High-performance and Quantum Computing for Strongly Correlated Problems

Werner Dobrautz

CASUS Institute Talk

January 15, 2025

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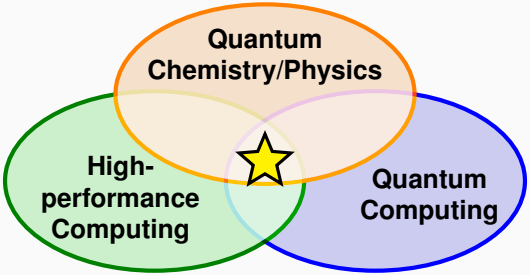
Outline

- Background and Motivation
- High-performance Computing for Strong Correlation
- Quantum Computing for Strong Correlation
- Summary and Outlook

Background and Motivation

Scientific Background and Research Profile



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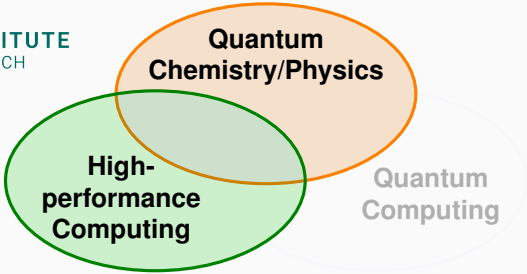
MAX PLANCK INSTITUTE
FOR SOLID STATE RESEARCH

PhD 2019
Prof. Ali Alavi



- **Quantum Monte Carlo** methods for strongly correlated problems
- **Resource reduction** and embedding
- Study of **transition metal** clusters

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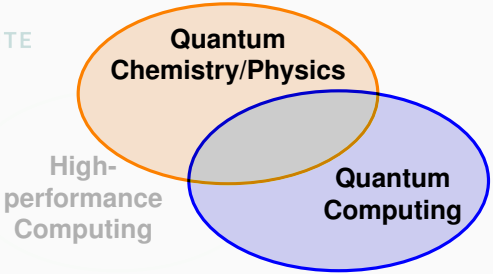


CHALMERS
UNIVERSITY OF TECHNOLOGY

IBM
Academic Network

Prof. Martin Rahm
Dr. Ivano Tavernelli

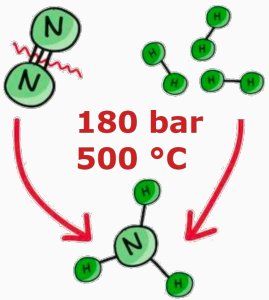
MARIE CURIE ACTIONS

- **Quantum Monte Carlo** methods for strongly correlated problems
- **Resource reduction** and embedding
- Study of **transition metal** clusters

- **Algorithm development:** Quantum imaginary time evolution
- **Error mitigation** and classical optimization
- **Resource reduction:** Qubits and circuit depth

Motivation: Haber-Bosch process and biological nitrogen fixation

Haber-Bosch Process



- **Crucial for fertilizer production**
- 2% of world's energy consumption
- 3% of global carbon emissions
- 5% of natural gas consumption

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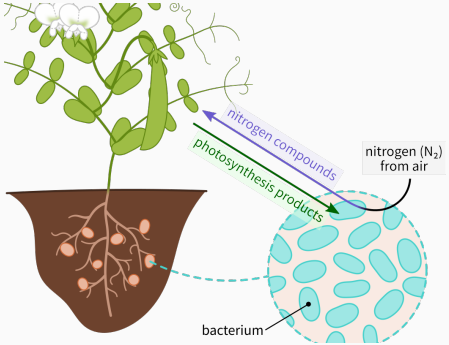
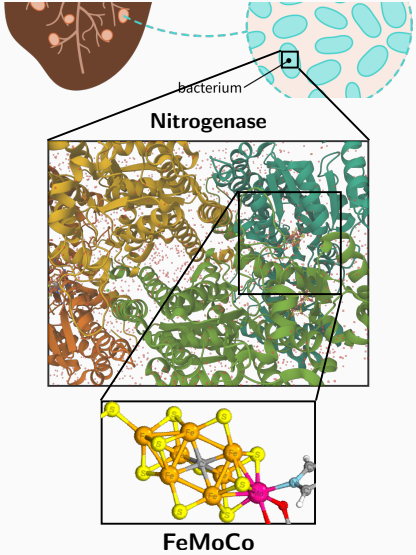
Biological nitrogen fixation



- **Ambient pressure and temperature**
- Not yet understood → Bio-catalysts for more efficient and greener ammonia production

Problem: Strongly correlated transition metal compounds

- **Transition metal clusters** act as catalysts: Iron-Molybdenum cofactor (FeMoCo) and other iron-sulfur clusters
- **Experimental study very difficult!**



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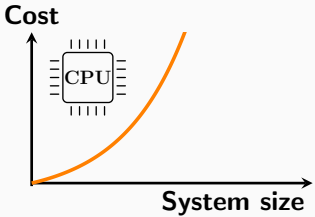
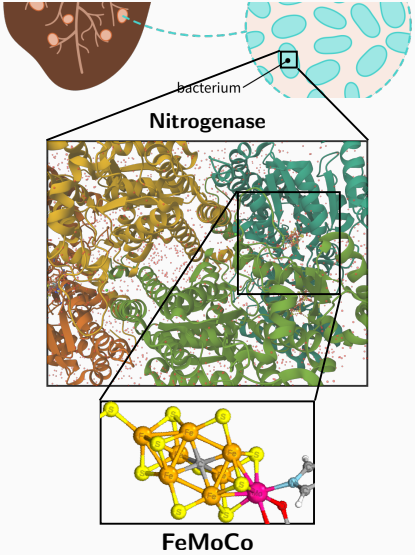
We have the equations at hand, but **exponentially costly** on classical computers!





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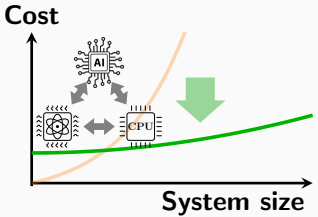
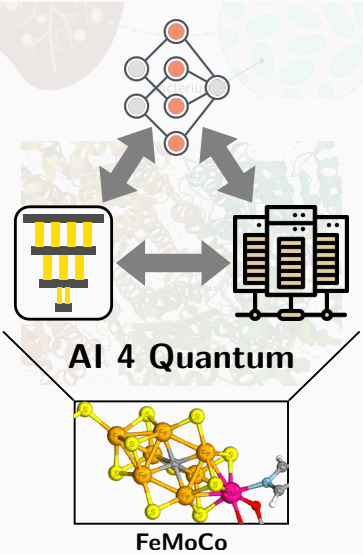
Use a combined AI, HPC and QC approach for a potential computational speedup





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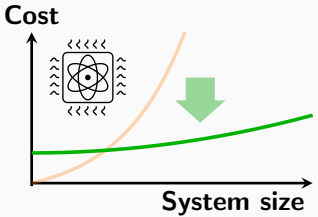
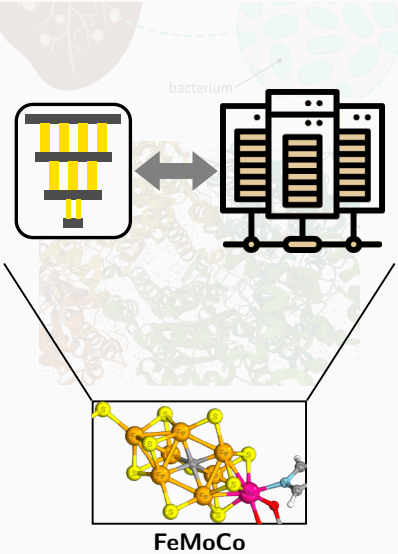
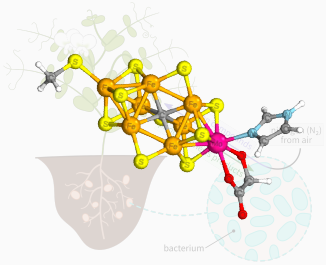
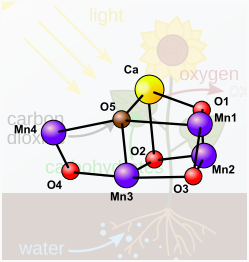
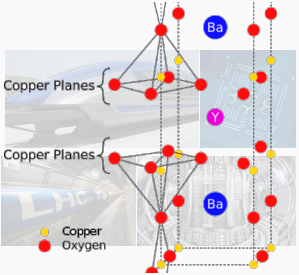




Quantum Chemistry – Theory, Workflow and Applications







Iron molybdenum cofactor (FeMoCo): nitrogen fixation of nitrogenase

Manganese Calcium Oxygen Clusters: Oxygen evolving clusters in photosystem II

2D Copper-Oxide planes in cuprates: unconventional high-T_c superconductivity

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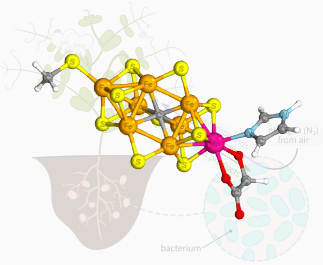

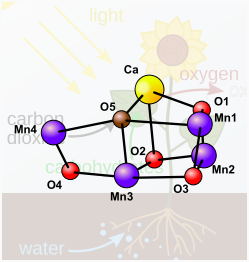

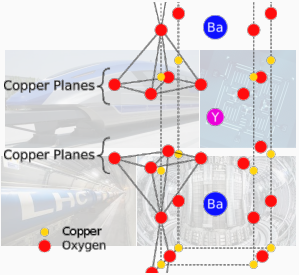

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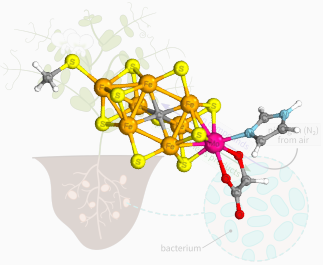

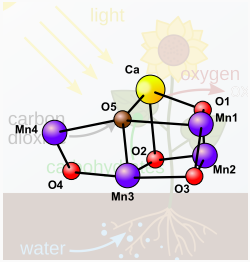

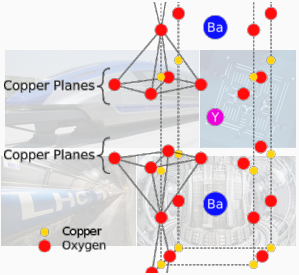

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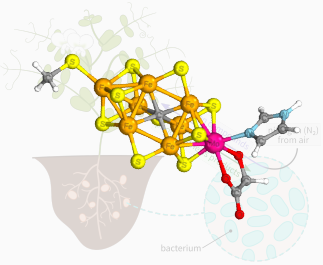

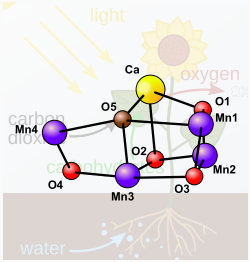

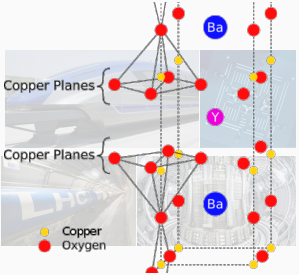

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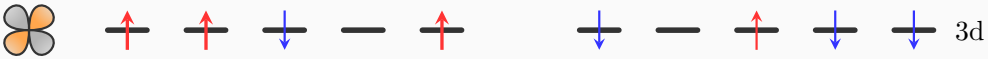
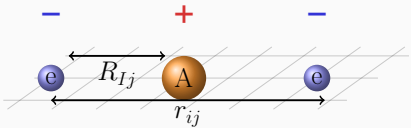


To obtain insight on the **chemical** and **physical properties** of these systems we need to **solve the Schrödinger equation**

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle\,, \qquad \hat{H}\,|\Psi(t)\rangle = i\frac{\partial}{\partial t}\,|\Psi(t)\rangle$$

All necessary information contained in electronic **molecular Hamiltonian**

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla^2_{\mathbf{r}_i}}_{\text{kinetic energy of e}^-} \underbrace{-\sum_{I,j}\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_j|}}_{\text{Attr. potential}} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{e}^- - \text{e}^- \text{ repulsion}}$$



Coulomb repulsion correlates all electrons of a system → analytic solution too complex → **approximations and computational approaches**

Quantum Chemistry – Electronic Structure Theory

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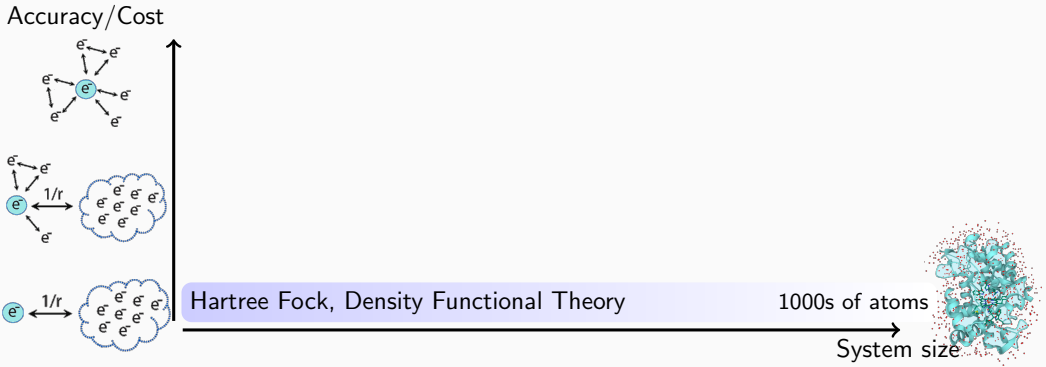

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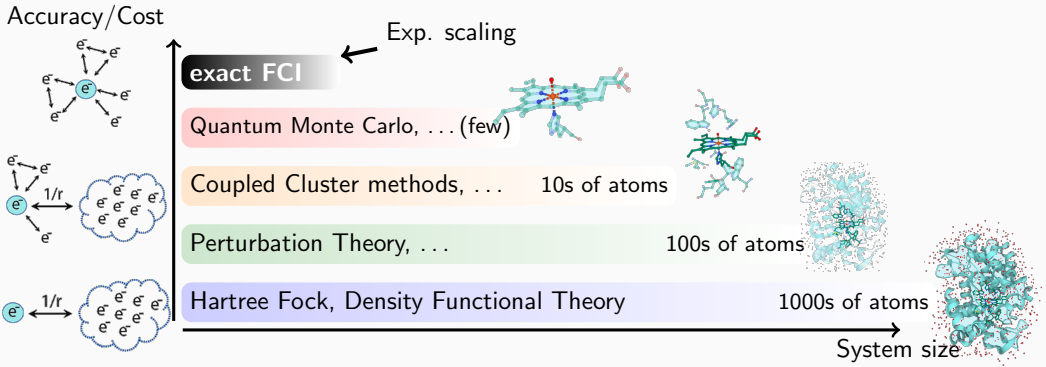

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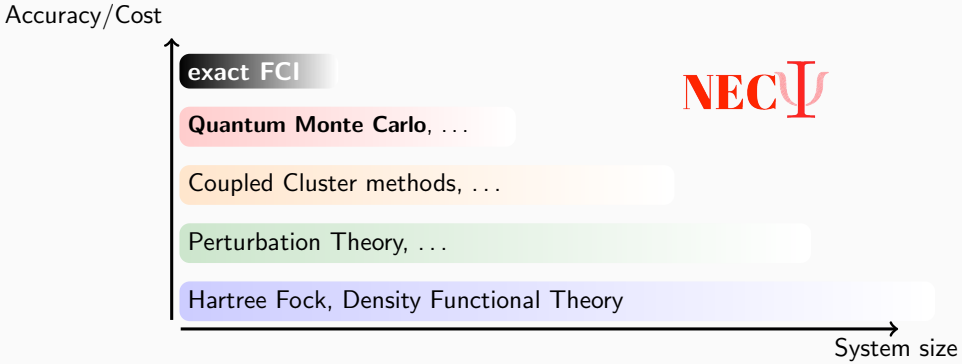

– **Main developer** of full configuration interaction quantum Monte Carlo (FCIQMC) code `NECI`: $\approx$ 30 developers, highly optimized for HPC

Targeting Real chemical accuracy at the EXascale

PRL 121, 056401 (2018); **JCP 153**, 034107 (2020); **JCTC 19**, 20, 6933 (2023)

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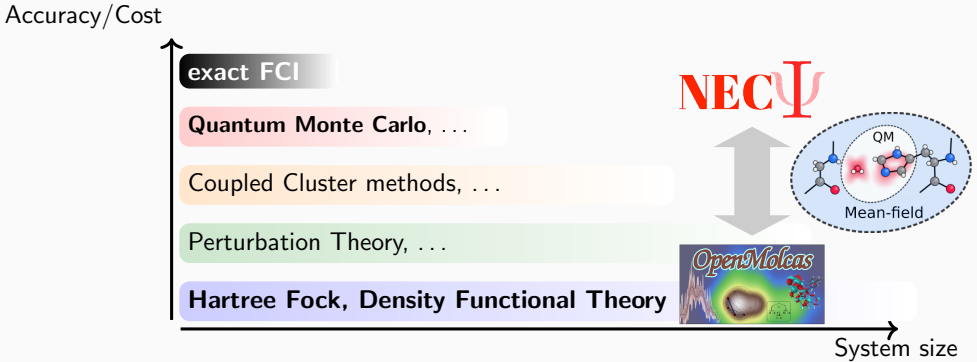

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– **Embedding** in form of complete active space self-consistent field:
$\rightarrow$ Interfaced FCIQMC as active space solver with `OpenMolcas`

TREX
Targeting Real chemical accuracy at the EXascale

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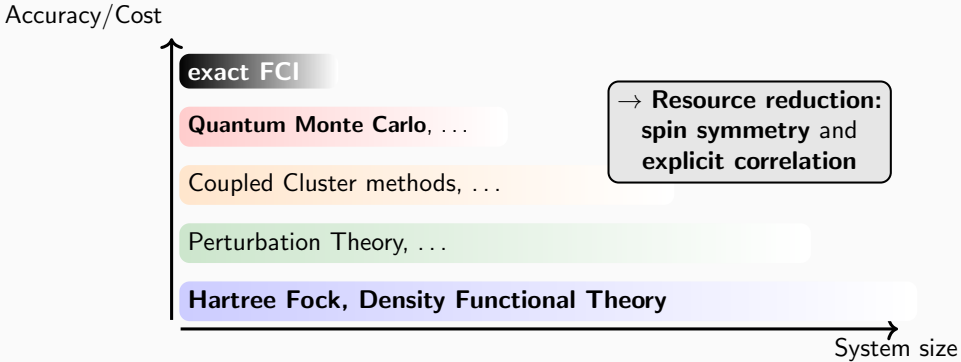

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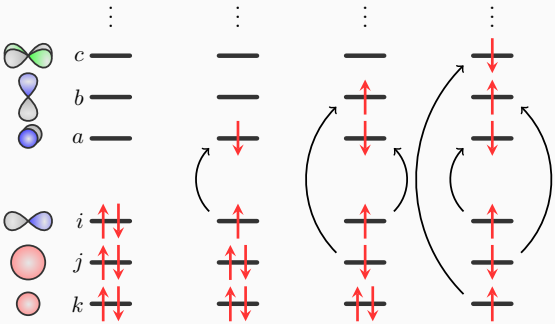
Exponential scaling of Full Configuration Interaction

FCI $\Rightarrow$ exact solution in a given basis: linear combination of determinants

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle \qquad \Rightarrow \qquad |\Psi\rangle = |\Phi_{HF}\rangle + \sum_i c_i\,|\Phi_i\rangle$$



$$|\Phi_{HF}\rangle \;+\; c_i^a\,|\Phi_i^a\rangle \;+\; c_{ij}^{ab}\,|\Phi_{ij}^{ab}\rangle + c_{ijk}^{abc}\,|\Phi_{ijk}^{abc}\rangle$$

All possible excitations from HF determinant

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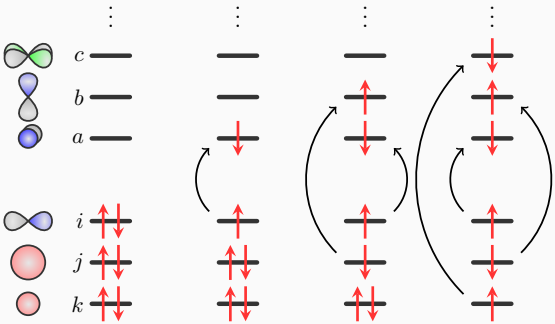

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All possible excitations from HF determinant

Number of states for given number of electrons and orbitals, active space (n_e, n_o)

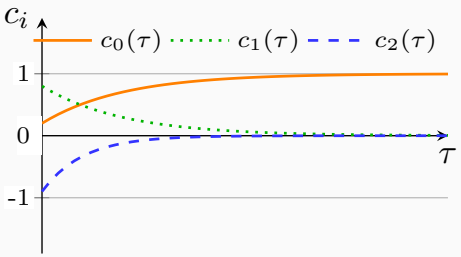
Mol.	#orbitals	#electrons	#states
H_2	2	2	4
LiH	4	4	36
Be_2	8	8	4900
H_2O	12	12	$\sim 8 \cdot 10^5$
C_2H_4	16	16	$\sim 16 \cdot 10^6$
F_2	18	18	$\sim 2 \cdot 10^9$

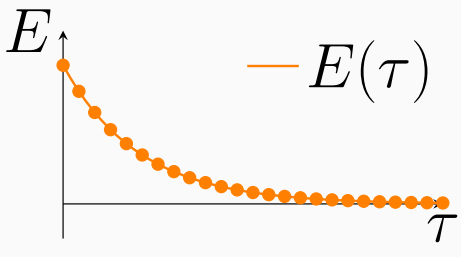
High-performance Computing for Strong Correlation

Imaginary Time Evolution

Imaginary-time evolution $\rightarrow$ method to project onto groundstate:

$$i\frac{\partial |\Psi\rangle}{\partial t} = \hat{H}|\Psi\rangle \quad \overset{\tau=it}{\rightarrow} \quad \frac{\partial |\Psi\rangle}{\partial \tau} = -\hat{H}|\Psi\rangle \quad \rightarrow \quad \boxed{|\Psi_0\rangle = \lim_{\tau\to\infty} \mathrm{e}^{-\hat{H}\tau}|\Phi(0)\rangle}$$





Full Configuration Interaction Quantum Monte Carlo – FCIQMC

- Based on the **imaginary-time** Schrödinger Eq.

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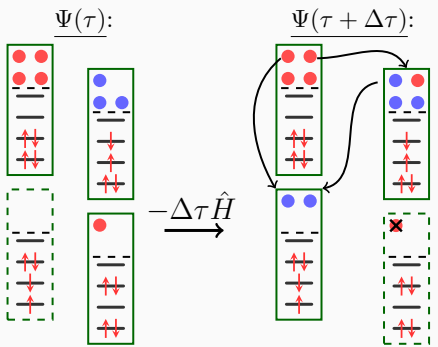
- Wavefunction, $|\Psi_0\rangle$, is stochastically sampled by a set of "walkers"



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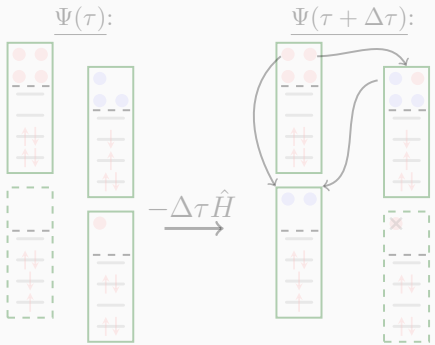
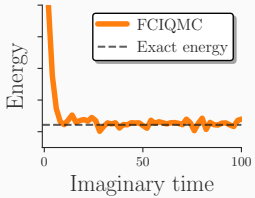


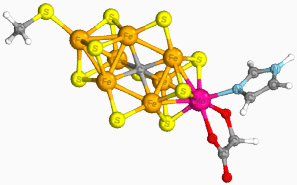


Highly-optimized for HPC. Excited state energies and properties for large active spaces $> (50e, 50o)$

My major contributions:
Implementation of **spin symmetry** and **transcorrelation**.

Booth, Thom, and Alavi, JCP, **131**, 054106 (2009); Guther, ..., **WD**, ..., Alavi, JCP, **153**, 034107 (**2020**); *https://github.com/ghb24/NECI_STABLE

Massively Parallel – Towards the Exascale



Markus Rampp @

MPCDF

MAX PLANCK
COMPUTING & DATA FACILITY

CAS(54e,54o) FeMoco molecule on 512 and 620 nodes @ Max-Planck Cobra HPC cluster

Walkers	Cores	Time/iteration	Ratio cores	Ratio time/iteration	Parallel efficiency (%)
32×10^9	19960	23.5	1.242	1.246	**99.68**
32×10^9	24800	18.8			

Ongoing work in the European Center of Excellence

Targeting Real Chemical Accuracy at the EXascale (TREX)

Interfaced with `Molpro`, `OpenMolcas`, `PySCF` and `VASP`

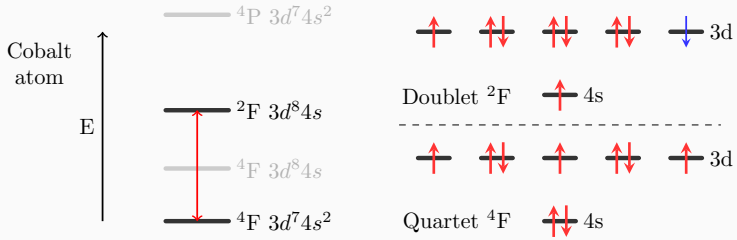
William Jalby @

TREX
Targeting Real chemical accuracy at the EXascale

Guther, ..., **WD**, ..., Alavi, JCP, **153**, 034107 (**2020**)

Spin Symmetry

Motivation: Potential Problems of a Slater determinant formulation



- Slater determinants (SDs) **no** spin-eigenfunctions
- No control and insight of total spin
- Narrow spin-gaps problematic

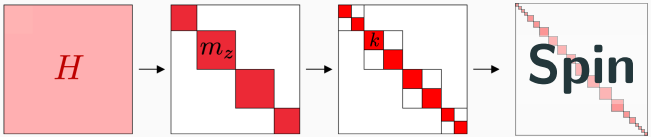
- Hard to obtain low-spin excited states
- Multi-reference open-shell low-spin excited state problematic for single-reference methods

$\Rightarrow$ Use a **spin-adapted basis**

WD, Smart and Alavi, JCP, **151**, 094104 (2019);

HPC Resource Reduction – Spin Symmetry

Symmetries reduce the computational cost, by block-diagonalizing the Hamiltonian



Spin symmetry: inherent to most electronic structure problems,
often not used, due to *impractical implementation.*

Efficient implementation in FCIQMC based on the **unitary group approach**[‡]

[†] **WD**, Smart and Alavi, JCP, **151**, 094104 (2019); [‡] Paldus, J. Chem. Phys. **61**, 5321 (1974) + Shavitt, Int. J. Quantum Chem., **12**, 131 (1977)

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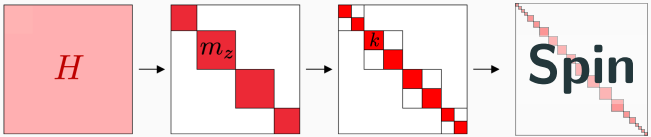

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Efficient implementation in FCIQMC based on the **unitary group approach**[‡]

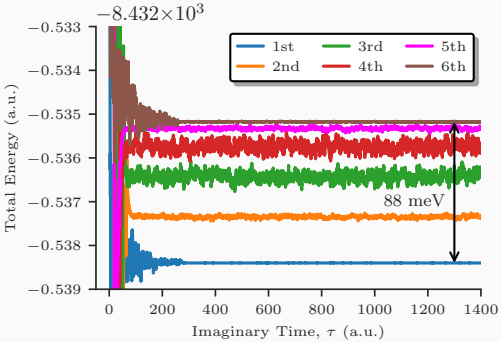
Benefits of a spin-symmetry adapted basis:

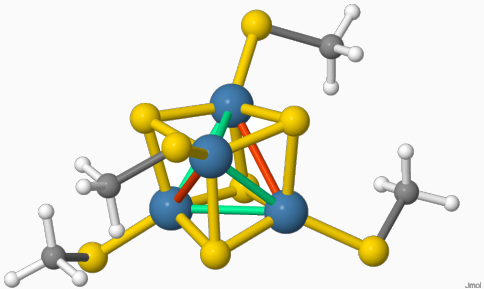
- Target specific spin-states
- Reduce Hilbert space/problem size

[†] **WD**, Smart and Alavi, JCP, **151**, 094104 (2019); [‡] Paldus, J. Chem. Phys. **61**, 5321 (1974) + Shavitt, Int. J. Quantum Chem., **12**, 131 (1977)

Results: Iron-sulfur clusters – Fe_4S_4

Energy and magnetic properties of Fe_4S_4 clusters:
Singlet spin states with 20 open shell orbitals.





Six lowest singlet states in (20e,20o) active space resolved within ≈ 3 mH

Li Manni, **WD**, Bogdanov, Guther, Alavi, JCP A **125** (22), 4727 (2021)

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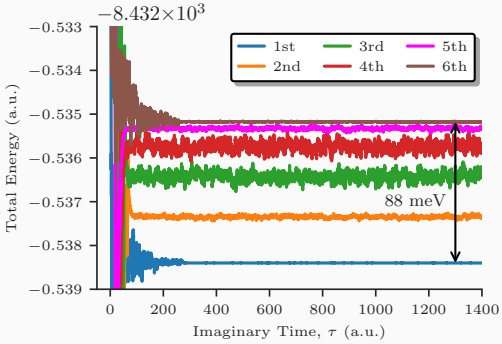

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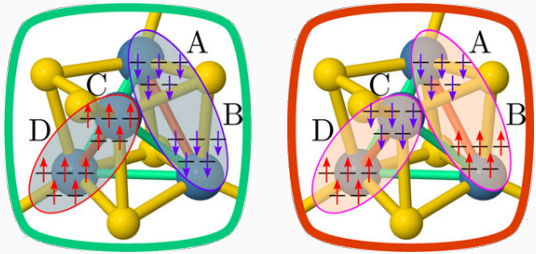
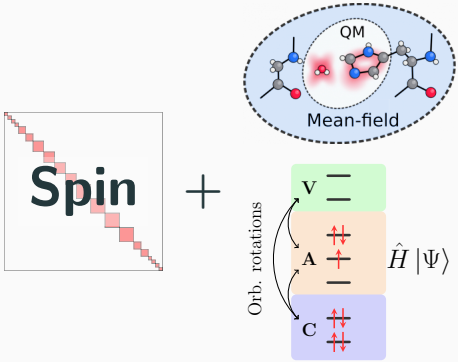


Access to wavefunction and spin information $\rightarrow$ reveals magnetic coupling of ground- and excited states

Li Manni, **WD**, Bogdanov, Guther, Alavi, JCP A **125** (22), 4727 (2021)

HPC Resource Reduction – Spin-symmetry and Embedding – Fe_2S_2

Combination of FCIQMC, spin-symmetry and embedding to study magnetic properties of iron-sulfur clusters



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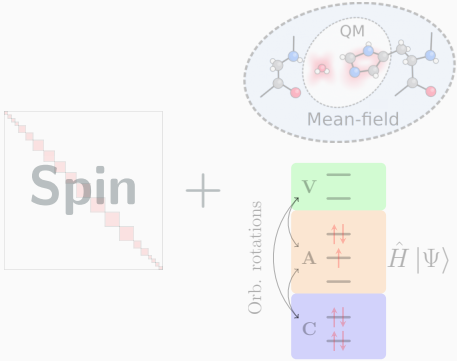

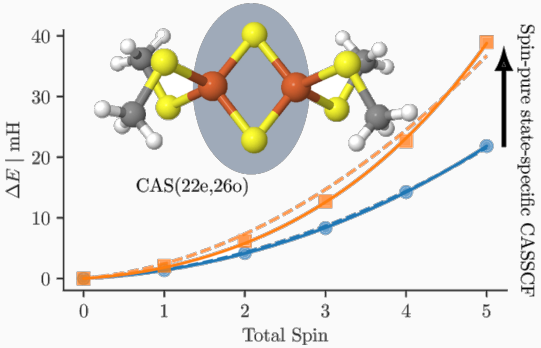

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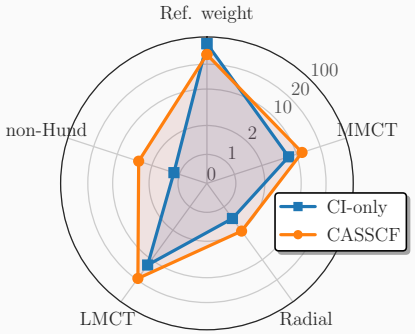

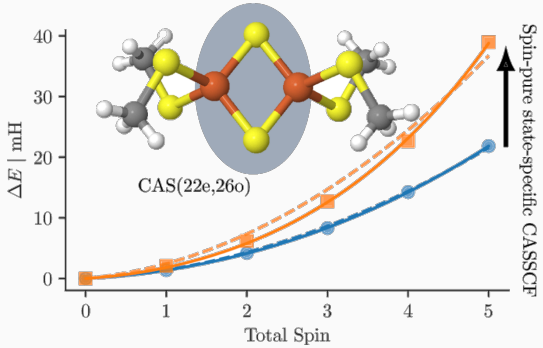

JCP **151**, 094104 (2019); JCTC **16**, 4, 2202 (2020); JPC A **125**, 22, 4727 (2021); PRB **104**, 235102 (2021); PRB **105**, 195123 (2022); PRB **107**, 064405 (2023)

WD, Weser, Bogdanov, Alavi, Li Manni, JCTC **17** (9), 5684 (2021)

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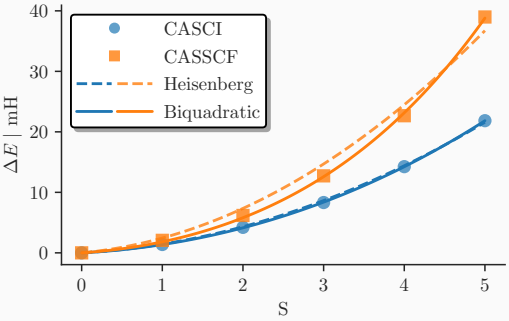
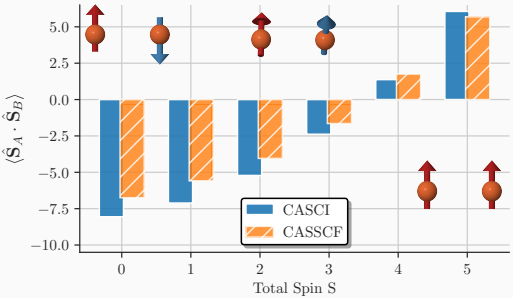


Linear Heisenberg

$$\hat{H} = J\,\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$$

CASCI: $J = 1.44$ mH

CASSCF: $J = 2.45$ mH



Biquadratic Heisenberg

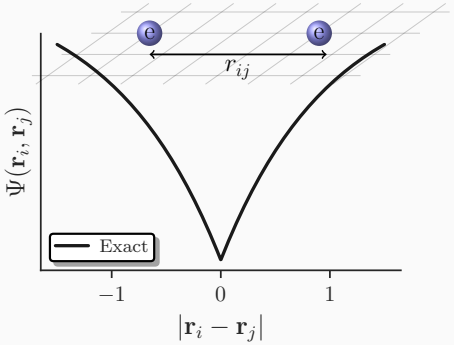
$$\hat{H} = J'\,\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B + K\left(\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B\right)^2$$

CASCI: $J' = 1.47$ mH and $K = 0.007$ mH

CASSCF: $J' = 2.70$ mH and $K = 0.054$ mH

Transcorrelation

Cusp condition: Singularity of Coulomb potential ($\sim \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$)
$\rightarrow$ sharp cusp of exact wavefunction $\Psi(\{\mathbf{r}\})$ at electron coalescence ($|\mathbf{r}_i - \mathbf{r}_j| = 0$)



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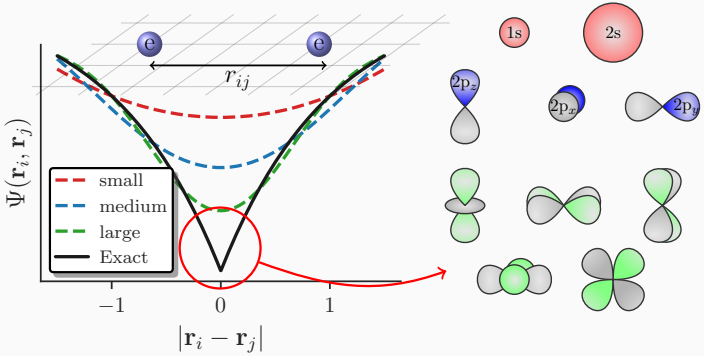

HPC – Resource Reduction: Basis sets

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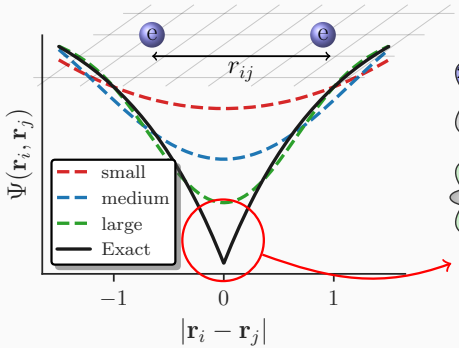
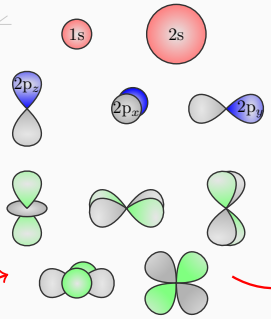
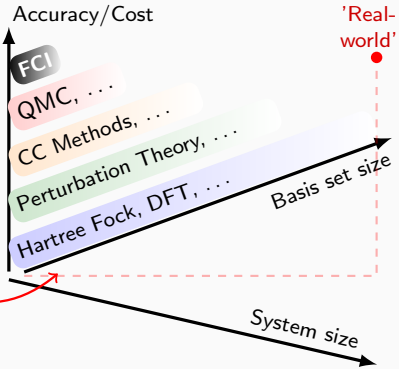
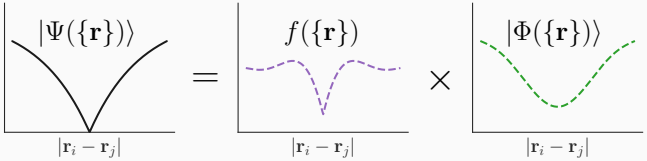






HPC – Resource Reduction: Transcorrelation (TC)



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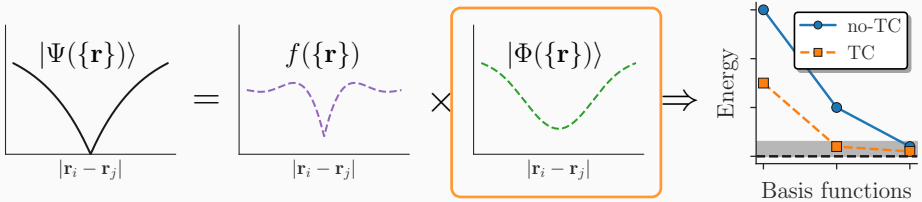

WD, Luo, Alavi, PRB **99** (7), 075119 (2019); Cohen, Luo, Guther, **WD**, Tew, Alavi, JCP **151** (6), 061101 (2019);

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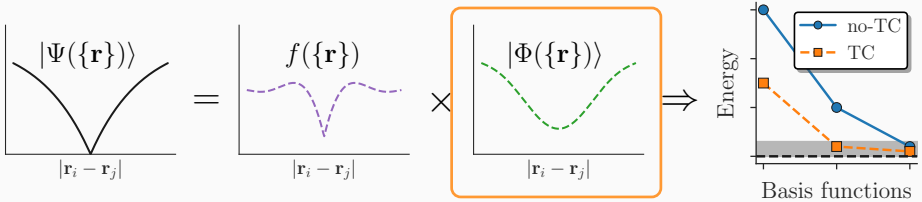

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle \quad \rightarrow \quad |\Psi\rangle = \mathrm{e}^{\hat{J}}\,|\Phi\rangle \quad \rightarrow \quad \overbrace{\mathrm{e}^{-\hat{J}}\,\hat{H}\,\mathrm{e}^{\hat{J}}}^{\hat{H}_{\mathrm{TC}}}\,|\Phi\rangle = E\,|\Phi\rangle$$

$|\Phi\rangle$ easier to represent with less basis functions → immense resource reduction

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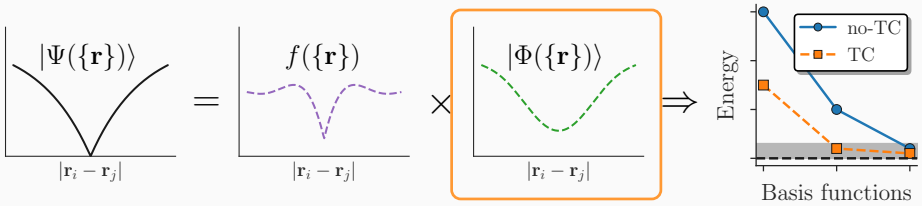

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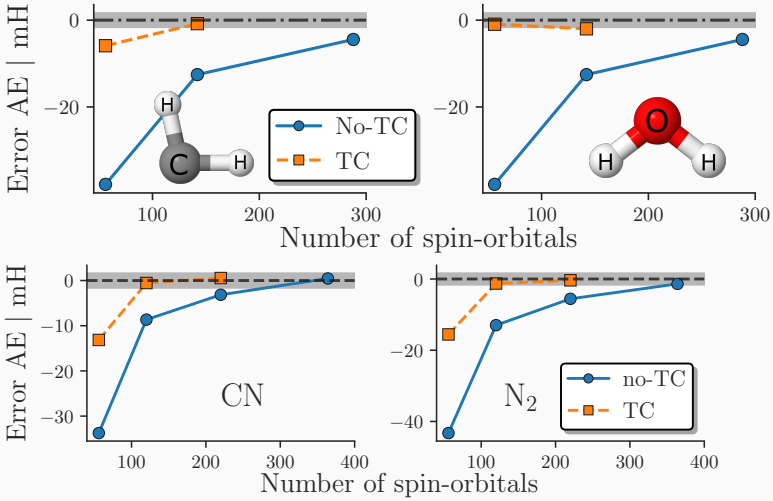
$\hat{H}_{\mathrm{TC}}$ is non-Hermitian and has 3-body terms

WD, Luo, Alavi, PRB **99** (7), 075119 (2019); Cohen, Luo, Guther, **WD**, Tew, Alavi, JCP **151** (6), 061101 (2019);

HPC – Resource Reduction: Transcorrelation – Results



WD, Cohen, Alavi, Giner, JCP **156** (23), 234108 (2022); Haupt, Hosseini, López Ríos, **WD**, Cohen, Alavi, JCP **158**, 224105 (2023)

Quantum Computing for Strong Correlation

Classical bit

0 1

Quantum bit = qubit

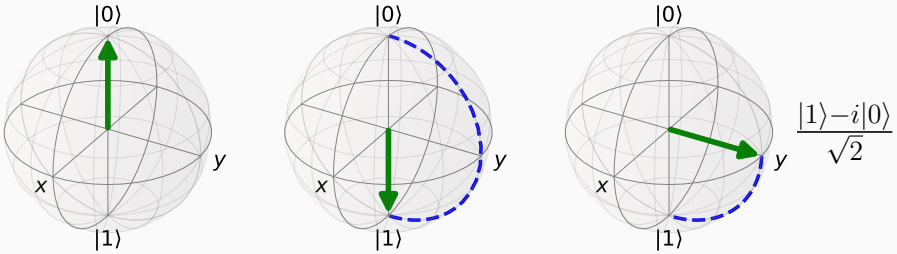
$$a\,|0\rangle \quad + \quad b\,|1\rangle$$

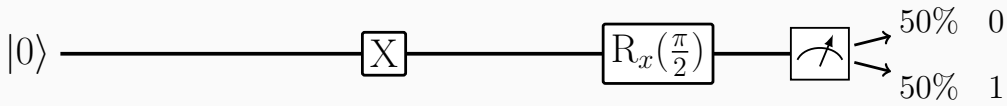
Quantum bit = qubit

$$a\,|0\rangle \quad + \quad b\,|1\rangle$$

$$|a|^2 + |b|^2 = 1$$

Qubits – Bloch Sphere





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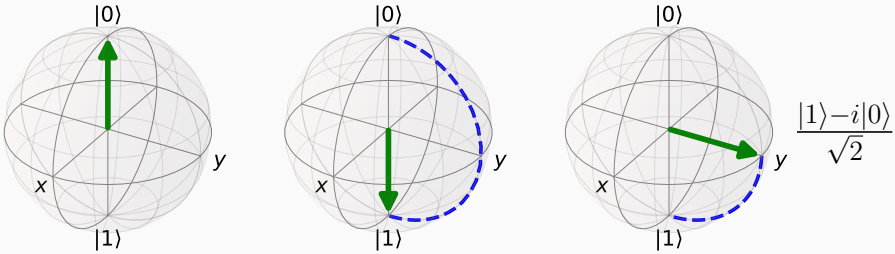

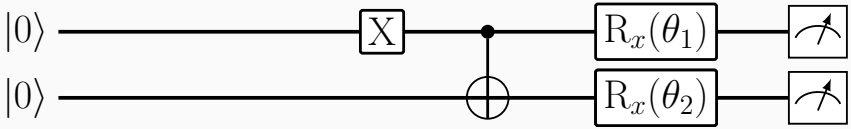

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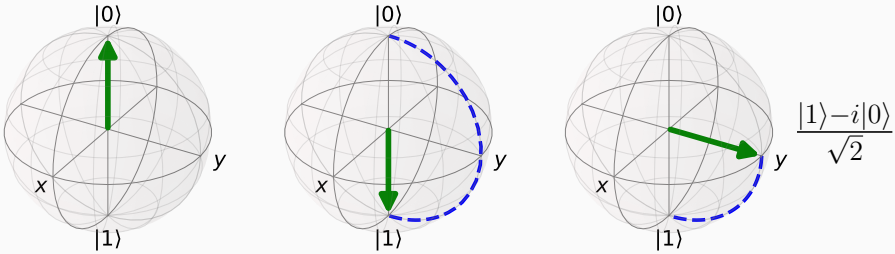

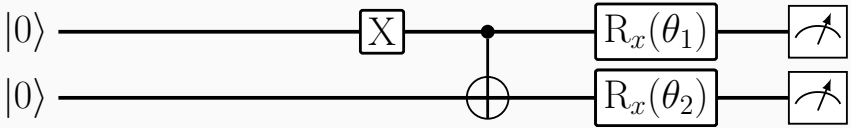

$$|\Psi\rangle \approx \hat{U}(\boldsymbol{\theta})\,|\mathbf{0}\rangle$$

Multiple Qubits – Entanglement

Bringing **two** qubits together:

$$|\Psi\rangle = \overbrace{(|0\rangle + |1\rangle)}^{\text{qubit 1}} \otimes \overbrace{(|0\rangle + |1\rangle)}^{\text{qubit 2}} = |00\rangle + |01\rangle + |10\rangle + |11\rangle \qquad \text{4 states}$$

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Three qubits:

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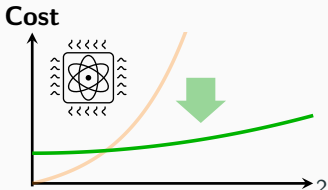
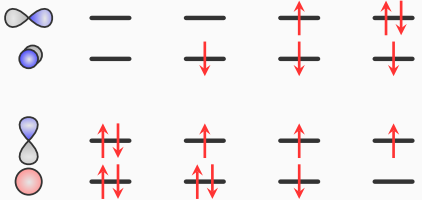
N qubits can encode exponentially many (2^N) states.
40 qubits enough to encode the $\sim 2 \cdot 10^9$ states of F_2!
$\rightarrow$ Need new **quantum algorithms** to use this potential advantage!



How can Quantum Computing help Quantum Chemistry?

2^N states

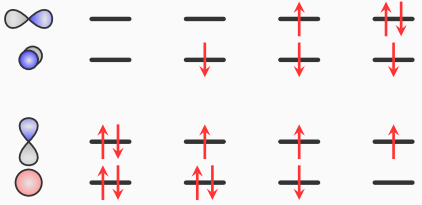


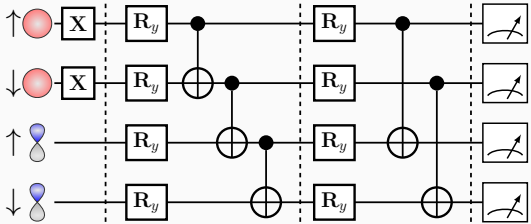
$|\Phi_{\mathrm{HF}}\rangle = |1100\rangle\,, |\Phi_i^a\rangle = |1010\rangle\,, \ldots$

How can Quantum Computing help Quantum Chemistry?

Fermion to qubit mapping

2^N states ⟶ N qubits





$|\Phi_{\mathrm{HF}}\rangle = |1100\rangle\,, |\Phi_i^a\rangle = |1010\rangle\,, \ldots$

- Map our problem (Hamiltonian/basis functions) onto quantum hardware/qubits
  - Qubits encode occupation of spin-orbitals $\in [0, 1]$

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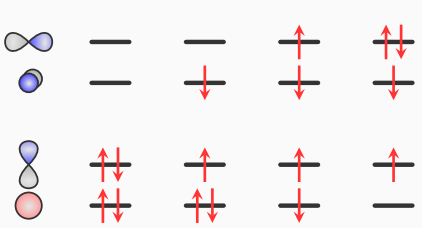

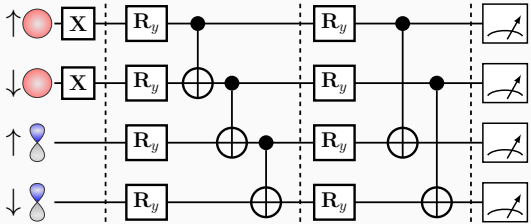

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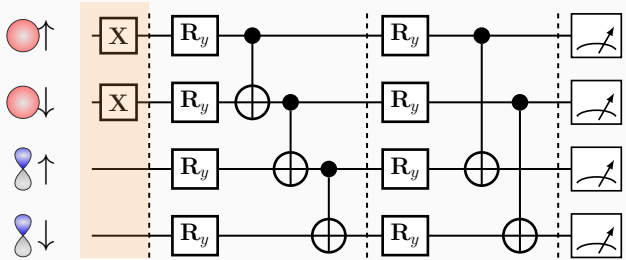
→ Use quantum algorithms for ground-, excited states, dynamics, ...

Quantum Chemistry on Quantum Hardware

1) Prepare an initial state $|\Phi_0\rangle$:

$$|\Phi_0\rangle = \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$



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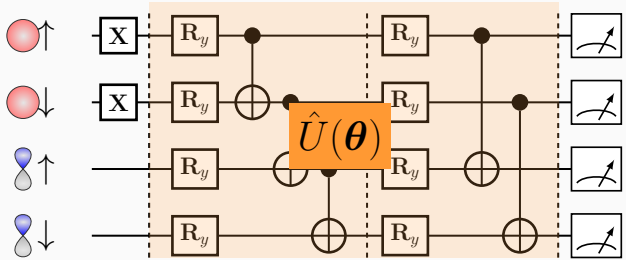


2) Perform **unitary** operations of chosen quantum algorithm:

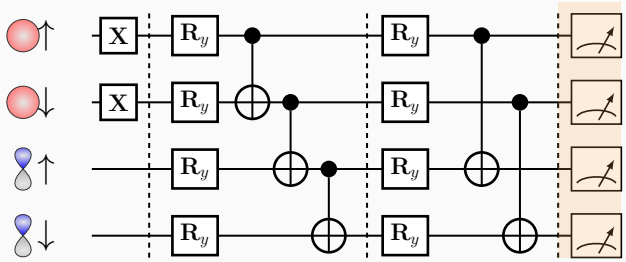
$$|\Phi\rangle = \hat{U}\,|\Phi_0\rangle = a_1 \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} + a_2 \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} + \cdots + a_{2^N} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

Quantum Chemistry on Quantum Hardware

1) Prepare an initial state $|\Phi_0\rangle$:

$$|\Phi_0\rangle = \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

3) Measure observable $\langle \hat{O} \rangle$

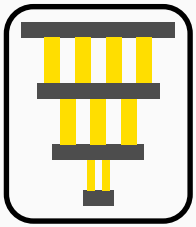


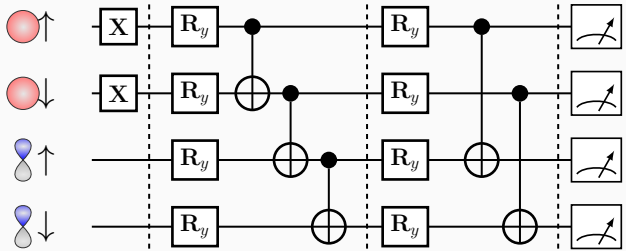
2) Perform **unitary** operations of chosen quantum algorithm:

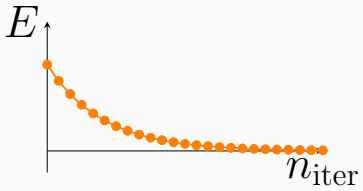
$$|\Phi\rangle = \hat{U}\,|\Phi_0\rangle = a_1 \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} + a_2 \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} + \cdots + a_{2^N} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

$\sim$ 15mK

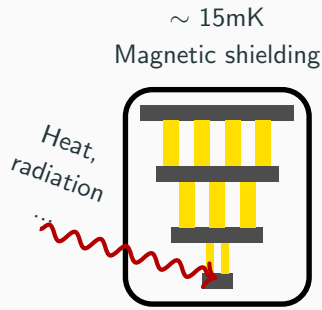
Magnetic shielding

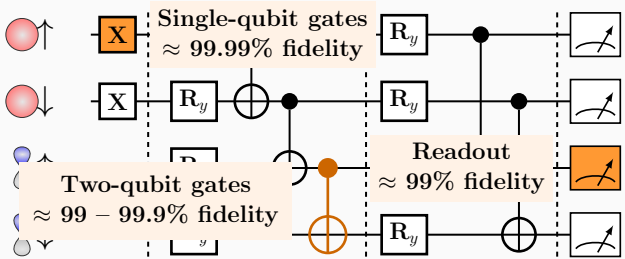






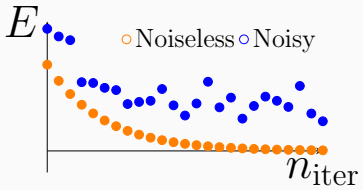
Quantum Chemistry on Quantum Hardware



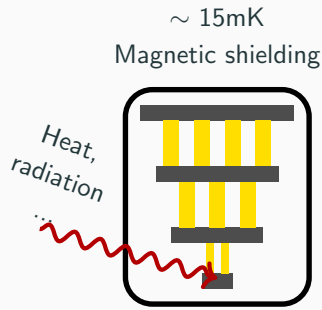


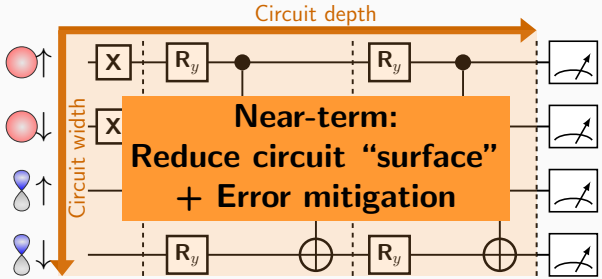
Effect of noise:

- Bit flip: $|0\rangle \leftrightarrow |1\rangle$
- Phase flip: $|0\rangle \leftrightarrow -|0\rangle$
- Decoherence: $|0\rangle + |1\rangle \rightarrow |0\rangle + e^{i?}|1\rangle$
- ...



Quantum Chemistry on Quantum Hardware





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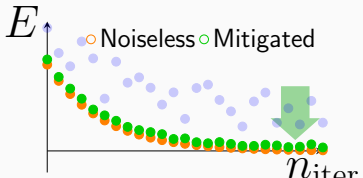
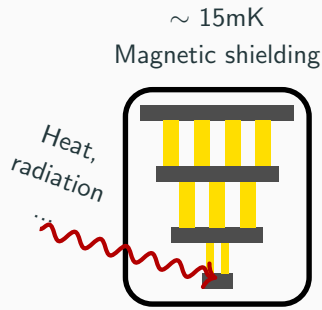
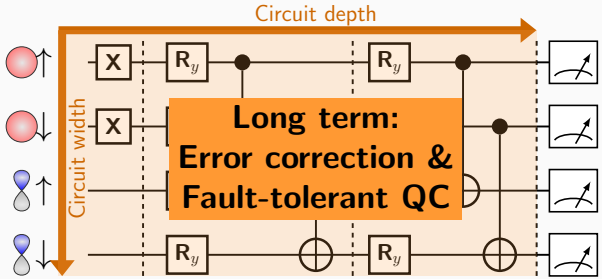


Quantum Chemistry on Quantum Hardware

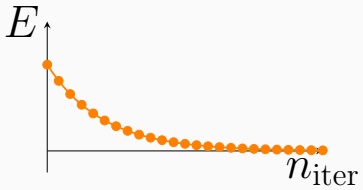




Use many physical qubits to encode a logical qubit:

$11111 \to 1$ $\quad$ $11\mathbf{0}11 \to 1$

$00000 \to 0$ $\quad$ $0\mathbf{1}000 \to 0$



Transition toward fault-tolerance

NISQ:

- Noisy and small quantum devices
- Limited utility
- Hybrid approaches

Fault-tolerant QC:
Quantum advantage

- Shor's and Grover's algorithm
- Quantum phase estimation

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Continuous transition to fault-tolerant QC:

- Develop intuition on quantum algorithm development
- Transferability of developed algorithms to FT regime
- Feedback for experimentalists to improve devices

– Near-term utility and relevant applications
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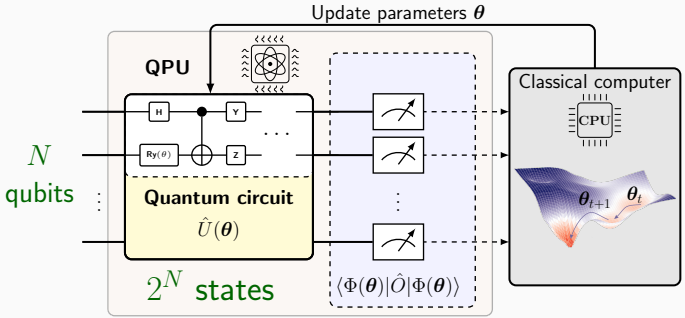
Near-term approaches and our work

NISQ Era – Hybrid Quantum-Classical Approach

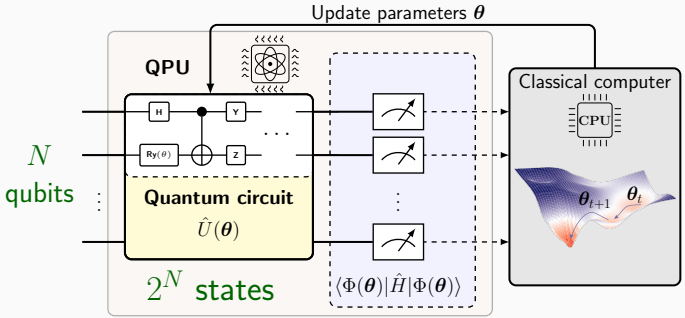
Use benefits of both quantum and classical resources



- Use short-depth quantum circuits that fit current hardware
- Improve on classical estimates by non-classical states
- Store quantum state with exponentially fewer resources

NISQ Era – Hybrid Quantum-Classical Approach

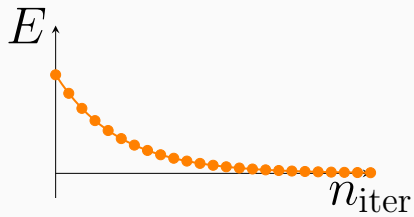
Use benefits of both quantum and classical resources



Variational Quantum Eigensolver

$$E(\boldsymbol{\theta}) = \langle\Phi(\boldsymbol{\theta})|\,\hat{H}\,|\Phi(\boldsymbol{\theta})\rangle$$

Quantum Imaginary Time Evolution



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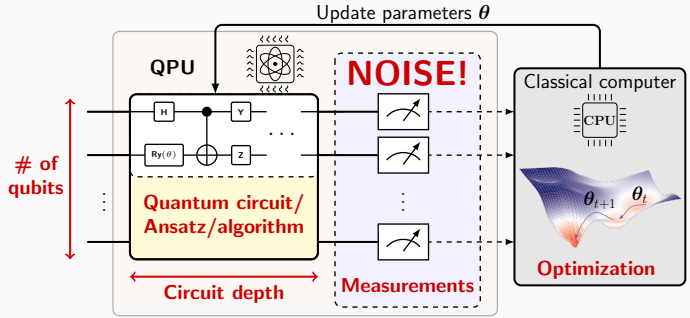

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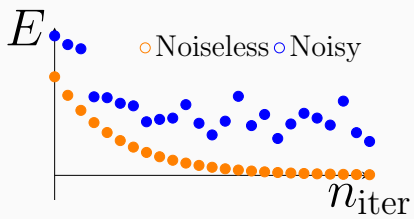

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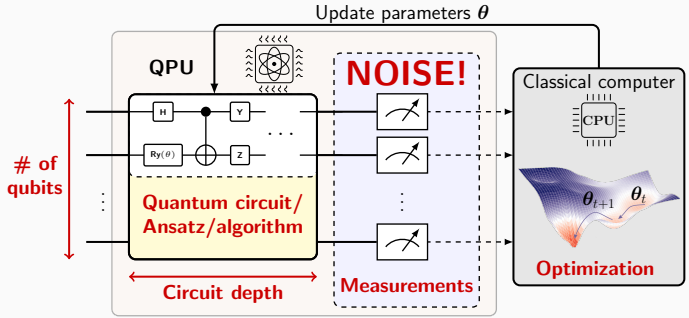
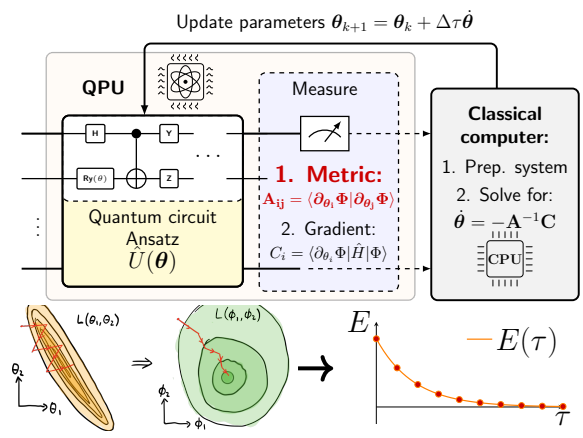


- Algorithms:
  Quantum imaginary time evolution (QITE)
- Classical optimization
- Resource reduction:
  Qubits and circuit depth
- Error mitigation

Quantum Computing – Algorithms and Classical Optimization

Orders of magnitude increased accuracy for quantum many-body problems on quantum computers via an exact transcorrelated method, *Phys. Rev. Research* **5**, 023174 (2023), I. O. Sokolov*, **W. Dobrautz***, H. Luo, A. Alavi, I. Tavernelli

Variational Quantum Imaginary Time Evolution:



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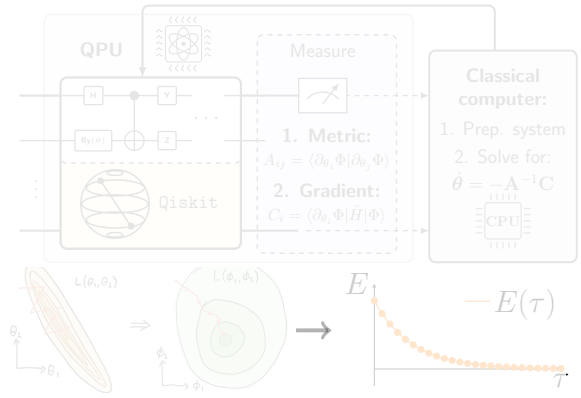
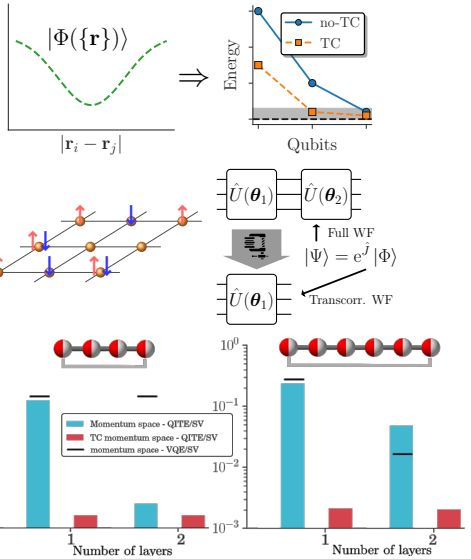
Variational Quantum Imaginary Time Evolution:

Update parameters $\theta_{k+1} = \theta_k + \Delta\tau\dot{\theta}$





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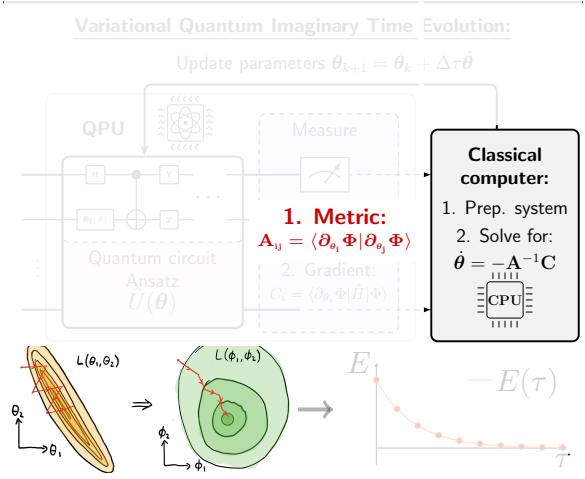
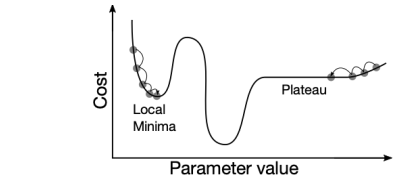
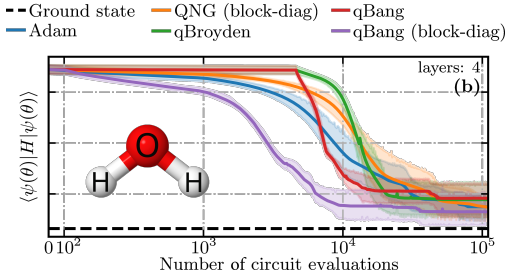
Optimizing Variational Quantum Algorithms with qBang: Efficiently Interweaving Metric and Momentum to Tackle Flat Energy Landscapes,
D. Fitzek, R. S. Jonsson, **W. Dobrautz**, C Schäfer, Quantum **8**, 1313 (2024)







Quantum Computing – Reference-state Error Mitigation (REM)

Reference-State Error Mitigation: A Strategy for High Accuracy Quantum Computation of Chemistry, *J. Chem. Theory Comput.*, **19**, 3, 783 (2023)

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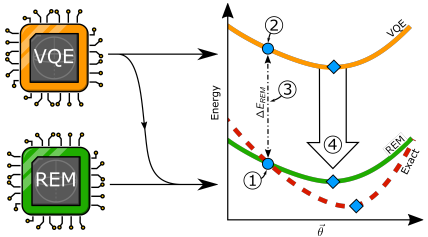

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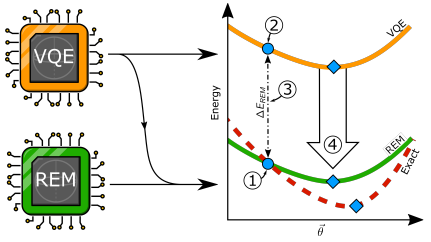

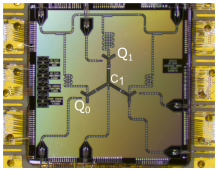

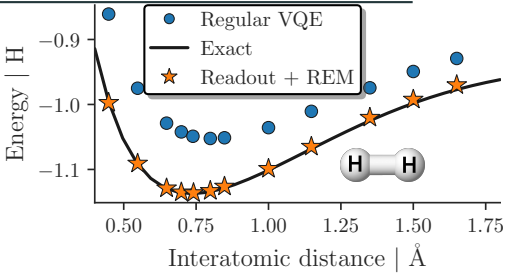

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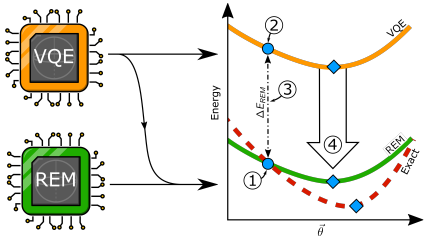

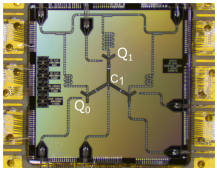

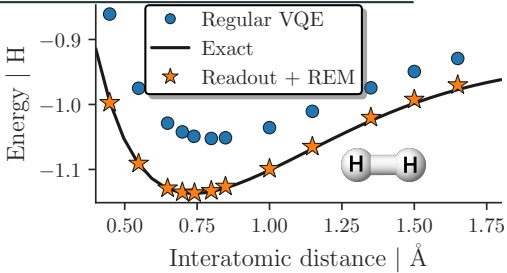

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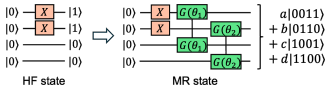

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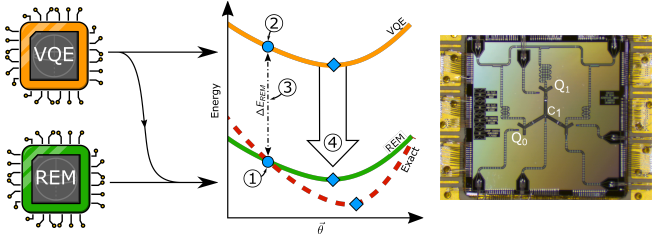

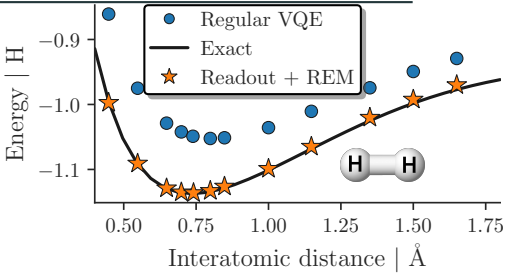

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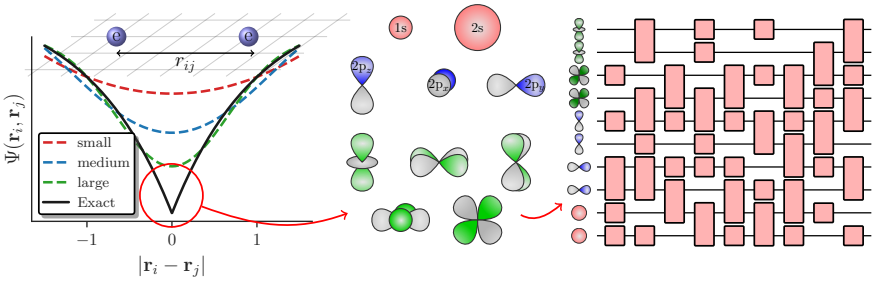
– **Electron density**: M. Skogh, P. Lolur, **W. Dobrautz**, C. Warren, J. Biznárová, A. Osman, G. Tancredi, J. Bylander, M. Rahm, Chemical Science **15**, 2257 (2024)

Resource Reduction: Qubits and circuit depth



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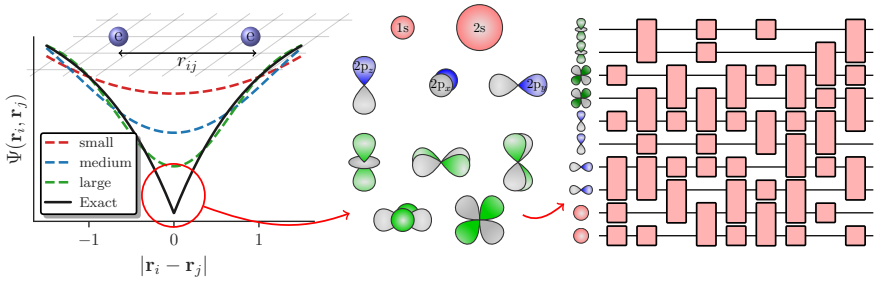

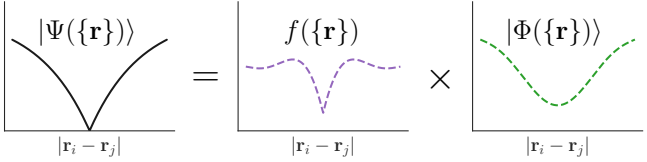

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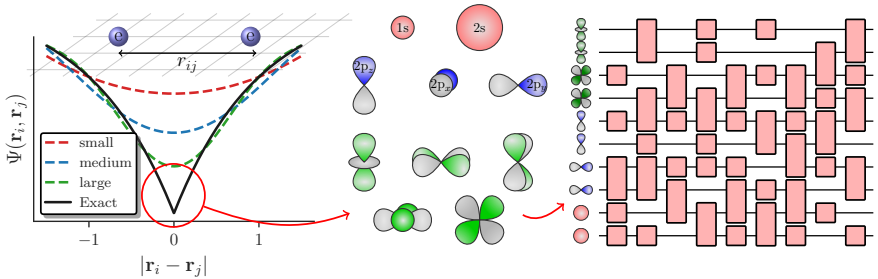
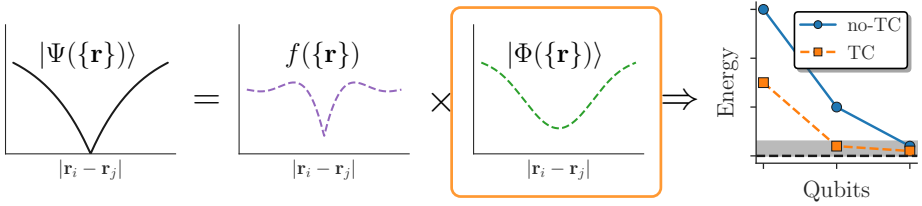
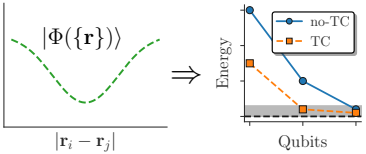
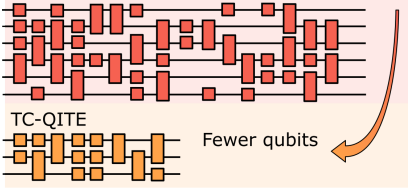




Quantum Computing – Resource Reduction – Transcorrelation



Smaller basis $\rightarrow$ fewer qubits



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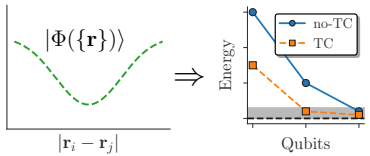

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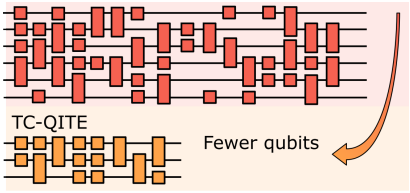
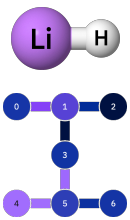
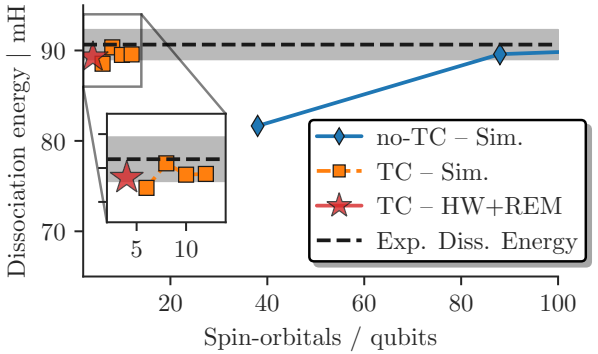
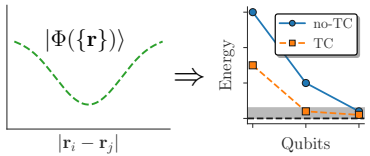


Towards real chemical accuracy on current quantum hardware through the transcorrelated method, J. Chem. Theory Comput. **20**, 10, 4146 (2024)
W. Dobrautz, I. O. Sokolov, K. Liao, P. Lopez Rios, M. Rahm, A. Alavi, I. Tavernelli

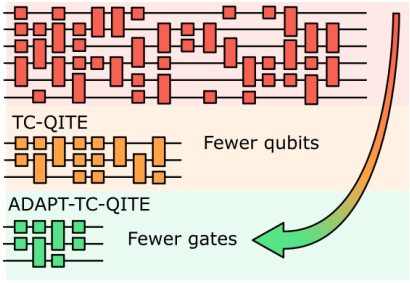




Quantum Computing – Resource Reduction – Transcorrelation



Smaller basis → fewer qubits



Towards real chemical accuracy on current quantum hardware through the transcorrelated method, J. Chem. Theory Comput. **20**, 10, 4146 (2024)
W. Dobrautz, I. O. Sokolov, K. Liao, P. Lopez Rios, M. Rahm, A. Alavi, I. Tavernelli

Reducing quantum circuit depth for noise-resilient quantum chemistry,
E. Magnusson, A. Fitzpatrick, S. Knecht, M. Rahm, **W. Dobrautz**,
Faraday Discussions on *Correlated Electronic Structure* (2024)

Summary and Outlook

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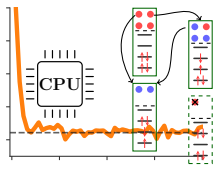

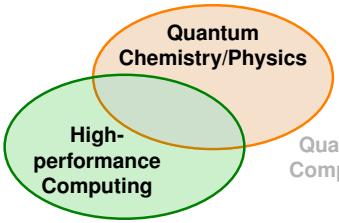

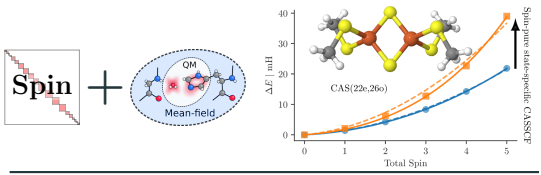

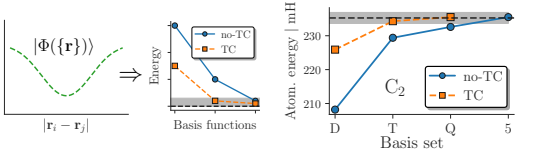

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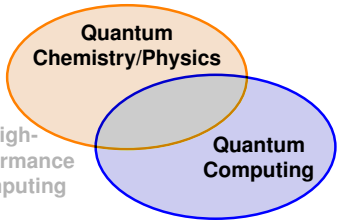

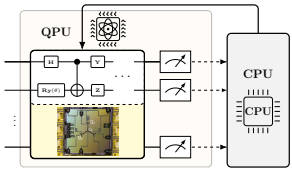

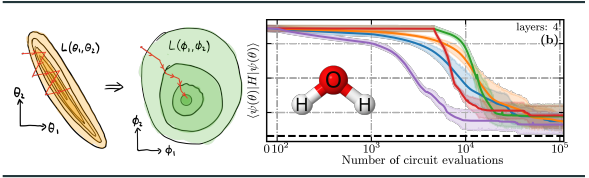

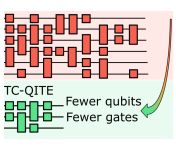

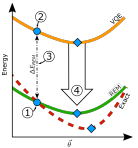

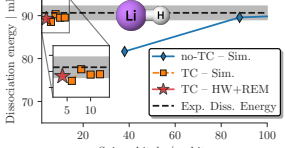

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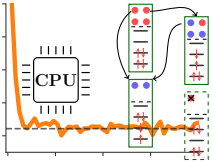

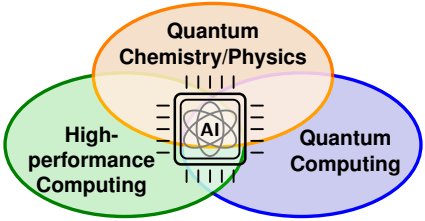

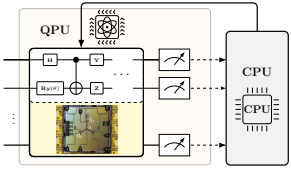

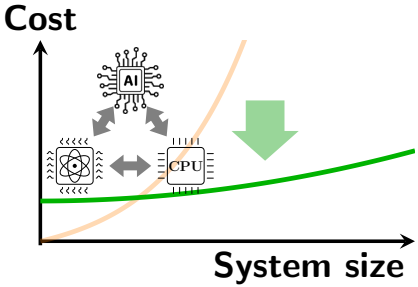

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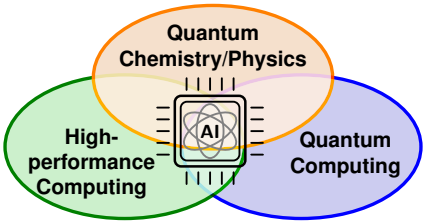
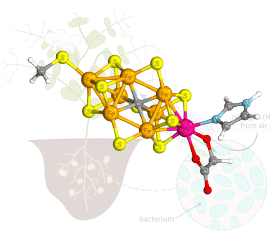
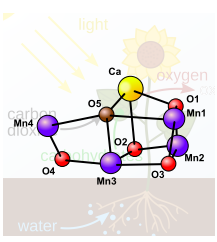
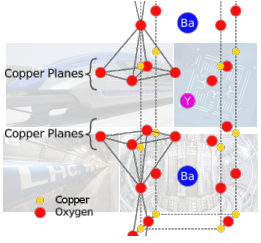




Iron molybdenum cofactor (FeMoCo): nitrogen fixation of nitrogenase



Manganese Calcium Oxygen Clusters: Oxygen evolving clusters in photosystem II



2D Copper-Oxide planes in cuprates: unconventional high-T_c superconductivity

Thank you for your attention!

qHPC-GREEN – BMBF JRG

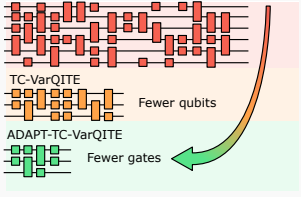
HPC+QC toolkit to study strongly correlated quantum chemistry problems

Simulation of bio-chemical transition metal compounds relevant for the **green energy transition**

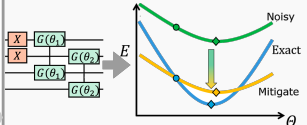
WP1

Resource reduction:

- Accurate calculations for relevant problems – Quantum imaginary time evolution
- Transcorrelation, active spaces, spin-symmetry and adaptive quantum Ansätze

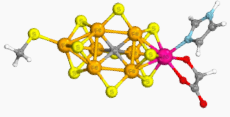


Error mitigation:



Relevant applications:

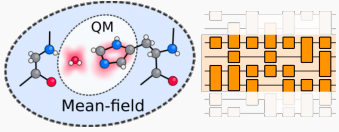
Electronic structure of transition metal complexes



WP2

Algorithms and software for relevant insights:

- Electronic properties
- Quantum embedding
- Excited states
- Efficient QC+HPC implementation



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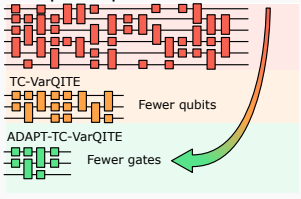

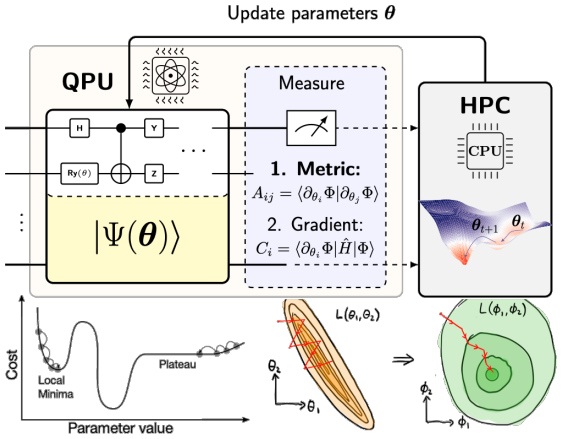

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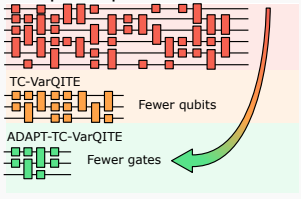
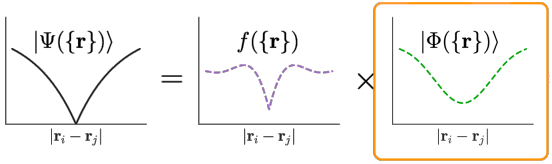
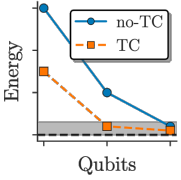
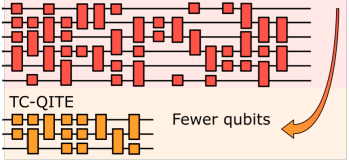




$$\hat{H}_{\mathrm{TC}} = f^{-1}\hat{H}f \quad \Rightarrow \quad \hat{H}_{\mathrm{TC}}|\Phi\rangle = E|\Phi\rangle$$





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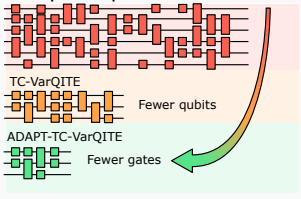

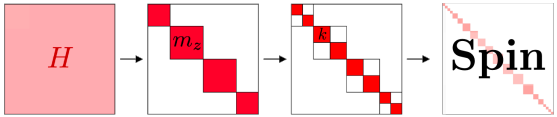

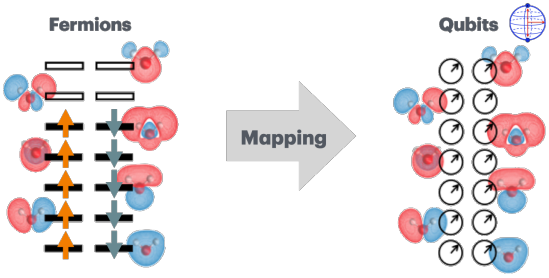

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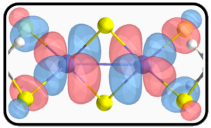
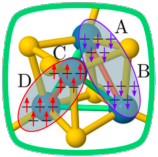
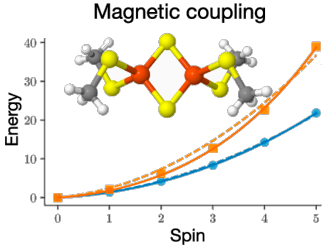
Electron densities



Spin-correlations



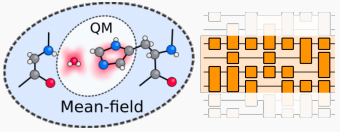
Magnetic coupling



WP2

Algorithms and software for relevant insights:

- **Electronic properties**
- Quantum embedding
- Excited states
- Efficient QC+HPC implementation



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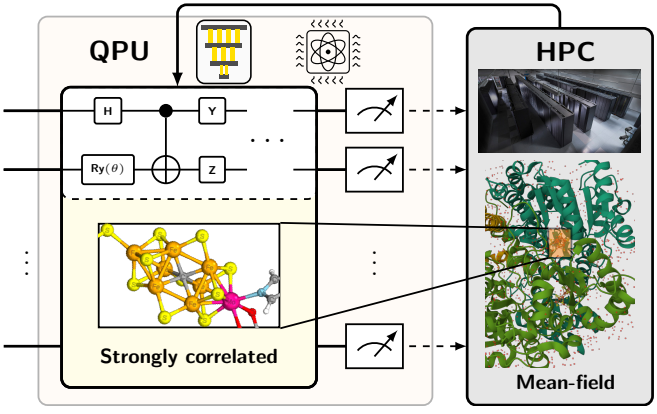

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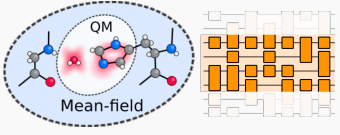

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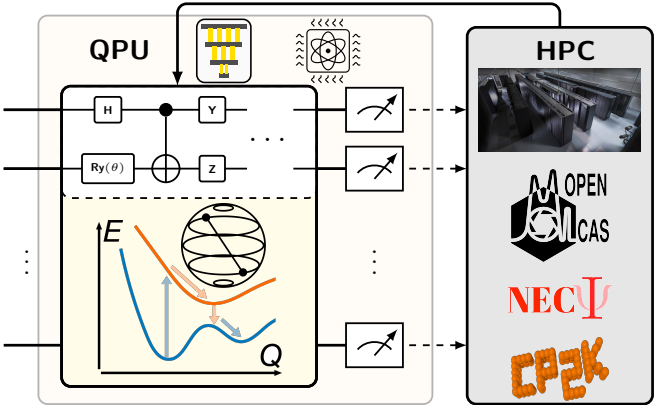

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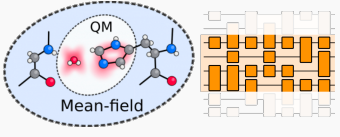

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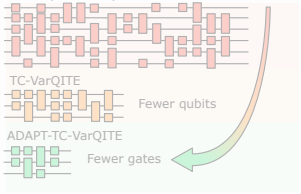
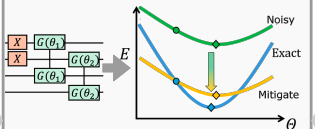


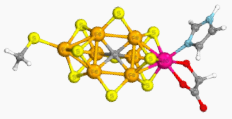
WP1-2

Error mitigation:



Relevant applications:

Electronic structure of transition metal complexes



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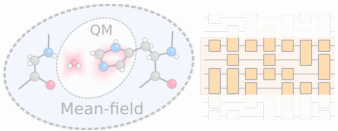
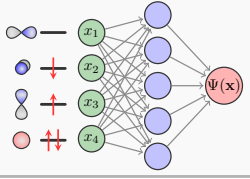


AI 4 Quantum

Novel ML approaches for the computational study of complex quantum systems

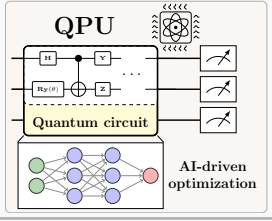
Neural Network States for Quantum Matter

- Compress exponential complexity of target solution, $\Psi(\mathbf{x})$
- Reinforcement learning approach
- Resource reduction: physics-informed, symmetry-preserving neural quantum states



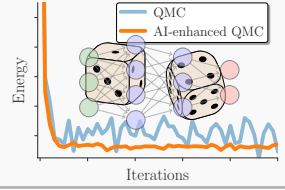
AI-driven Quantum Computing Approaches

- Increase noise-resilience and optimization of quantum algorithms
- ML optimization of quantum circuit Ansätze for $\Psi(\mathbf{x})$: Gates, parameters $\boldsymbol{\theta}$ and transferability



AI-enhanced Quantum Monte Carlo Methods

- Extend reach and acc. of QMC
- AI-enhanced FCIQMC: Agent-based sampling of exponential state space
- Big data ML approach for optimal sampling



Quantum.AI

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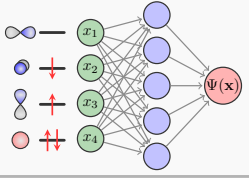
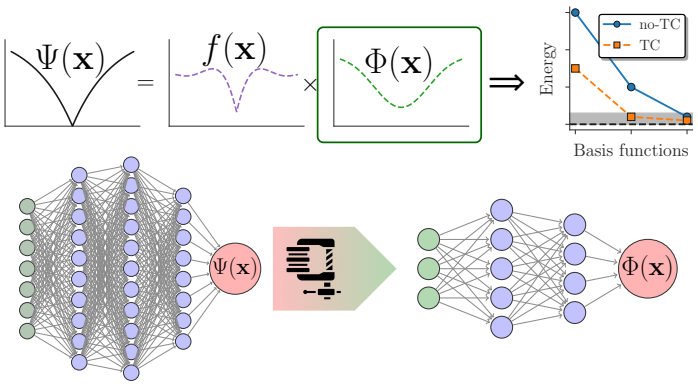
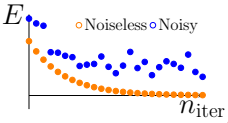
- **Resource reduction: physics-informed**, symmetry-preserving neural quantum states

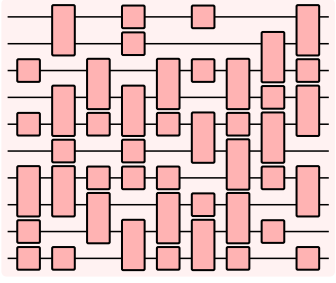




AI 4 Quantum

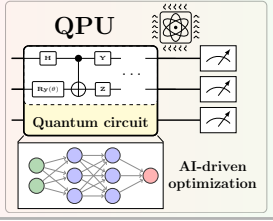
Novel ML approaches for the computational study of complex quantum systems





AI-driven Quantum Computing Approaches

- Increase noise-resilience and optimization of quantum algorithms
- ML optimization of quantum circuit Ansätze for $\Psi(\mathbf{x})$: Gates, parameters $\boldsymbol{\theta}$ and transferability



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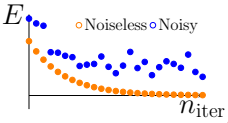

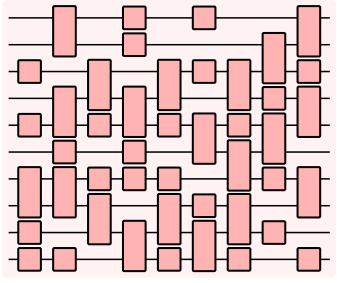

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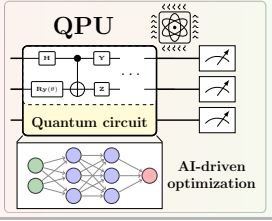

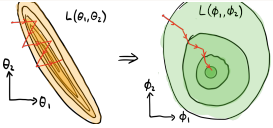

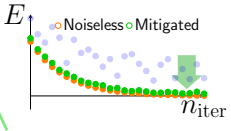

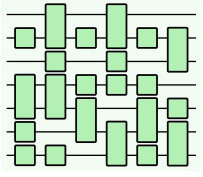

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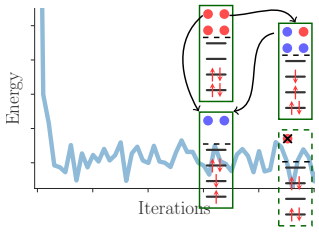

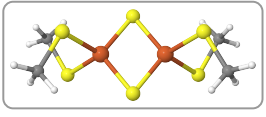

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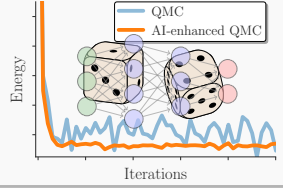
- Extend reach and acc. of QMC
- AI-enhanced FCIQMC: Agent-based sampling of exponential state space
- Big data ML approach for optimal sampling



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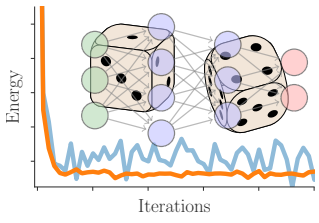

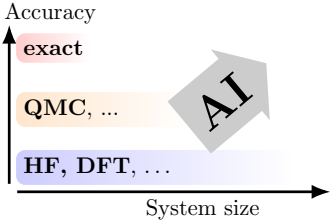

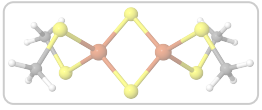

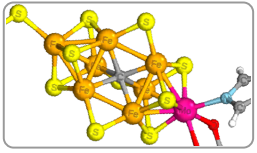

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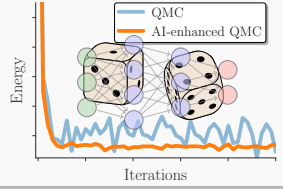
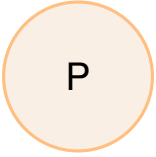


Vision of the field



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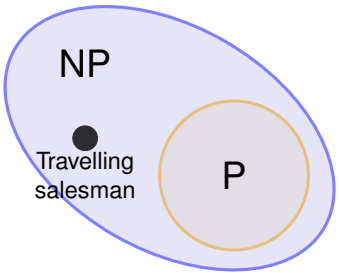

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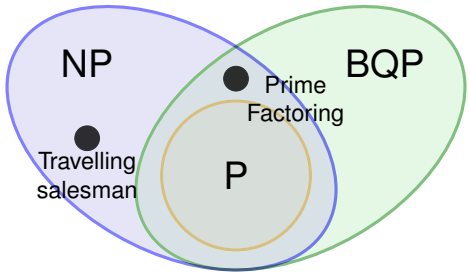

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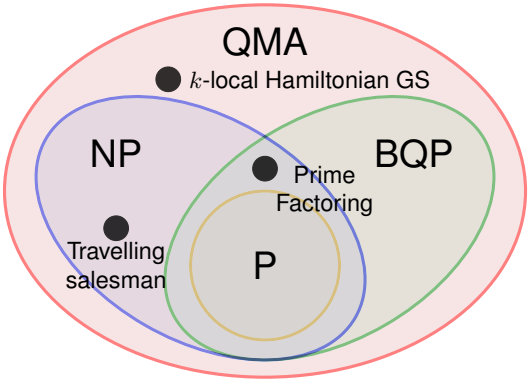

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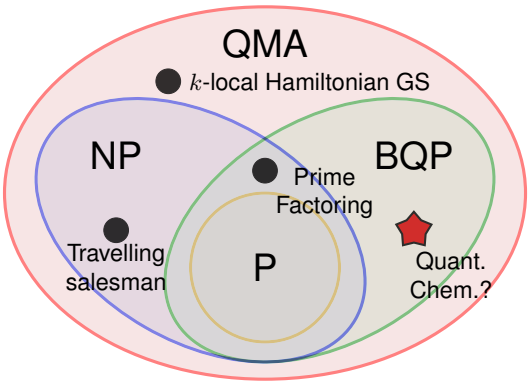

- Hartree-Fock is in QMA
  – PCCP, **15**, 397
- Even if GS search is in QMA
  – PRX Quantum **3**, 020322
  maybe we still find efficient algorithms
- Quantum dynamics is known to be efficient
  $\rightarrow$ Quantum phase estimation
  – arXiv:quant-ph/0606179

Possible Quantum Advantage – Quantum Phase Estimation

Unitary op. Phase

$$\hat{U}|\Psi\rangle = \mathrm{e}^{i\theta}|\Psi\rangle$$

Eigenstate

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$$\hat{U}\left|\Psi\right\rangle = \mathrm{e}^{i\theta}\left|\Psi\right\rangle$$

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Schrödinger eq.

$$\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle$$

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$$\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle$$

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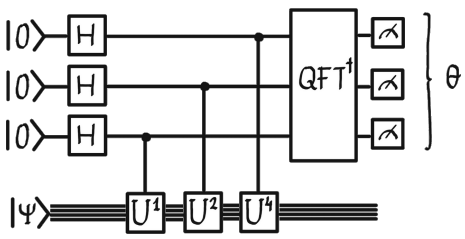

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No matrix diagonalization!
Subroutine of Shor's algorithm

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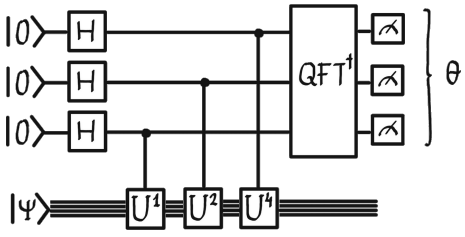

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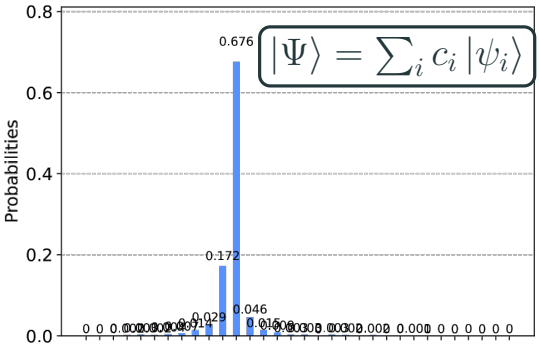

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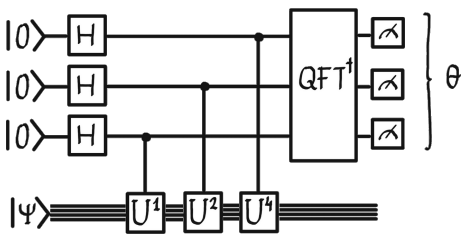

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$$\downarrow$$

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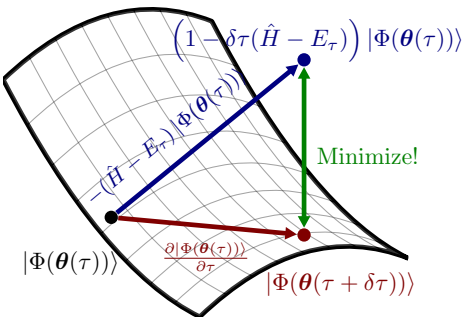
- Many qubits, deep circuits → requires error corrected quantum devices
- State preparation: how to get good approximations of $|\Psi\rangle$?

VarQITE

Map imaginary-time evolution to parameters $\boldsymbol{\theta}(\tau)$ of Ansatz $|\Phi(\boldsymbol{\theta}(\tau))\rangle \approx |\Psi(\tau)\rangle$



- Imag-time Schrödinger equation, for small $\delta\tau$:

$$\mathrm{e}^{-\delta\tau(\hat{H}-E_\tau)} \approx (1-\delta\tau(\hat{H}-E_\tau))$$

- Variation of $|\Phi(\boldsymbol{\theta}(\tau))\rangle$ w.r.t. to parameters $\partial\theta$:

$$|\Phi(\boldsymbol{\theta}(\tau+\delta\tau))\rangle \approx |\Phi(\boldsymbol{\theta}(\tau))\rangle + \sum_j \frac{\partial\,|\Phi(\boldsymbol{\theta}(\tau))\rangle}{\partial\theta_j}\frac{\partial\theta_j}{\partial\tau}\delta\tau$$

- McLachlan's variational principle

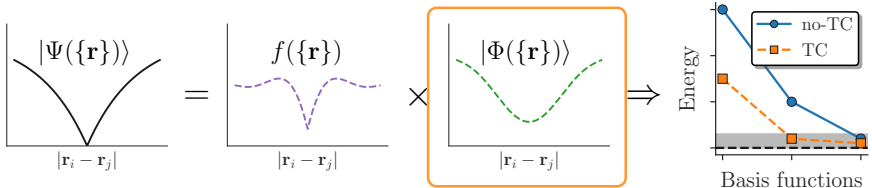
$$\delta\left|\left(\frac{\partial}{\partial\tau}+(\hat{H}-E_\tau)\right)|\Phi(\boldsymbol{\theta}(\tau))\rangle\right| = 0$$

Evolution of parameters: $\dot{\boldsymbol{\theta}} = \mathbf{A}^{-1}\mathbf{C}, \quad A_{ij} = \frac{\partial\,\langle\Phi|}{\partial\theta_i}\frac{\partial\,|\Phi\rangle}{\partial\theta_j} \qquad C_i = -\frac{\partial\,\langle\Phi|}{\partial\theta_i}\hat{H}\,|\Phi\rangle$

McLachlan, Molecular Physics, 8(1),39 (1964); McArdle *et al.*, npj Quantum, 5, 75 (2019); Yuan *et al.* Quantum 3, 191 (2019);

Cusp Condition – The Transcorrelated (TC) Method

Form of the **cusp** is known* $\rightarrow$ describe it with a **wavefunction Ansatz**



The transcorrelated (TC) method: use a Jastrow Ansatz, $\mathrm{e}^{\hat{J}}$, with optimizable parameters J_{ij} (via VMC†) to transform the Hamiltonian:

$$|\Psi(\{\mathbf{r}\})\rangle = \exp\left[\sum_{ij} J_{ij} g(\tilde{r}_{ij})\right] |\Phi(\{\mathbf{r}\})\rangle \quad \rightarrow \quad \hat{H}\,|\Psi\rangle = E\,|\Psi\rangle \quad \rightarrow \quad \overbrace{\mathrm{e}^{-\hat{J}}\,\hat{H}\,\mathrm{e}^{\hat{J}}}^{\bar{H}_{\mathrm{TC}}} |\Phi\rangle = E\,|\Phi\rangle$$

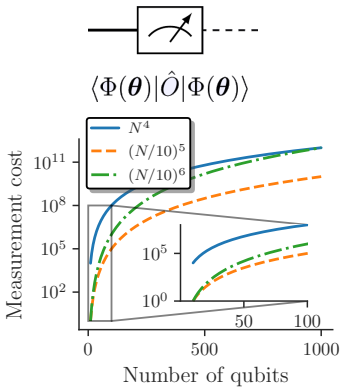
$|\Phi\rangle$ easier to represent with less basis functions $\rightarrow$ immense resource reduction

*Kato (1957); Boys and Handy (**1969**); Kutzelnigg (1985); **WD**, Luo, Alavi, PRB **99** (7), 075119 (2019); Cohen, Luo, Guther, **WD**, Tew, Alavi, JCP **151** (6), 061101 (2019); **WD**, Cohen, Alavi, Giner, JCP **156** (23), 234108 (2022); †Haupt, Hosseini, López Ríos, **WD**, Cohen and Alavi, JCP **158**, 224105 (2023);

Scaling of TC – Measurement Cost

$$\bar{H} = \sum_{pq,\sigma} h_q^p a_{p,\sigma}^\dagger a_{q,\sigma} + \frac{1}{2} \sum_{pqrs,\sigma\tau} \bar{V}_{rs}^{pq} a_{p,\sigma}^\dagger a_{q,\tau}^\dagger a_{s,\tau} a_{r,\sigma} - \frac{1}{6} \sum_{pqrstu,\sigma\tau\lambda} L_{stu}^{pqr} a_{p,\sigma}^\dagger a_{q,\tau}^\dagger a_{r,\lambda}^\dagger a_{u,\lambda} a_{t,\tau} a_{s,\sigma}$$

- Measurement formally scaling as N^6, with N being the number of orbitals
- Recently shown that N^6-scaling terms can be neglected to good accuracy*
- **xTC work on N^4-scaling approximation**‡
- **Order of magnitude less orbitals:** since also no core functions needed in basis set†
- **Shorter circuit depth**, due to more compact ground state!#



*WD *et al.*, Journal of Chemical Physics 156 (23), 234108 (2022); †Cohen, Luo, Guther, **WD**, Tew, Alavi, JCP **151** (6), 061101 (2019); ‡Christlmaier, Schraivogel, López Ríos, Alavi, Kats, JCP **159**, (1) 014113 (2023); #Sokolov, **WD**, Luo, Alavi, Tavernelli, PR Research **5** (2), 023174 (2023);

Similarity Transformation – Transcorrelated (TC) Method

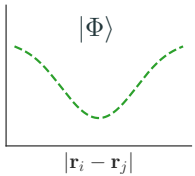
Describe the cusp condition and/or capture part of correlation with a correlated wavefunction Ansatz → incorporate into Hamiltonian!

Instead of $\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle$ solve the similarity transformed (ST) problem

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle\,, \quad \text{with} \quad |\Psi\rangle = \mathrm{e}^{\hat{J}}\,|\Phi\rangle$$

$$\mathrm{e}^{-\hat{J}} \rightarrow | \quad \hat{H}\,\mathrm{e}^{\hat{J}}\,|\Phi\rangle = E\,\mathrm{e}^{\hat{J}}\,|\Phi\rangle\,, \qquad \left(\hat{J}^\dagger = \hat{J}\right)$$

$$\left(\mathrm{e}^{-\hat{J}}\,\hat{H}\,\mathrm{e}^{\hat{J}}\right)|\Phi\rangle = E\,\mathrm{e}^{-\hat{J}}\,\mathrm{e}^{\hat{J}}\,|\Phi\rangle = E\,|\Phi\rangle$$



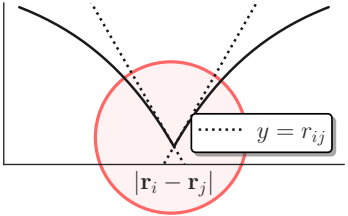
Baker-Campbell-Hausdorff (BCH) exp. to obtain TC Hamiltonian:

$$\bar{H} = \mathrm{e}^{-\hat{J}}\,\hat{H}\,\mathrm{e}^{\hat{J}} = \hat{H} + [\,\hat{H}, \hat{J}\,] + \frac{1}{2}\,[\,[\,\hat{H}, \hat{J}\,], \hat{J}\,] + \ldots$$

For the molecular Hamiltonian the BCH exp. terminates at 2nd order, as only kinetic energy operators in $\hat{H}$ do not commute with $\hat{J}$!

Hirschfelder, JCP, **39**, 3145 (1963); Boys and Handy, Proc. R. Soc. A (**1969**); **WD**, Luo, Alavi, PRB **99** (7), 075119 (2019); Cohen, Luo, Guther, **WD**, Tew, Alavi, JCP **151** (6), 061101 (2019); **WD**, Cohen, Alavi, Giner, JCP **156** (23), 234108 (2022)

Explicitly Correlated methods



Linear behavior in electron-electron distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ for small r_{ij}!

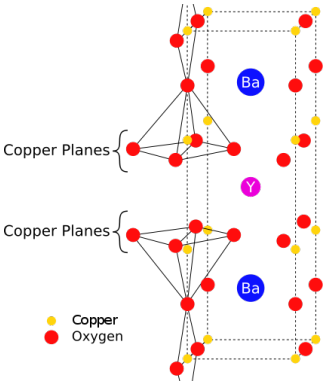
R12 methods*: $\quad |\Psi\rangle = r_{ij}\,|\Phi\rangle$

F12 methods†: $\quad |\Psi\rangle = f(r_{ij})\,|\Phi\rangle\,, \quad f(r_{ij}) = \dfrac{1-\exp(-\gamma r_{ij})}{\gamma}$

Jastrow Ansatz‡: $\quad |\Psi\rangle = \mathrm{e}^{\hat{J}}\,|\Phi\rangle\,, \quad \hat{J} = \sum_{ij} J_{ij} g(\tilde{r}_{ij})$

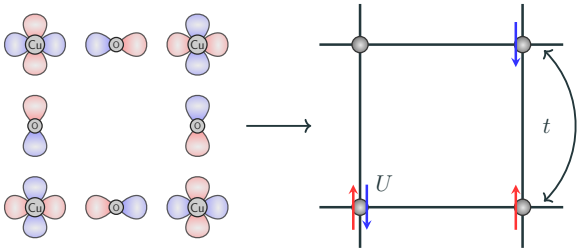
* Kutzelnigg, Theoretica chimica acta 68, 445 (1985); † Ten-no, J. Chem. Phys. 121, 117 (2004); ‡ Jastrow, Phys. Rev. **98**, 1479 (1955);

High-T_C Superconductors and the Hubbard Model



YBCO

Mapping to an effective lattice model:



The Hubbard Hamiltonian

$$\hat{H} = -t \sum_{\langle i,j \rangle, \sigma} \left(c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c. \right) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

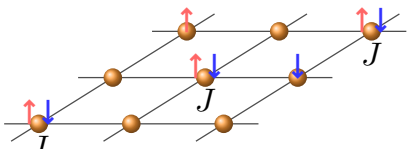
Strong interaction $\Rightarrow$ highly multiconfigurational

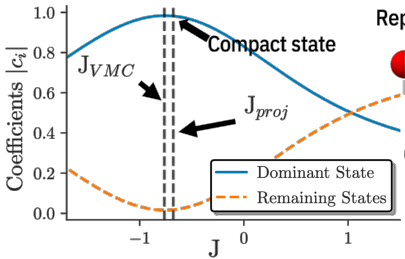
Hubbard, 1963; Kanamori, 1963; Gutzwiller; 1963; Anderson, 1987; Emery, 1987; Zhang and Rice, 1988; Bednorz and Müller, 1986

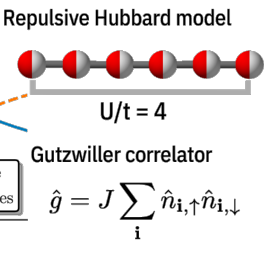
Reduce circuit depth with Transcorrelation

Suppress energetically unfavourable double occupancies via the *Gutzwiller* Ansatz:

$$\hat{g} = J \sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} : \qquad \hat{H} \quad \rightarrow \quad \mathrm{e}^{-\hat{g}}\,\hat{H}\,\mathrm{e}^{\hat{g}}$$







⇒ **Increased compactness** of the right EV, due to downfolding of correlations into Hamiltonian

⇒ Does the increased compactness/more single reference character have an impact on the necessary quantum Ansatz depth?

Gutzwiller, PRL 10, **159** (1963); Tsuneyuki, Prog. Theor. Phys. Supp., **176**, 134 (2008); Scuseria et al., PRB, **91**, 041114 (2015); **WD**, Luo, Alavi, PRB, **99**, 075119 (2019); Sokolov, **WD**, Luo, Alavi, Tavernelli, Physical Review Research 5 (2), 023174 (2023)

Full Configuration Interaction Quantum Monte Carlo

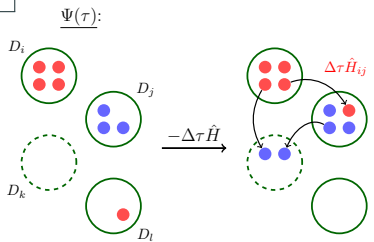
- *Projector MC method* based on the **imaginary-time Schrödinger equation**, stochastically sampling FCI wavefunction. Integration leads to an iterable equation:

$$i\frac{\partial\left|\Psi(t)\right\rangle}{\partial t} = \hat{H}\left|\Psi(t)\right\rangle \overset{\tau=it}{\rightarrow} \frac{\partial\left|\Psi(\tau)\right\rangle}{\partial\tau} = -\hat{H}\left|\Psi(\tau)\right\rangle \rightarrow \left|\Psi_{GS}\right\rangle \propto \lim_{\tau\rightarrow\infty} \mathrm{e}^{-\tau\hat{H}}\left|\Phi(\tau=0)\right\rangle$$

- *First order* Taylor expansion $\mathrm{e}^{-\Delta\tau\hat{H}} \approx 1-\Delta\tau\hat{H}$ leads to the *working equation:*

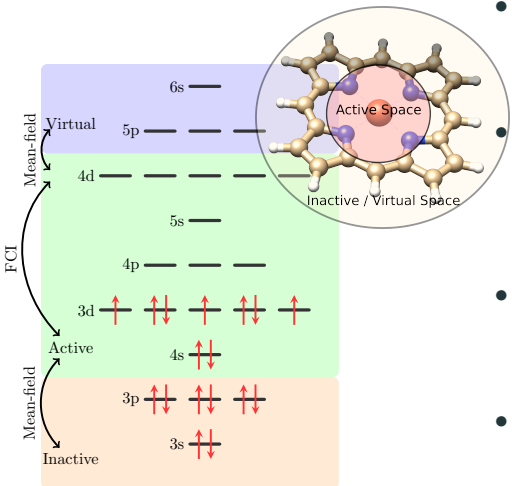
$$\boxed{c_i(\tau+\Delta\tau) = \left[1-\Delta\tau H_{ii}\right]c_i(\tau) - \Delta\tau\sum_{j\neq i} H_{ij}c_j(\tau)} \quad \text{for } c_i \text{ in } \left|\Psi(\tau)\right\rangle = \sum_i c_i\left|D_i\right\rangle$$

- Solved stochastically by the *population dynamics* of **"walkers"** in the discrete Slater determinant (SD) Hilbert space.
- **Multireference method** and highly accurate solutions for system sizes $> (50e, 50o)$ possible.



Booth, Thom, and Alavi, JCP, **131**, 054106 (2009); Guther, ..., **WD**, ..., Alavi, JCP, **153**, 034107 (**2020**)

Complete active space self-consistent field method (CASSCF)



- Well-established **embedding method** in quantum chemistry for the treatment of strongly correlated electron systems
- **Active space** consisting of the most important orbitals and electrons treated exactly. Configuration interaction solver (**FCIQMC**) yields ground state energy and wavefunction $|\Psi_0\rangle$
- Effect of the **environment** (Inactive/Virtual space) accounted for at the mean-field level by orbital rotations.
- **One- and two-body reduced density matrices** in the active space are needed!

$$\rho_{ij}^{\sigma} = \langle \Psi_0 | a_{i\sigma}^{\dagger} a_{j\sigma} | \Psi_0 \rangle$$

Roos, Taylor, Sigbahn, Chem. Phys., **48, 2**, 157 (1980)

The (Graphical) Unitary Group Approach

- **Spin-free** formulation of non-relativistic Hamiltonian:

$$\hat{H} = \sum_{ij}^{n} t_{ij}\, \hat{E}_{ij} + \frac{1}{2} \sum_{ijkl}^{n} V_{ijkl} \left(\hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} \right)$$

- Spin-preserving (singlet) excitation operators:

$$\hat{E}_{ij} = \hat{c}^{\dagger}_{i\uparrow} \hat{c}_{j\uparrow} + \hat{c}^{\dagger}_{i\downarrow} \hat{c}_{j\downarrow}, \quad \text{with} \quad [\, \hat{E}_{ij}, \hat{\mathbf{S}}^2 \,] = 0$$

- *same commutation relations* as **generators** of the Unitary Group $U(n)$
- Gel'fand-Tsetlin (GT) basis: **invariant** and **irreducible**, same storage cost as SDs
- **Efficient** matrix element calculation and excitation generation entirely via the Graphical Unitary Group Approach (GUGA)*, without reference to SDs

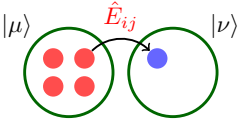
Paldus, J. Chem. Phys. **61**, 5321 (1974); Gel'fand and Tsetlin, Doklady Akad. Nauk SSSR, **71**, 1017 (1950), *Shavitt, Int. J. Quantum Chem., **12**, 131 (1977

Spin-free RDMs with GUGA-FCIQMC for CASSCF

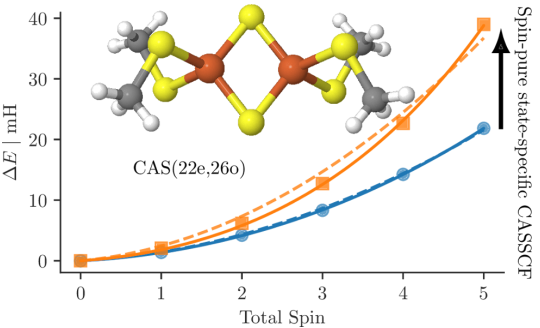
Sample one- and two-body RDMs in excitation process:

$$\rho_{ij} = \langle \Psi | \hat{E}_{ij} | \Psi \rangle = \sum_{dd'} c_d^{(\mathrm{I})} c_{d'}^{(\mathrm{II})} \langle d' | \hat{E}_{ij} | d \rangle,$$

$$\Gamma_{jl,ik} = \frac{1}{2} \langle \Psi | \hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} | \Psi \rangle$$



- Modest computational overhead
- Interfaced with `OpenMolcas`*
- (22e,26o) active space of Fe_2S_2 model system
- Reveals necessary higher order terms in Heisenberg mapping



*Overy *et al.*, JCP, **141**, 244117 (2014); †**WD**, Weser, Bogdanov, Alavi, Li Manni, JCTC **17** (9), 5684 (2021)