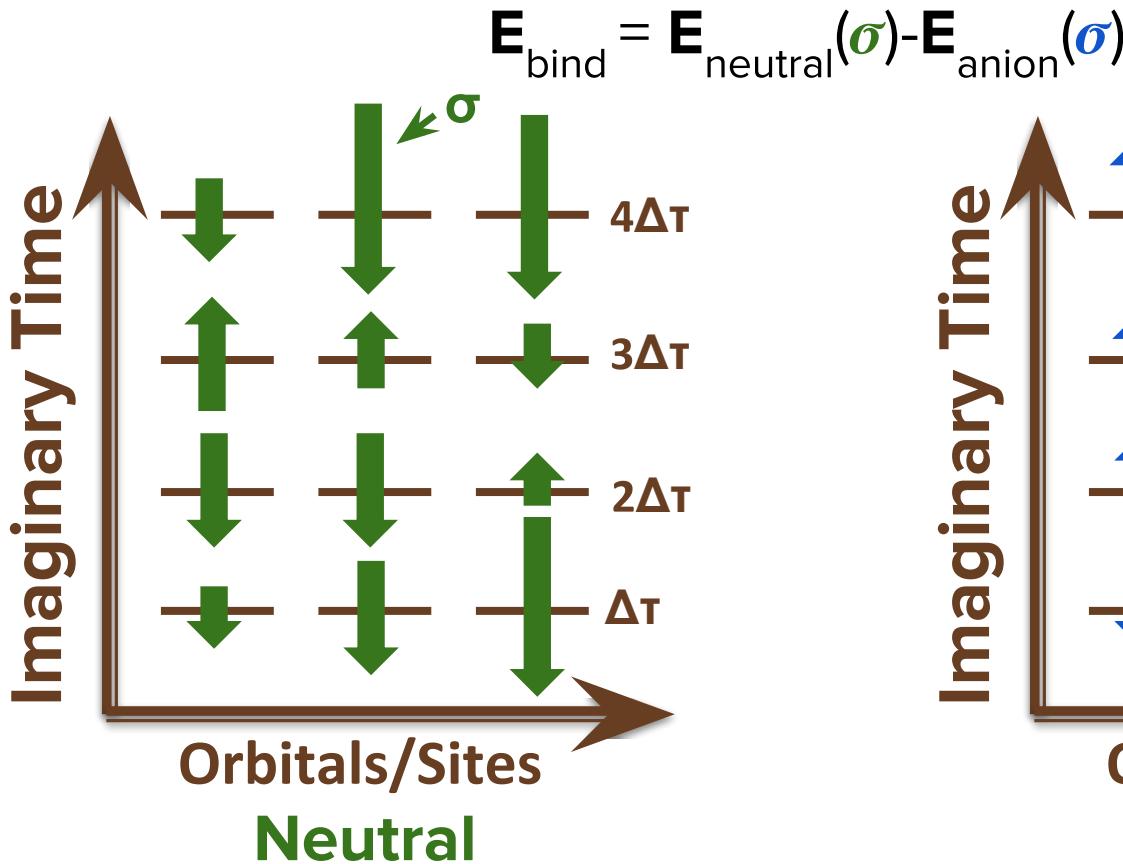
$$V(\vec{r}) \sim \sum_{n=0}^{\infty} \frac{M_n(\theta, \varphi)}{r^{n+1}}$$
$$= \frac{M_0}{r^1} + \boxed{\frac{M_1(\theta)}{r^2}} + \frac{M_2(\theta, \varphi)}{r^3} + \frac{M_3(\theta, \varphi)}{r^4} + \dots$$

- **Critical Dipole Moment:** >1.625 D
- **Average Distance Between Electron and Neutral Core:** 10-100s Å
- **Molecular Electron Binding Energies:** >10s cm⁻¹



UN-CORRELATED AFQMC

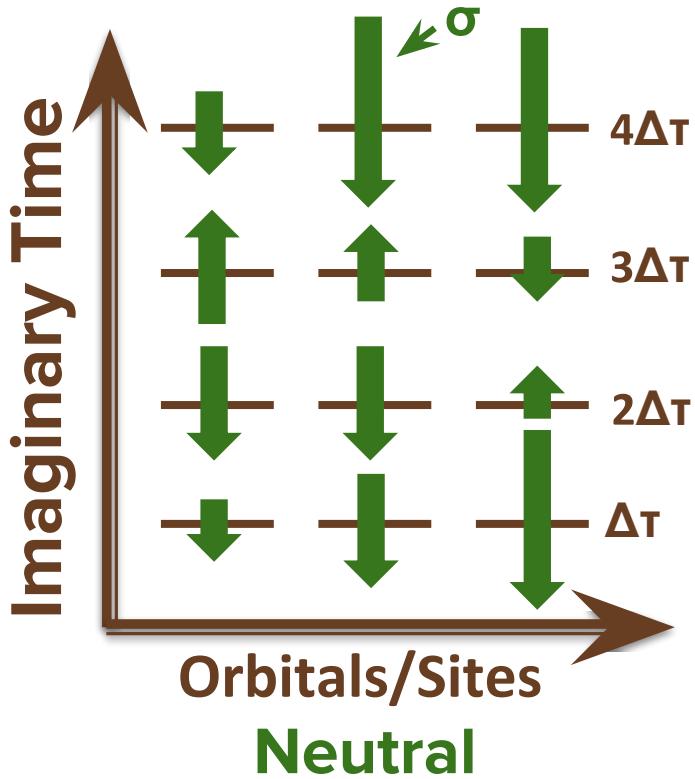
Typically, energies are averaged over different sets of fields.



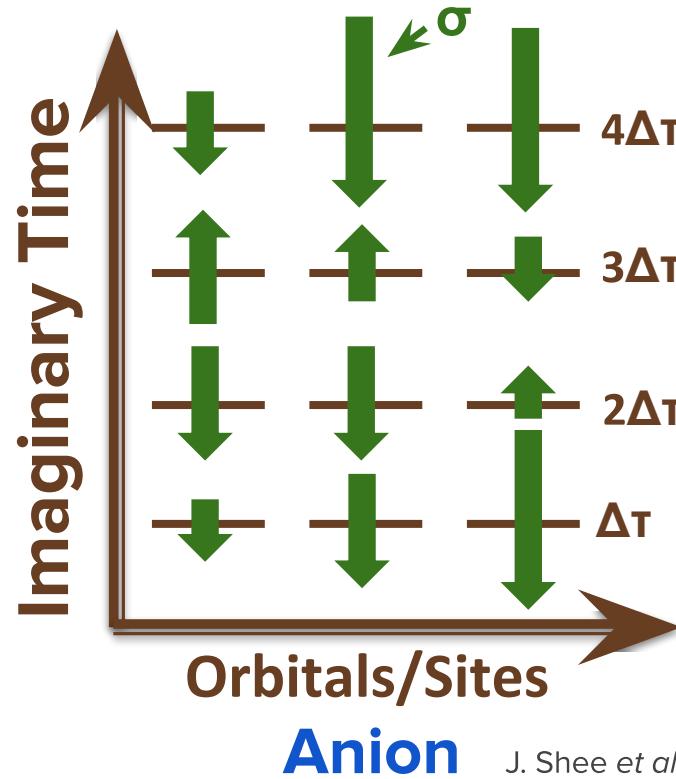
CORRELATED AFQMC

Reduces statistical errors by using the same set of fields.

$$\mathbf{E}_{\text{bind}} = \mathbf{E}_{\text{neutral}}(\sigma) - \mathbf{E}_{\text{anion}}(\sigma)$$



Neutral

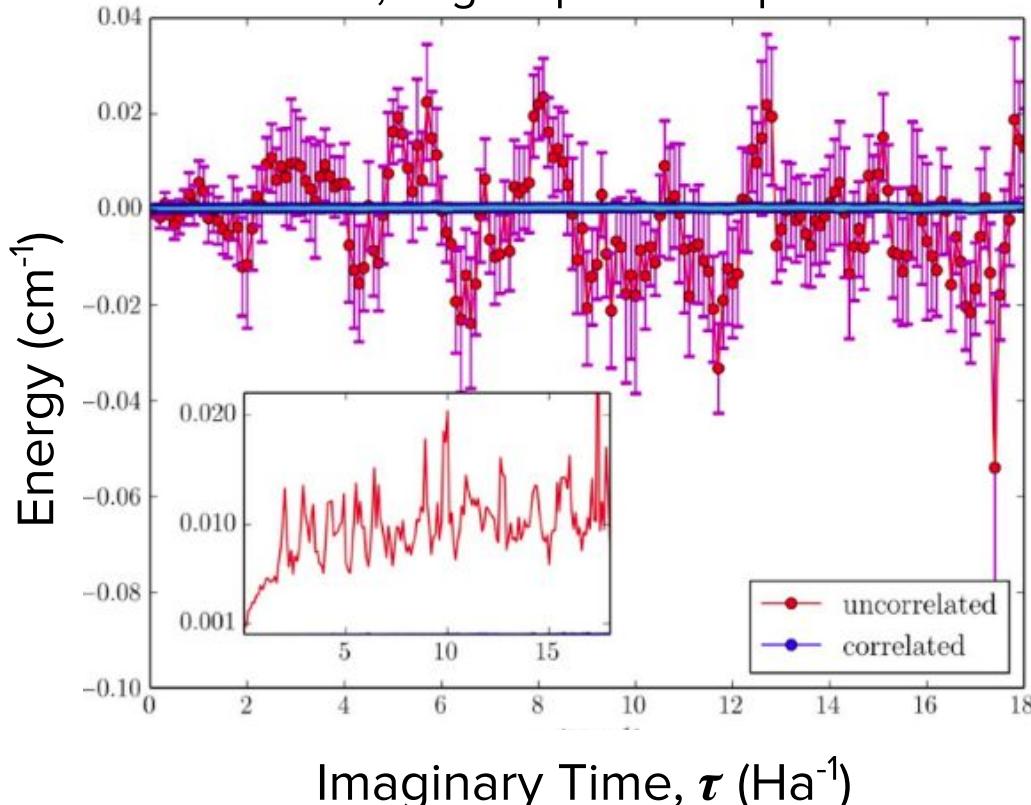


Anion

CORRELATED SAMPLING AFQMC RESULTS

C-AFQMC for CH_3CN Anion

UHF trial, aug-cc-pvdZ+7s7p basis set



For 384 Walkers and 17 Repeats

- Uncorrelated Fluctuations of $10,000 \text{ cm}^{-1}$
- Correlated Fluctuations of 24 cm^{-1}

C-AFQMC Simulations Were Performed With Two Orders of Magnitude Fewer Time Slices Than DMC Simulations

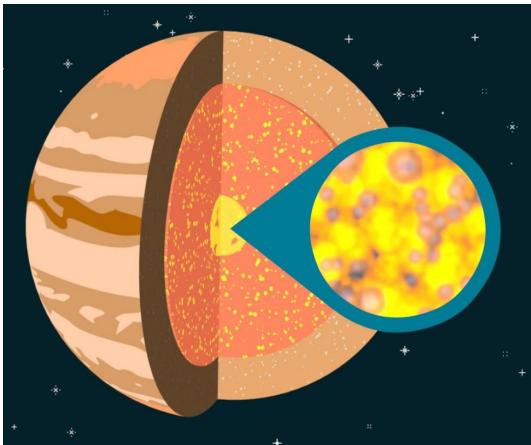
PREDICTED BINDING ENERGIES

Table 1. EBEs and Dipole Moments of Selected Species from Experiment and Self-Consistent Field [HF], Coupled Cluster [CCSD(T)], DMC, and C-AFQMC Calculations

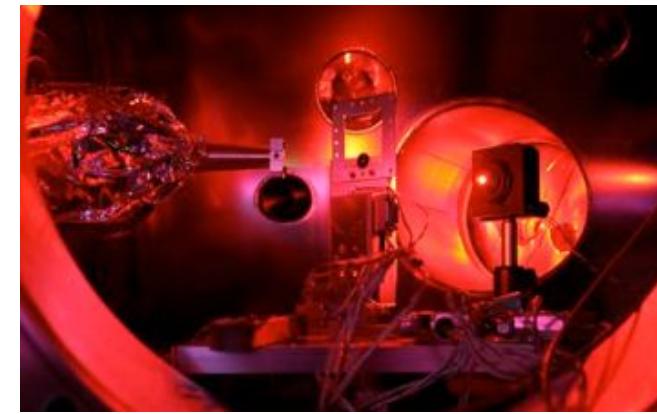
	dipole moment (D)	experiment	Δ SCF ^a	CCSD(T) ^a	DMC ^b	C-AFQMC ^c
SO	1.55 ⁶²	not bound	-3.84	-4.13	-308.20 \pm 70.82	-4.54 \pm 0.64
HCN	2.98 ⁶²	13 ⁶³	11.00	7.44	46.17 \pm 45.30	10.80 \pm 2.95
CH ₂ CHCN	3.87 ⁶²	56–87 ^{12,64}	43.30	61.87	106.63 \pm 58.12	65.70 \pm 11.03
CH ₃ CN	3.92 ⁶²	93–145 ^{12,64}	50.83	103.00	93.83 \pm 36.21	95.85 \pm 9.73
C ₂ H ₂	4.14 ⁶⁵	170 \pm 50 ⁶⁶	54.61	162.08	151.22 \pm 64.25 ^d	132.45 \pm 9.43 ^e
C ₂ H ₂ O ₃	4.55 ⁶²	194 \pm 24 ⁶⁷	103.13	163.31	213.98 \pm 116.15	157.70 \pm 17.96

- Using modest amounts of simulation time, C-AFQMC was able to achieve CCSD(T) accuracies
- Error bars were 1-2 orders of magnitude smaller than DMC error bars
- No particular signs of a phaseless approximation bias

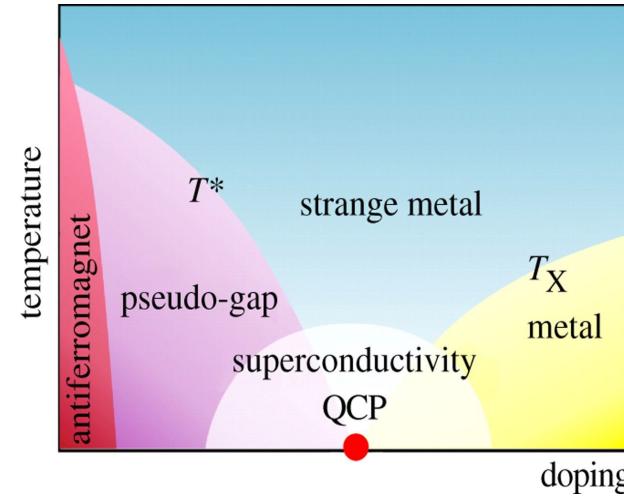
MOTIVATION: NEED FOR TEMPERATURE



Planetary
Astrophysics/
Geophysics



Laser-Generated
Plasmas and
Laser-Induced Chemistry



Solid/Model Phase
Diagrams

MOTIVATION: Existing Methodologies

Ground State

DMRG

Coupled Cluster

Diffusion MC

CAS/RAS

Perturbation Theory

DFT/HF

Full CI/ED

AFQMC

Finite Temperature

SEET

Path Integral MC

Continuous Time QMC

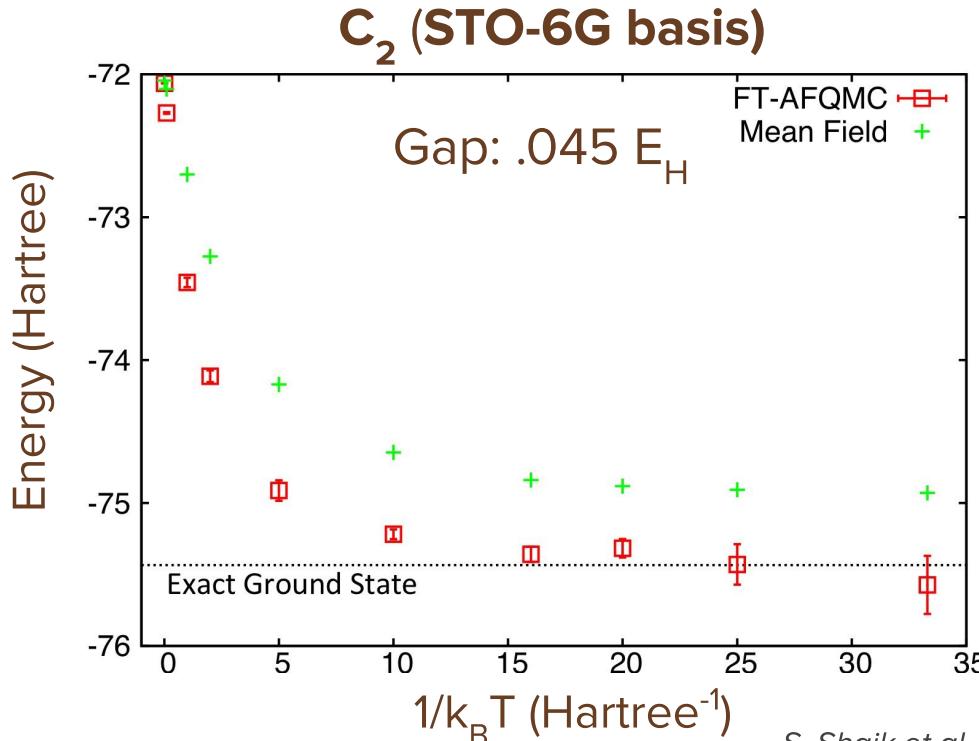
Determinantal QMC

Mean Field Theory

Full CI/ED

FINITE TEMPERATURE CHEMISTRY: C₂

AFQMC can readily be redeveloped into a finite temperature method, which opens the door to phase diagrams.



Calculation of Observables:

$$\langle \hat{O} \rangle = \frac{\text{Tr}[\hat{O} e^{-\beta(\hat{H}-\mu\hat{N})}]}{\text{Tr}[e^{-\beta(\hat{H}-\mu\hat{N})}]}$$

Partition Function:

$$\Xi = \text{Tr} \left(\lim_{\Delta\tau \rightarrow 0} \prod_l^L e^{-\Delta\tau(\hat{H}-\mu\hat{N})} \right)$$

ONGOING
CHALLENGES AND
OPPORTUNITIES

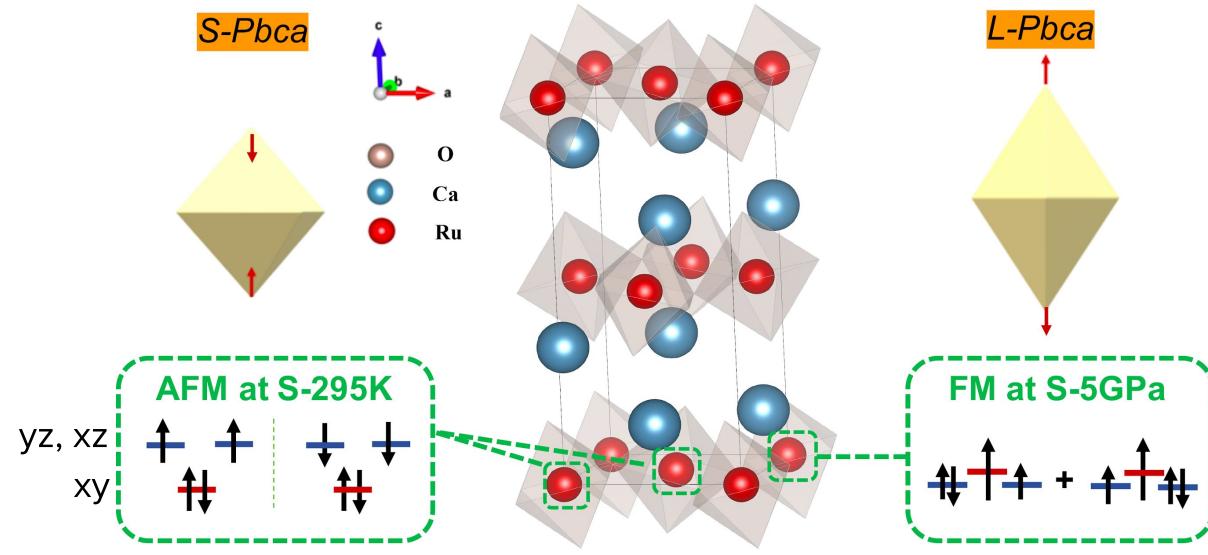
CHALLENGES AND OPPORTUNITIES

- **Speed: Our Scaling Is $O(N^3)$**
 - But N (Basis Size) Can Be Very Large for Realistic Systems
 - Tensor Decompositions Have Been Proposed To Reduce Scaling, But Still High
- **Achieving Chemical Accuracy for Transition Metals**
 - Transition metals, lanthanides, and actinides are critical to chemical catalysis, condensed matter physics
 - Sufficient accuracy to capture metal bonds? At what expense?
 - To Describe Reactions: Need Free Energies, Barriers, Gradients **[Must Go Beyond Energy!]**

BACKUP SLIDES

GOING BEYOND BENCHMARKS: Ca_2RuO_4

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- Low Temperature (<300 K), Low Pressure (< 0.5 GPa): Antiferromagnetic Insulator with S-Pbca structure
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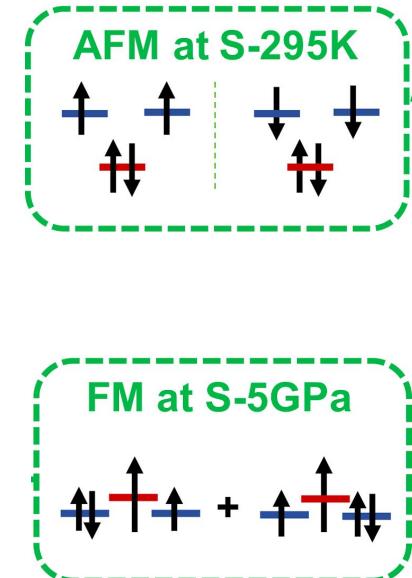
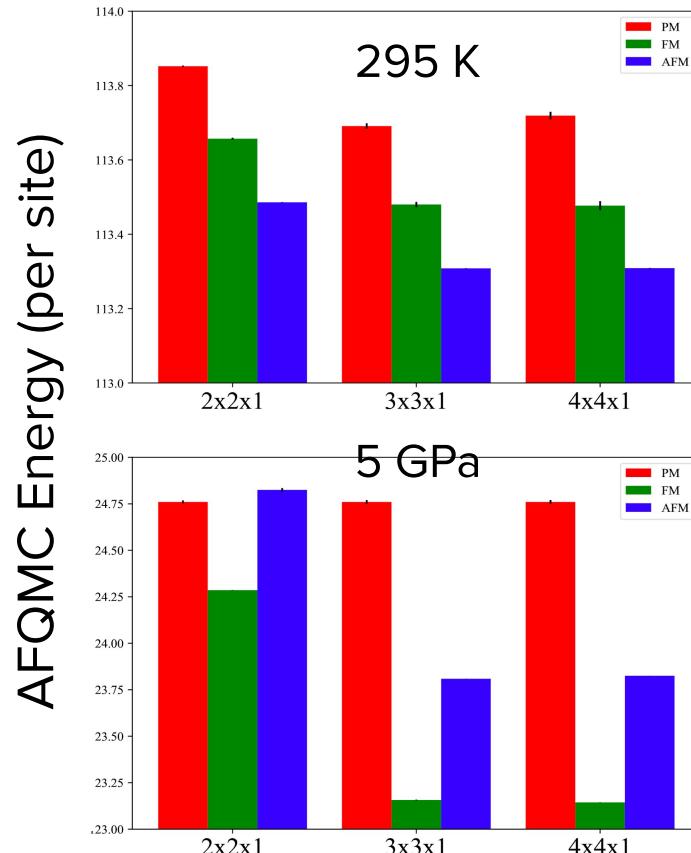


Low T, Low P → High T, High P

Can AFQMC (and DMFT) predict these transitions?

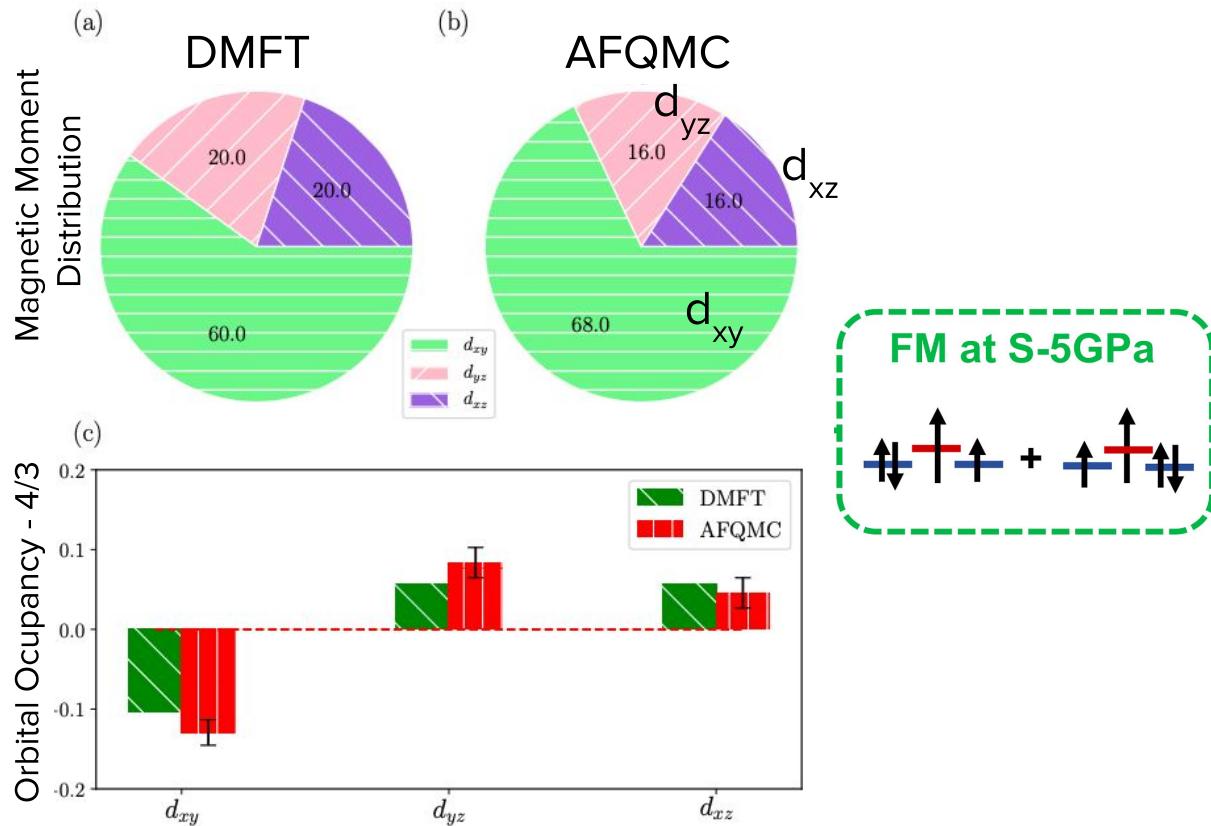
MAGNETIC ORDERING IN Ca_2RuO_4

- AFM clearly found for the S-295K structure; FM found for the S-5GPa structure
- Parameterized 3-Band HK Model for AFQMC and DMFT calculations from Maximally Localized Wannier Functions
- Used five structures obtained from experiment: S-295K, S-400K, S-1GPa, S-3GP, S-5GPa
- $U = 2.3 \text{ eV}$, $J = .35 \text{ eV}$ from previous simulations



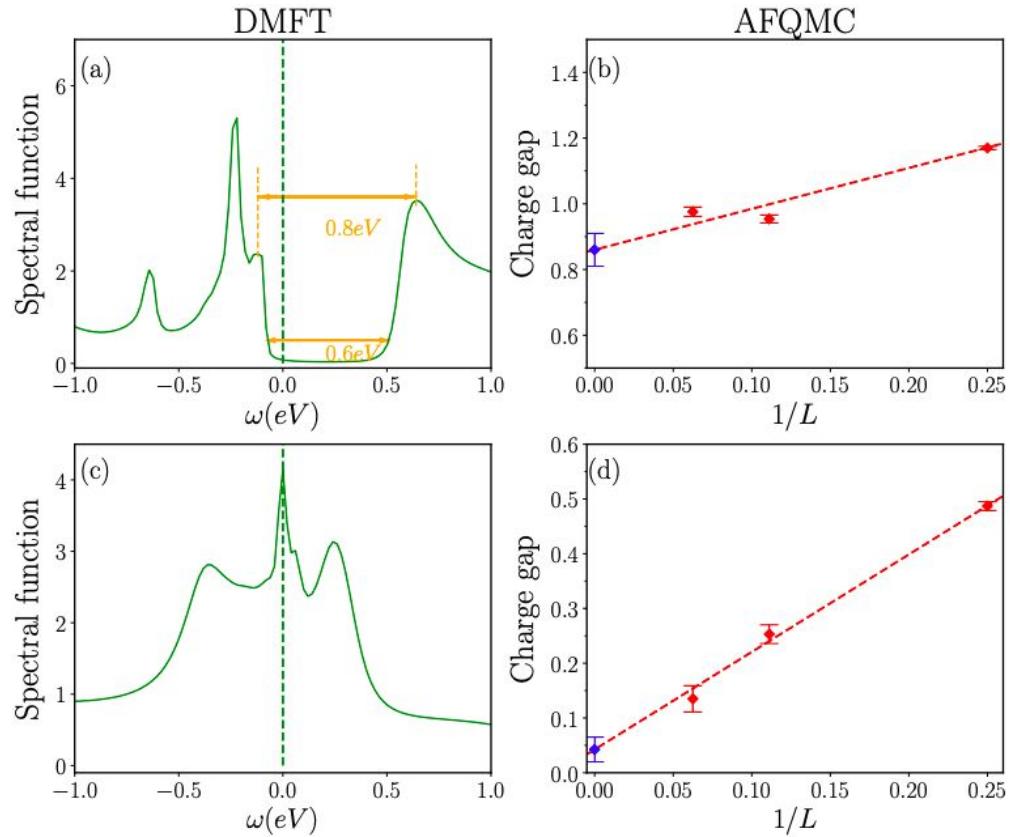
MAGNETIC ORDERING IN Ca_2RuO_4

- AFQMC and DMFT predict similar magnetic moment distributions in the FM, 5GPa phase
- With a small Δ , the d_{xz} and d_{yz} orbitals fill, leaving the moment to be determined by the d_{xy} orbital



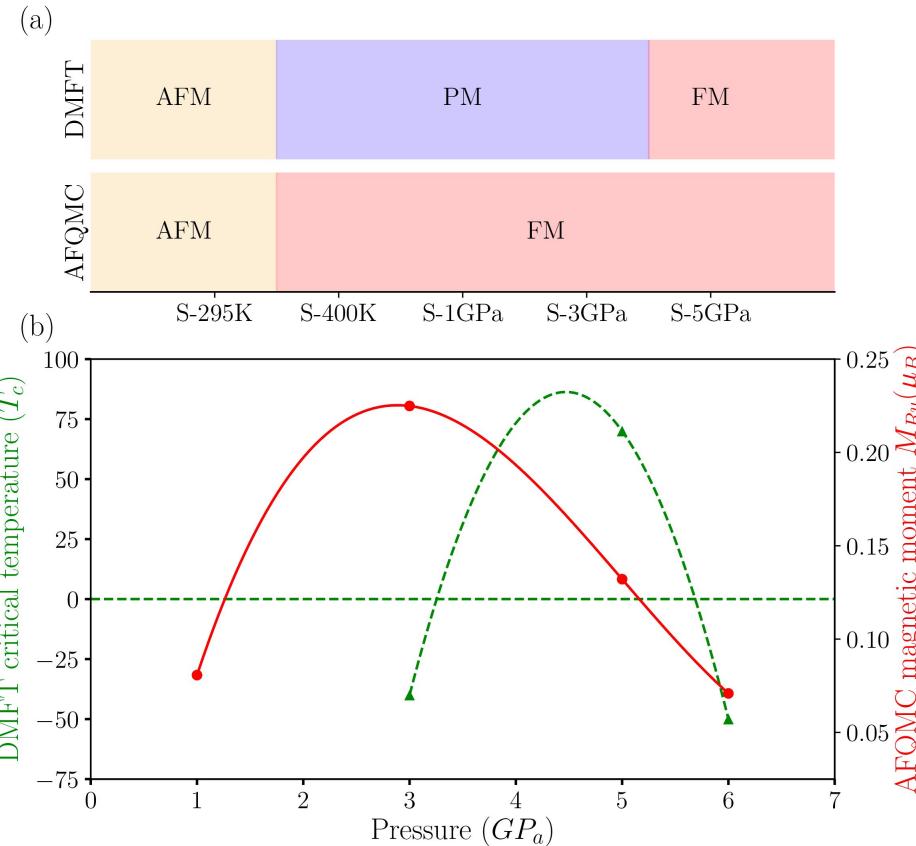
INSULATING BEHAVIOR Ca_2RuO_4

- AFQMC and DMFT *both* classify the S-295 K structure as an insulator and the S-5GPa structure as a metal
- Approximated in DMFT from gap in analytically continued spectral functions; approximated in QMC via the charge gap



FULL Ca_2RuO_4 PHASE DIAGRAM

- AFQMC and DMFT agree for S-295K and S-5GPa, but disagree at other pressures/temperatures
- Disagreement may stem from the presence of a mixed state at intermediate pressures observed experimentally
- The methods quantitatively disagree regarding critical temperatures



Determinant Quantum Monte Carlo (DQMC)

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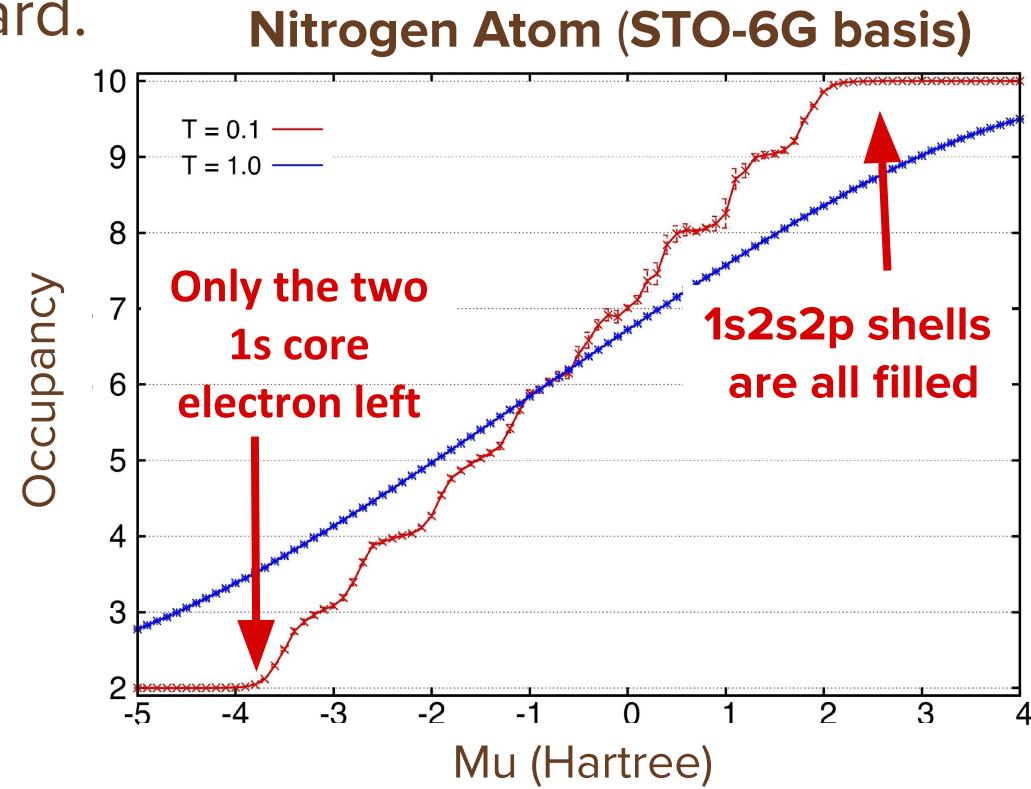
Trace Over Partition Function:

$$\Xi = \sum_{\vec{\sigma}} \text{Det}[I + B_{\uparrow}^L(\vec{\sigma}_L) \dots B_{\uparrow}^1(\vec{\sigma}_1)] \text{Det}[I + B_{\downarrow}^L(\vec{\sigma}_L) \dots B_{\downarrow}^1(\vec{\sigma}_1)]$$

Constraining the Occupancy

Constraining occupancies in the grand canonical ensemble turns out to be straightforward.

- Clear plateaus may be found for each integer electron number
- This facilitates constraining occupancies by selecting the proper chemical potentials
- Although adaptations to the canonical ensemble can be made



Simple Atomic/Molecular Benchmarks

Simple benchmarks for which exact results may be obtained manifest mH accuracy.

Beryllium Atom (MIDI basis)

$1/k_B T$	ED (exact)	AFQMC	MFT
0.01	-10.812530	-10.812(7)	-10.803770
0.1	-11.486682	-11.48(2)	-11.395784
1	-13.990088	-13.991(5)	-13.829351
5	-14.260043	-14.26(2)	-14.174662
10	-14.396622	-14.395(2)	-14.309152
20	-14.478346	-14.482(2)	-14.436926
50	-14.484593	-14.485(1)	-14.474763
100	-14.484595	-14.485(2)	-14.475035

$1/k_B T$ is given in units of Hartree⁻¹; all ED, AFQMC, and MFT energies are given in Hartree.