Reducing the Circuit Footprint for Noise-Resilient Quantum Chemistry via Transcorrelation and Adaptive Ansätze

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Quantinuum Seminar

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INSTITUTE OF

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Diese Maßnahme wird mitfinanziert mit Steuermitteln auf Grundlage des vom Sächsischen Landtag beschlossenen Haushalts.

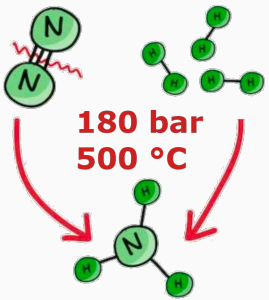
Outline

- Background and Motivation
- Transcorrelation to reduce the computational footprint on quantum hardware
- Results: Hubbard model and *ab initio* quantum chemistry problems
  - Hubbard model – Reduce circuit depth
  - *Ab initio* problems – Reduce circuit width (qubits)
- Adaptive Circuit Ansätze
- Conclusions

Background and Motivation

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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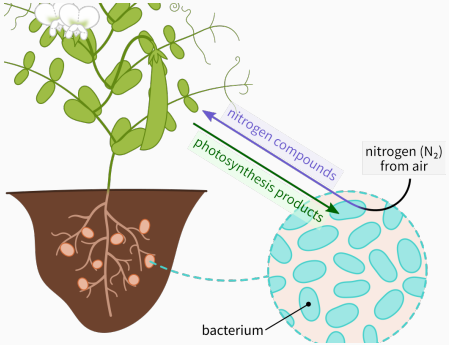
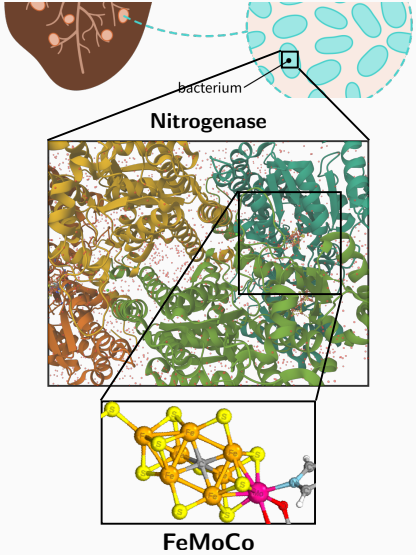
Biological nitrogen fixation



- **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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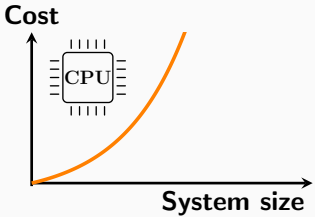
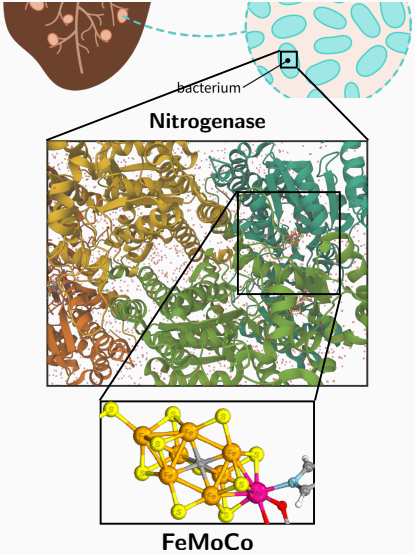
→ Numerical studies of relevant quantum phenomena necessary → $\hat{\mathbf{H}}\,|\mathbf{\Psi}\rangle = \mathbf{E}\,|\mathbf{\Psi}\rangle$

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





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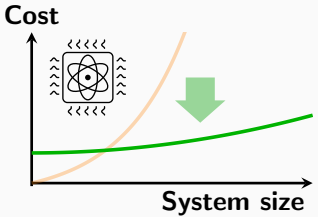
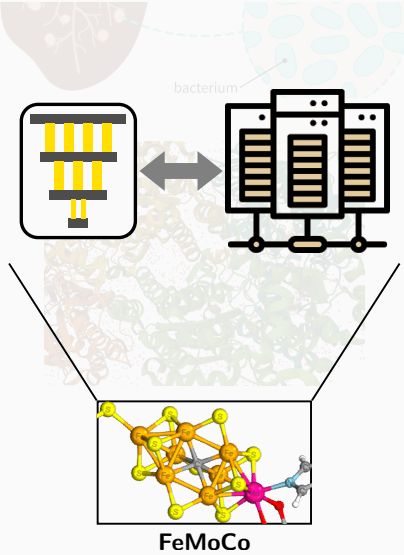
Use a combined **HPC and QC** approach for a potential computational speedup



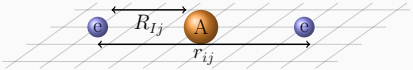


To obtain insight on the **chemical** and **physical properties** of these systems we need to **solve the Schrödinger equation**

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

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

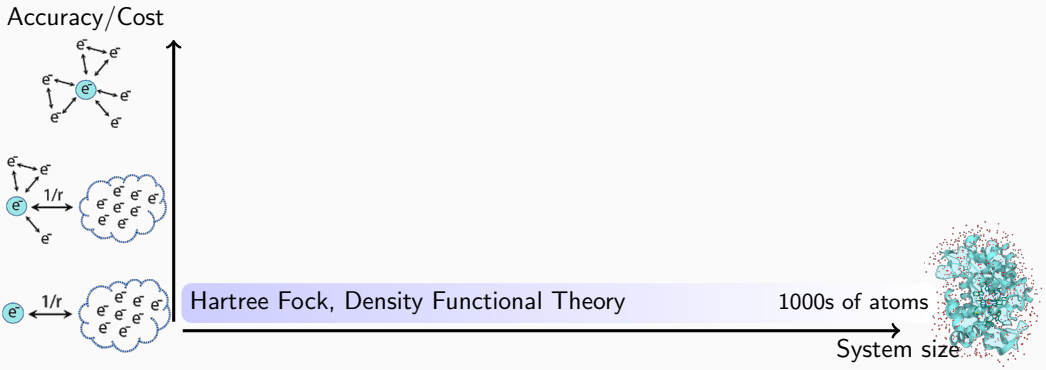
$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla^2_{\mathbf{r}_i}}_{\text{kinetic energy of e}^-} \underbrace{-\sum_{I,j}\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_j|}}_{\text{Attr. potential}} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{e}^- - \text{e}^- \text{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



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

Hierarchy of Methods and Theories

Depending how accurately we treat correlation: various methods and **levels of theory** to solve the Schrödinger equation



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

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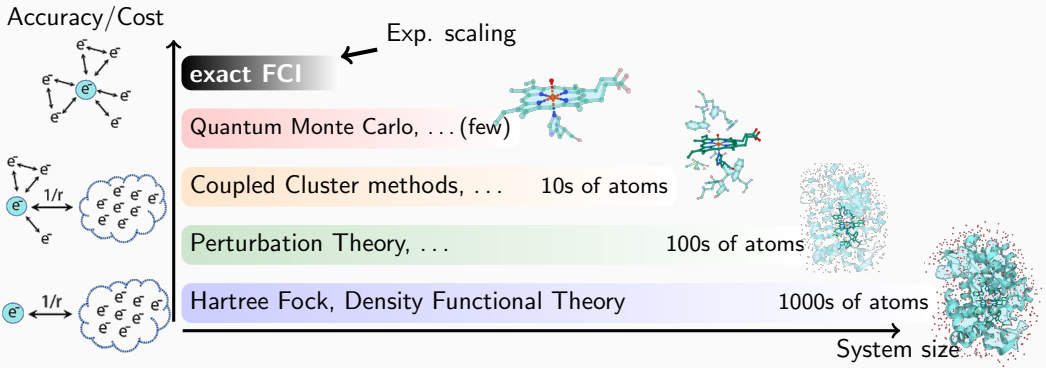

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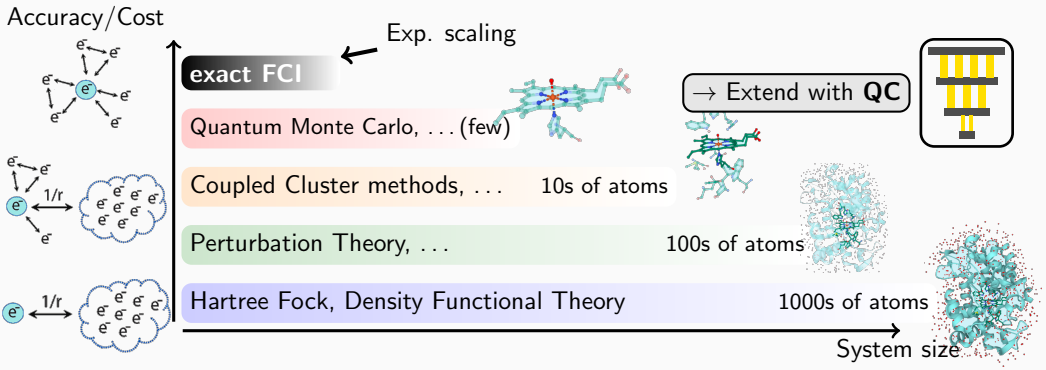

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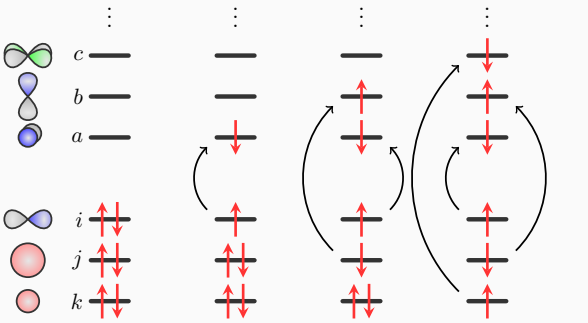
Exponential scaling of Full Configuration Interaction

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

$$|\Psi\rangle = |\Phi_{HF}\rangle + \sum_i c_i |\Phi_i\rangle$$



All possible excitations from HF determinant

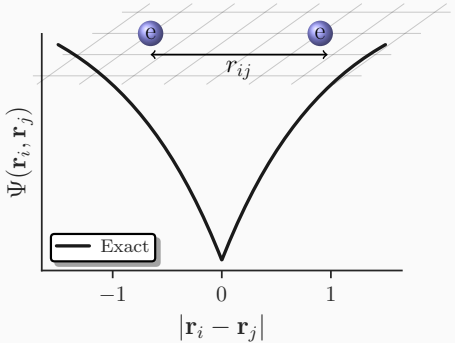
Number of possible states for given number of electrons, N, and orbitals, n, $\sim \binom{N}{n}$

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	$\sim 2 \cdot 10^9$

Problems for accurate description: Cusp condition

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 ($|\mathbf{r}_i - \mathbf{r}_j| = 0$)

$$\hat{H} \propto -\frac{1}{2}\sum_i \nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \qquad \hat{H}\,|\Psi(\{\mathbf{r}\})\rangle = E_0\,|\Psi(\{\mathbf{r}\})\rangle$$



Kato, Communications on Pure and Applied Mathematics **10** (2), 151 (1957)

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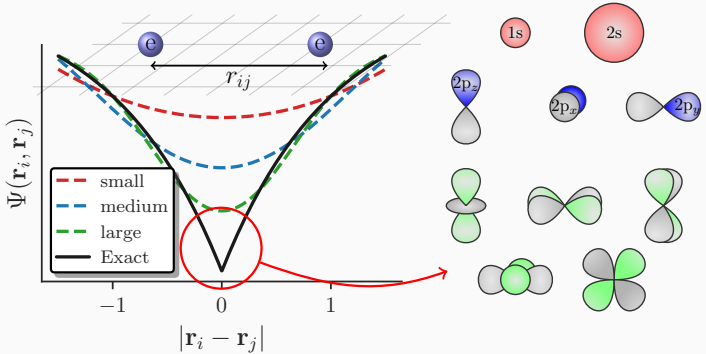

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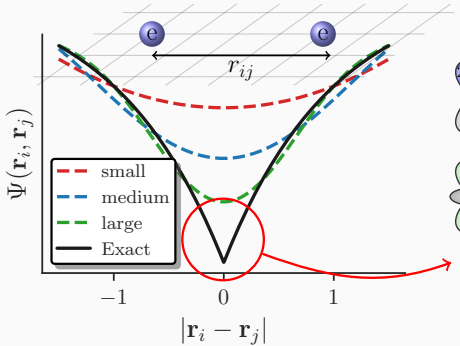

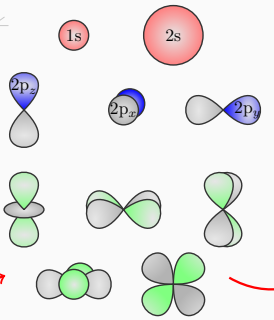

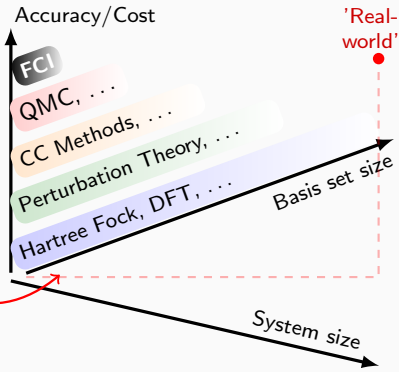

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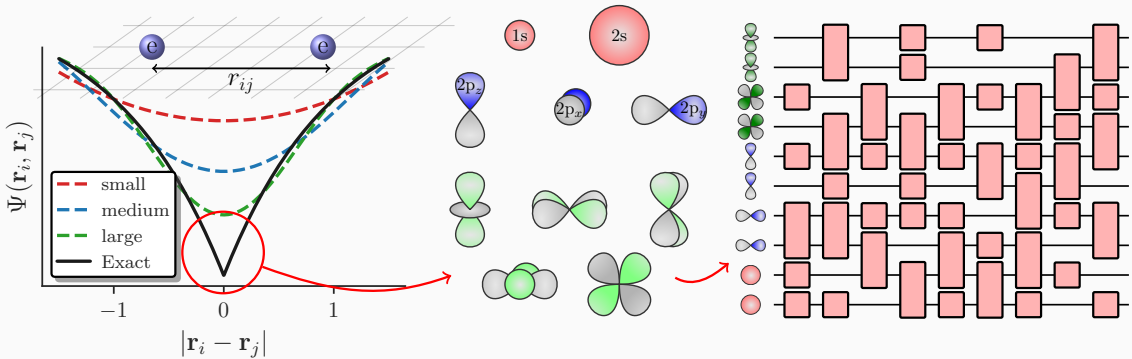

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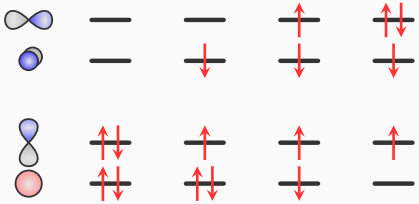
The Case for Quantum

How can Quantum Computing help Quantum Chemistry?

2^N states

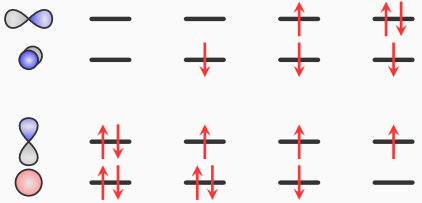


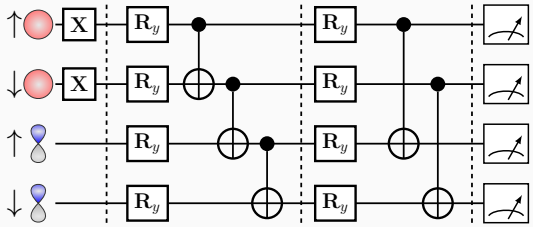
$|\Phi_{\mathrm{HF}}\rangle = |1100\rangle\,, |\Phi_i^a\rangle = |1010\rangle\,, \ldots$

How can Quantum Computing help Quantum Chemistry?

Fermion to qubit mapping

2^N states ⟶ N qubits





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

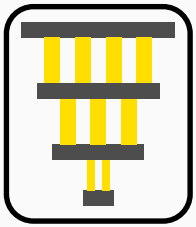
- Map our problem (Hamiltonian/basis functions) onto quantum hardware/qubits
  - Qubits encode occupation of spin-orbitals $\in [0, 1]$

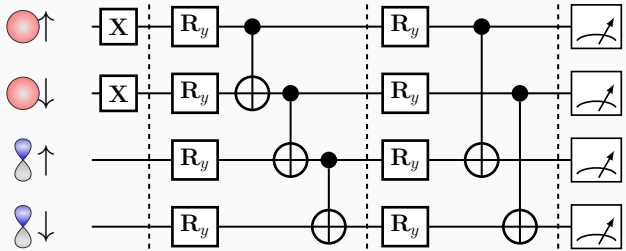
$\rightarrow$ Use quantum algorithms for ground-, excited states, dynamics, ...

* Jordan-Wigner, Bravyi-Kitaev, (Ann. Phys. **298**, 210 (2002)), Parity encoding ...

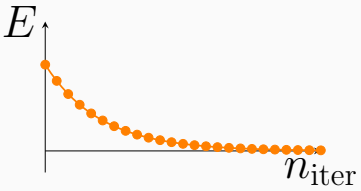
$\sim$ 15mK

Magnetic shielding

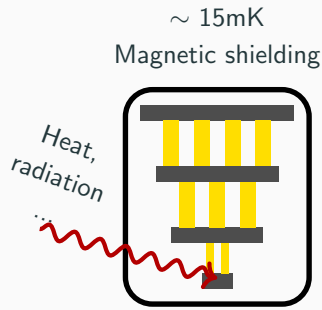


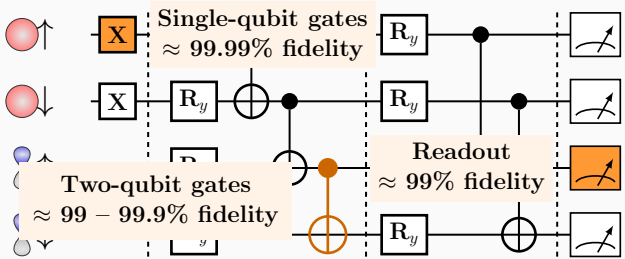


Variational Quantum Eigensolver:



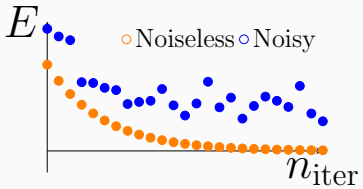
Quantum Chemistry on Quantum Computers





Effect of noise:

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



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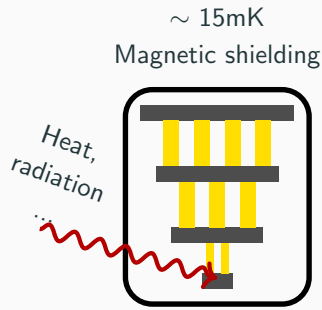

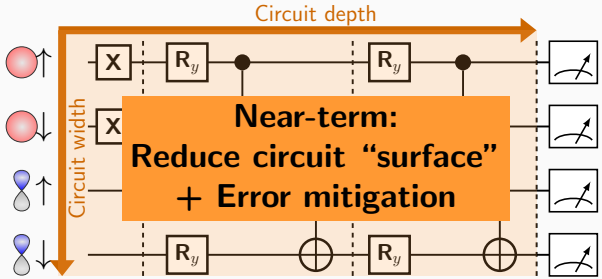

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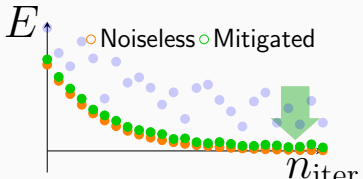
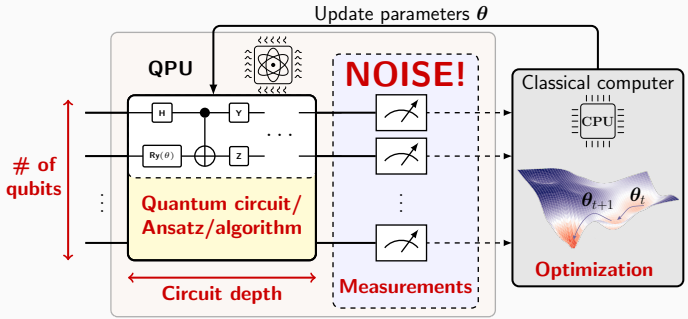


Near-term approaches and our work

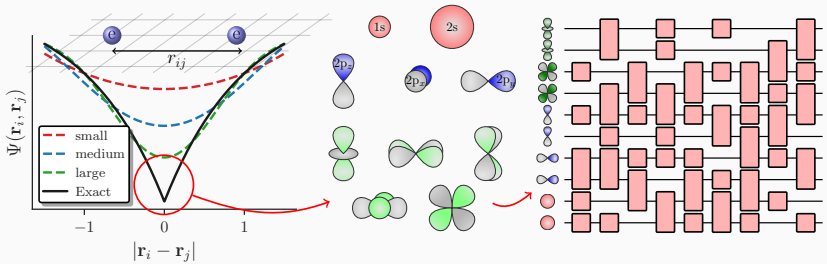
Hybrid Quantum-Classical: Use benefits of both quantum and classical resources



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

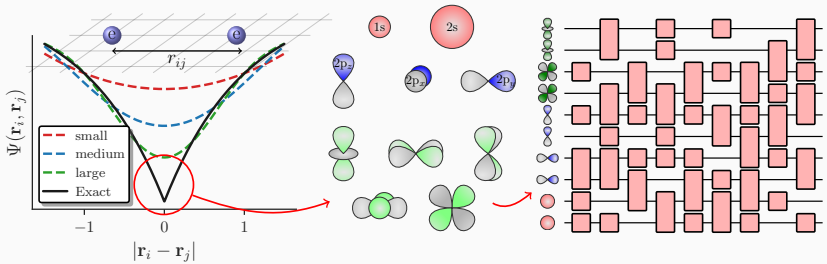
Transcorrelation to reduce the computational footprint on quantum hardware

Resource Reduction: Qubits and circuit depth



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

Resource Reduction: Qubits and circuit depth



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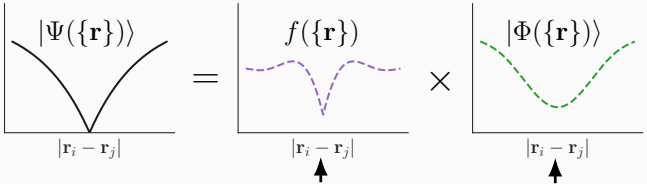

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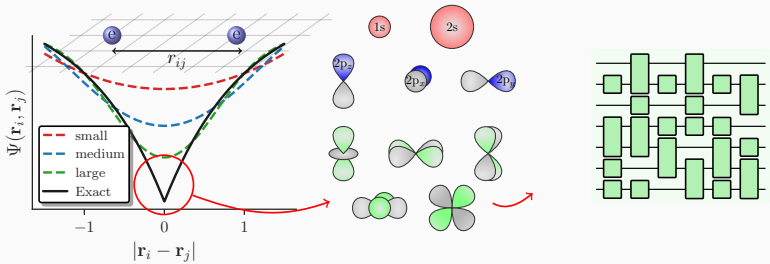

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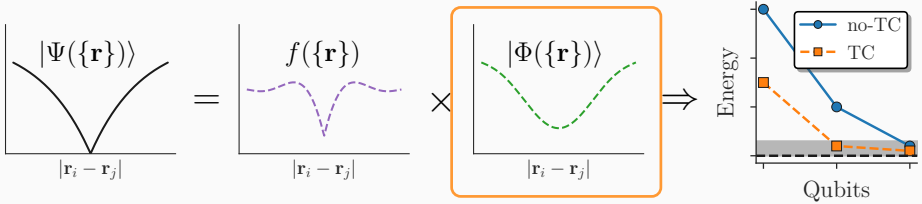
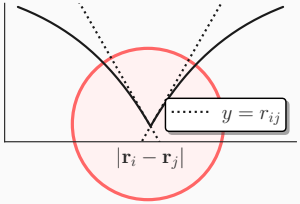


Explicitly Correlated methods



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

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

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

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

J_{ij} are optimizable parameters and $g(\tilde{r_{ij}})$ polynomials dependent on the electron positions.
We use VMC# to classically optimize the Jastrow factor $\hat{J}$, which scales as $\mathcal{O}(n_{\mathrm{el}}^3)$

* Kutzelnigg, Theoretica chimica acta 68, 445 (1985); † Ten-no, J. Chem. Phys. 121, 117 (2004); ‡ Jastrow, Phys. Rev. **98**, 1479 (1955); #Haupt, Hosseini, López Ríos, **WD**, Cohen and Alavi, JCP **158**, 224105 (2023);

Cusp Condition – The Transcorrelated (TC) Method

The transcorrelated (TC) method: use a Jastrow Ansatz, $\mathrm{e}^{\hat{J}}$, with optimizable parameters J_{ij} (via VMC†) to describe the cusp condition and/or capture part of correlation.

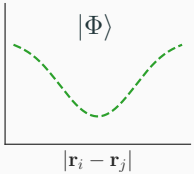
$$|\Psi(\{\mathbf{r}\})\rangle = \exp\left[\sum_{ij} J_{ij} g(\tilde{r}_{ij})\right] |\Phi(\{\mathbf{r}\})\rangle$$

Incorporate $\mathrm{e}^{\hat{J}}$ into Hamiltonian and solve a similarity transformed problem:

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

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

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



$|\Phi\rangle$ 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);

Similarity Transformation – Transcorrelated (TC) Method

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 $\hat{J}$!

$$\begin{aligned}\bar{H} &= \hat{H} - \sum_i \left(\frac{1}{2}\nabla_i^2\hat{J} + (\nabla_i\hat{J})\nabla_i + \frac{1}{2}(\nabla_i\hat{J})^2\right) \\ &= \hat{H} - \sum_{i<j}\hat{K}(\mathbf{r}_i,\mathbf{r}_j) - \sum_{i<j<k}\hat{L}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k)\end{aligned}$$

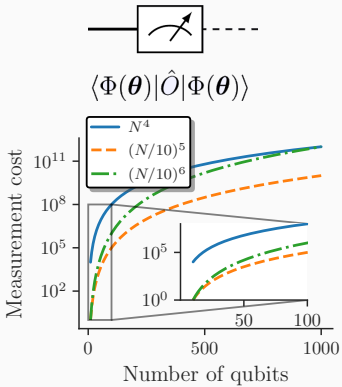
- Exact transformation
- 3-body terms and non-Hermitian!
- **Rapid basis set convergence!**

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)

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
- 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);

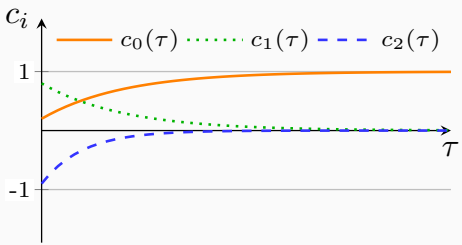
Since the TC Hamiltonian is non Hermitian, variational algorithms like VQE are not applicable!

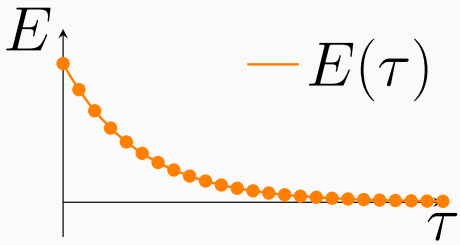
$\rightarrow$ Quantum Imaginary Time Evolution!

(Quantum) Imaginary Time Evolution – QITE

→ Solve for the **right** eigenvector of non-Hermitian $\bar{H}$ by projecting on the ground state with **(quantum) imaginary-time evolution (QITE)**

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





Variational Ansatz-based QITE – VarQITE

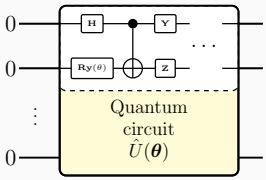
(Normalized) imaginary-time (Wick-rotated) Schrödinger equation

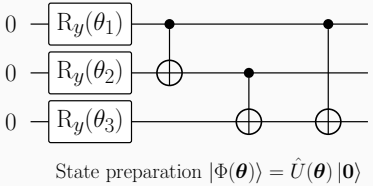
$$\frac{\partial \left|\Psi(\tau)\right\rangle}{\partial \tau} = -(\hat{H} - E_\tau)\left|\Psi(\tau)\right\rangle \quad \rightarrow \left|\Psi(\tau)\right\rangle = \mathrm{e}^{-\delta\tau(\hat{H}-E_\tau)}\left|\Psi(0)\right\rangle$$

$$\text{with} \quad E_\tau = \left\langle\Psi(\tau)\right| \hat{H} \left|\Psi(\tau)\right\rangle$$

would yield the ground state, but **non-unitary** $\mathrm{e}^{-\tau(\hat{H}-E_\tau)}$ not possible on a QC!
Approximate $|\Psi(\tau)\rangle$ with an "Ansatz" with parametrized unitary gates:

$$\left|\Psi(\tau)\right\rangle \approx \left|\Phi(\boldsymbol{\theta}(\tau))\right\rangle = \hat{U}(\boldsymbol{\theta}(\tau))\left|\mathbf{0}\right\rangle$$



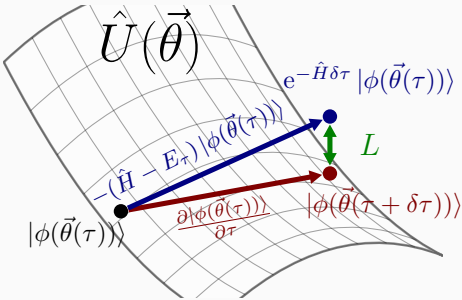


State preparation $\left|\Phi(\boldsymbol{\theta})\right\rangle = \hat{U}(\boldsymbol{\theta})\left|\mathbf{0}\right\rangle$

McArdle *et al.*, npj Quantum, 5, 75 (2019); Yuan *et al.* Quantum 3, 191 (2019);

VarQITE – Details

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 $\delta\tau$:

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

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

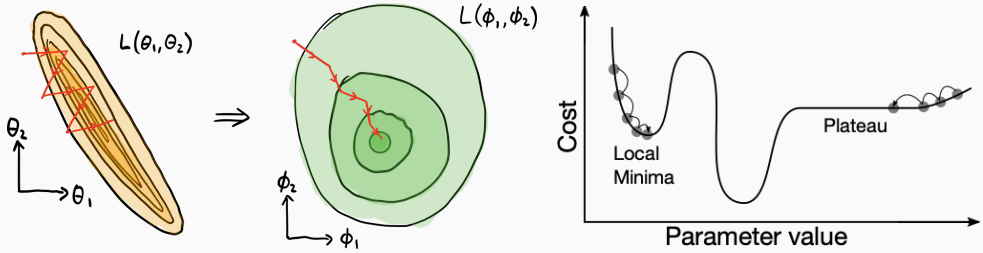
McLachlan, Molecular Physics, 8(1),39 (1964); McArdle *et al.*, npj Quantum, 5, 75 (2019); Yuan *et al.* Quantum 3, 191 (2019);

VarQITE – Connection to Quantum Natural Gradient

- Incorporate the geometry of the Ansatz, $|\Phi(\boldsymbol{\theta})\rangle = \hat{U}(\boldsymbol{\theta})\,|0\rangle$, with metric:

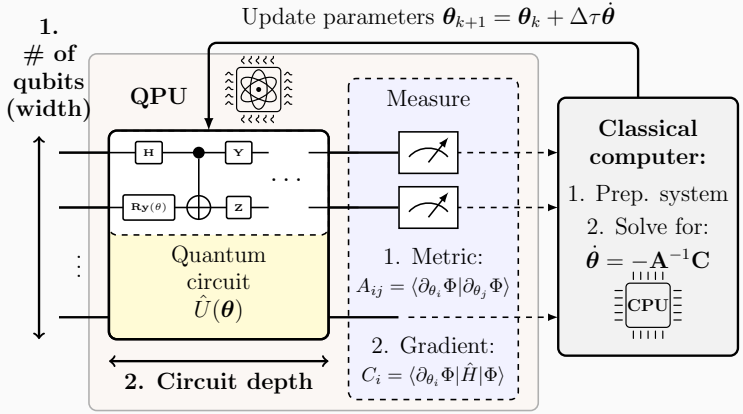
$$A_{ij} = \frac{\partial \langle \Phi|}{\partial \theta_i} \frac{\partial |\Phi\rangle}{\partial \theta_j}$$

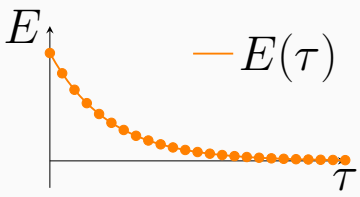
- *Natural gradient* update rule: $\dot{\boldsymbol{\theta}} = -\mathbf{A}^{-1}\boldsymbol{C}$



QITE Workflow

Can be performed in a NISQ-friendly hybrid approach





Sokolov, **WD**, Luo, Alavi, Tavernelli, Physical Review Research 5 (2), 023174 (2023)

VarQITE – Pros and Cons

Pros:

- No classical optimization
- Convergence (more) robust against noise
- Applicable to open/transport problems (**non Hermitian Hamiltonians**)

Cons:

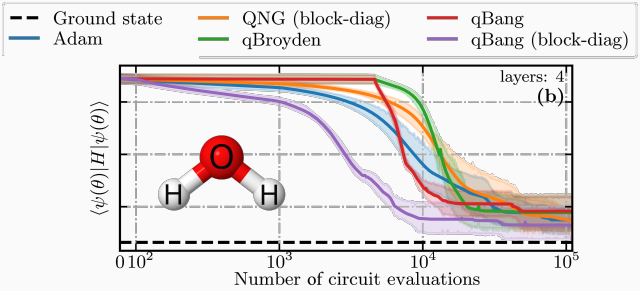
- 2^{nd} order method $\rightarrow$ metric $\mathbf{A}$ needs to be measured – n_θ^2 scaling with n_θ parameters
- $\mathbf{A}$ can be singular $\rightarrow$ inversion $\mathbf{A}^{-1}$ can problematic

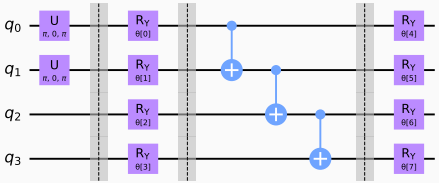
Improving classical optimization – qBANG – Quantum 8, 1313

Quasi-Newton approximation and an adaptive momentum (ADAM) approach to update the metric (with Sherman-Morrison formula direct update of $\mathbf{A}^{-1}$!)

$$\mathbf{A}_{k+1} \approx (1-\epsilon_k)\mathbf{A}_k + \epsilon_k \mathbf{C}_k \mathbf{C}_k^T$$

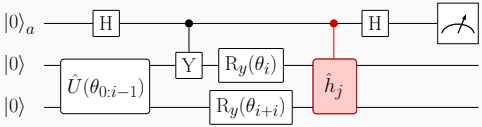
Immense reduction in circuit evaluations and improved convergence





VarQITE with non-Hermitian $\bar{H}$

Hermitian gradient (i.e. lin. comb. of unitaries): $C_i = \frac{\partial \langle \Phi |}{\theta_i} \hat{H} |\Phi\rangle, \quad \hat{H} = \sum_j c_j \hat{h}_j$



For TC: McArdle and Tew, arXiv:2006.11181

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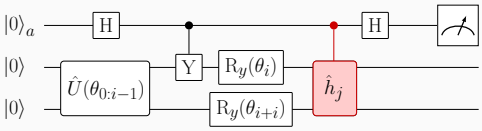
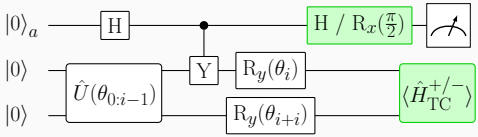


For TC: McArdle and Tew, arXiv:2006.11181



Sokolov, **WD**, et al, PR Res. 5 (2), 023174

In the TC case: split non-Hermitian Hamiltonian in Hermitian and anti-Hermitian part:

$$\hat{H}^{+}_{TC} = \hat{H}_{TC} + \hat{H}^{\dagger}_{TC}, \qquad \hat{H}^{-}_{TC} = \hat{H}_{TC} - \hat{H}^{\dagger}_{TC}$$

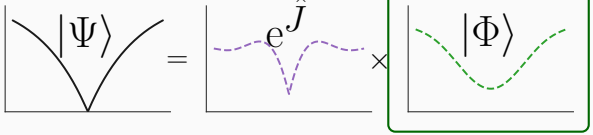
$$C_i = \frac{1}{2}\left(\langle\partial_{\theta_i}\Phi|\hat{H}_{TC}|\Phi\rangle + \langle\Phi|\hat{H}^{\dagger}_{TC}|\partial_{\theta_i}\Phi\rangle\right) = \frac{C^{+}_i + C^{-}_i}{4}$$

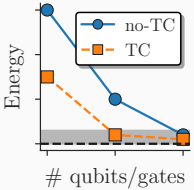
$$C^{+}_i = 2\langle\partial_{\theta_i}\Phi|\hat{H}^{+}_{TC}|\Phi\rangle, \qquad C^{-}_i = 2\langle\partial_{\theta_i}\Phi|\hat{H}^{-}_{TC}|\Phi\rangle$$

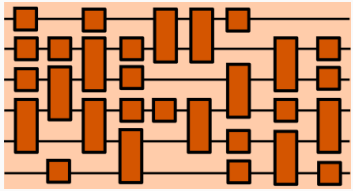
McArdle and Tew, arXiv:2006.11181 (2020); Sokolov, **WD**, Luo, Alavi, Tavernelli, Physical Review Research 5 (2), 023174 (2023) Schuld *et al.*, Phys. Rev. A 99, 032331 (2019)

Results: Hubbard model and ab initio quantum chemistry problems

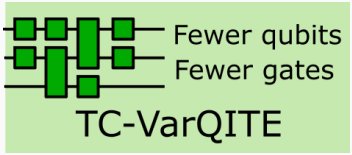
TC for QC – Motivation







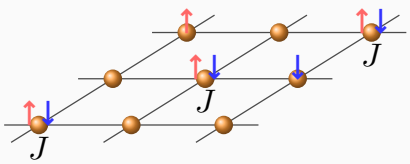
$$e^{-\hat{J}} \hat{H} e^{\hat{J}}$$

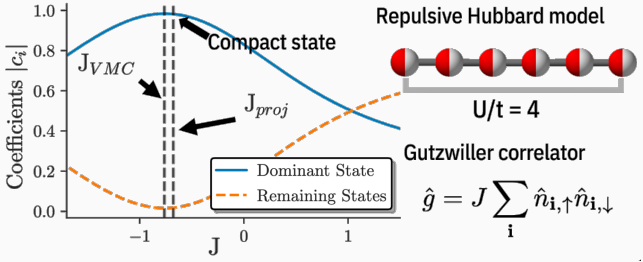


Reduce circuit depth with Transcorrelation

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

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



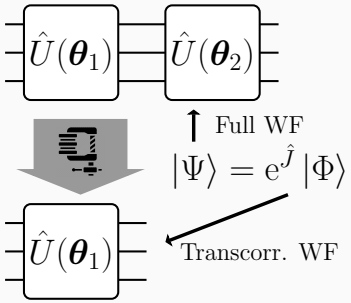


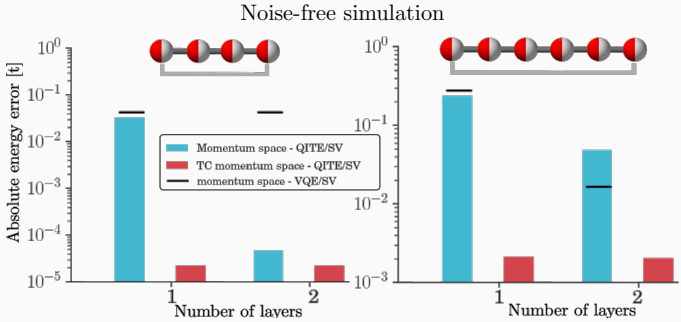
- **Increased compactness** of the right EV, due to downfolding of correlations into Hamiltonian
- Does the increased compactness/more single reference character have an impact on the necessary quantum Ansatz depth?

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)

Results – Hubbard model – Phys. Rev. Research 5 (2), 023174

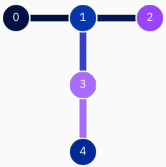
Transcorrelation ⇒ **shallower quantum circuits** for accurate results!

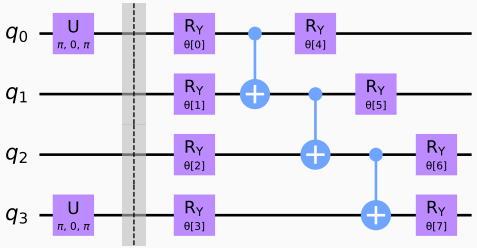




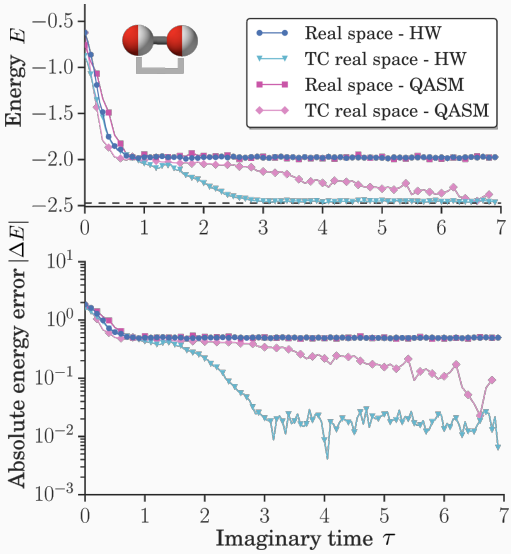
Noiseless statevector results, UCCSD Ansatz

Experimental results for the Hubbard model on ibmq_lima





Hardware-efficient RY Ansatz

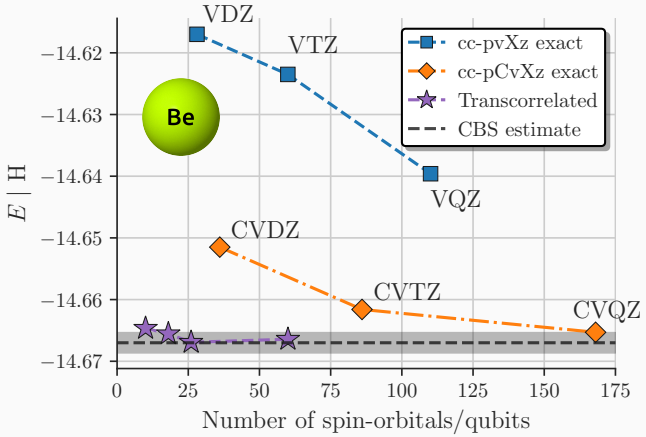


Sokolov, **WD**, Luo, Alavi, Tavernelli, Physical Review Research 5 (2), 023174 (2023)

Beryllium atom – JCTC 20 (10), 4146

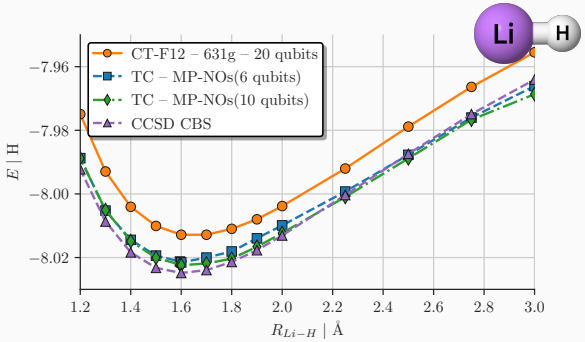
Beryllium atom – exact simulation of a quantum device (no noise)

Goal: complete basis set (CBS) limit → full description to compare with experiment

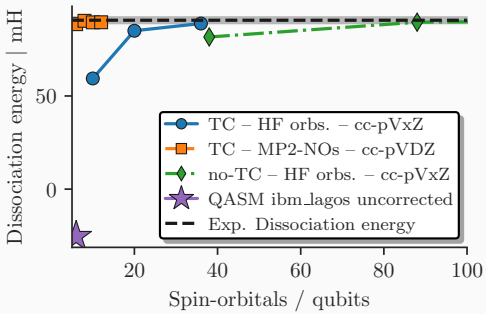


Lithium hydride – LiH – JCTC 20 (10), 4146

Lithium hydride – Potential energy surface and dissociation energy



Energy vs. bond distance – noiseless simulation



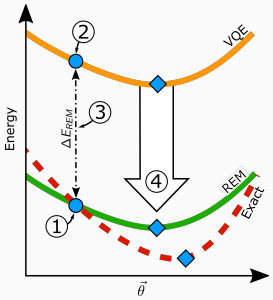
Noiseless and simulation of noisy quantum device (QASM) with hardware-efficient Ansatz

*CT-F12: Motta *et al.*, Phys. Chem. Chem. Phys. **22**, 24270, 2020; †Haeffler *et al.*, Phys. Rev. A, 1996, 53, 6, 4127 (1996); **WD**, Sokolov, Liao, Lopez Rios, Rahm, Alavi, Tavernelli, JCTC 20 (10), 4146

Reference-state Error Mitigation

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

P. Lolur, M. Skogh, **W. Dobrautz**, C. Warren, J. Biznárová, A. Osman, G. Wendin, J. Bylander, M. Rahm



- Classically compute exact reference energy (i.e. Hartree-Fock), $E(\boldsymbol{\theta}_{\mathrm{ref}})$
- Measure reference energy on noisy device $\mathcal{E}(\boldsymbol{\theta}_{\mathrm{ref}})$, with reference parameters $\boldsymbol{\theta}_{\mathrm{ref}}$
- Calculate REM correction: $\Delta E_{\mathrm{REM}} = \mathcal{E}(\boldsymbol{\theta}_{\mathrm{ref}}) - E(\boldsymbol{\theta}_{\mathrm{ref}})$
- Correct final VQE energy with REM correction

Reference-state Error Mitigation

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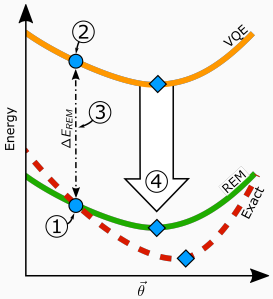
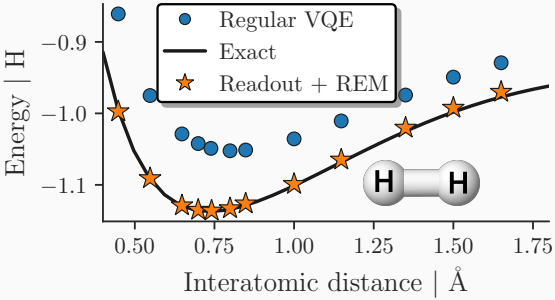


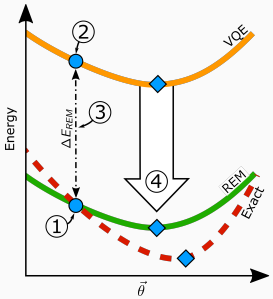


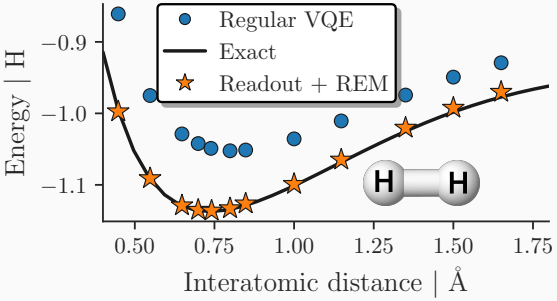
*Lolur, Skogh, **WD**, Warren, Biznárová, Osman, Tancredi, Wendin, Bylander, and Rahm, J. Chem. Theory Comput. 2023, **19**, 3, 783

Reference-state Error Mitigation

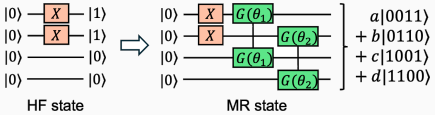
Reference-State Error Mitigation: A Strategy for High Accuracy Quantum Computation of Chemistry, *J. Chem. Theory Comput.*, **19**, 3, 783 (2023)

P. Lolur, M. Skogh, **W. Dobrautz**, C. Warren, J. Biznárová, A. Osman, G. Wendin, J. Bylander, M. Rahm





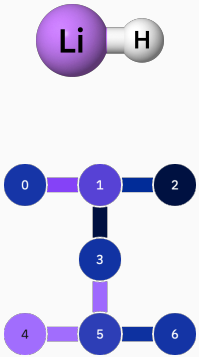
– **Multireference-state error mitigation for strong correlation**, H. Zou, E. Magnusson, H. Brunander, M. Rahm, **W. Dobrautz**, *to be submitted*

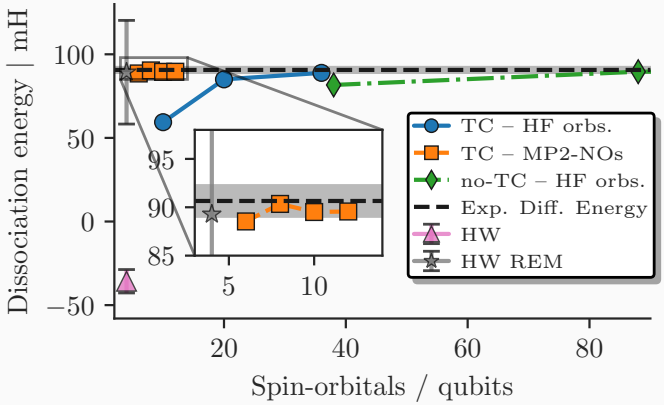


*Lolur, Skogh, **WD**, Warren, Biznárová, Osman, Tancredi, Wendin, Bylander, and Rahm, J. Chem. Theory Comput. 2023, **19**, 3, 783

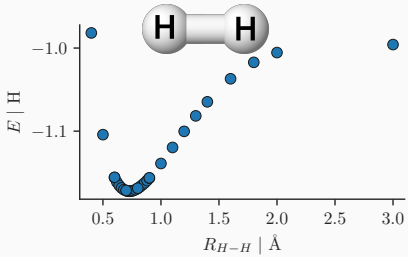
LiH – Experiment on IBM Quantum devices – JCTC 20 (10), 4146

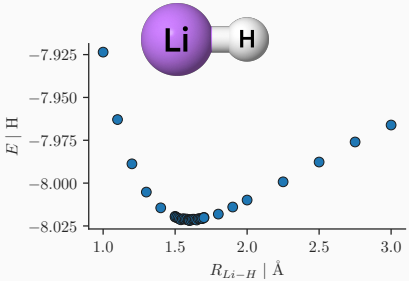
Hardware (HW) experiment: **lithium hydride** dissociation energy on `ibm_lagos`.
Hardware efficient RY Ansatz with linear entangling layer and parity encoding





Spectroscopic Constants

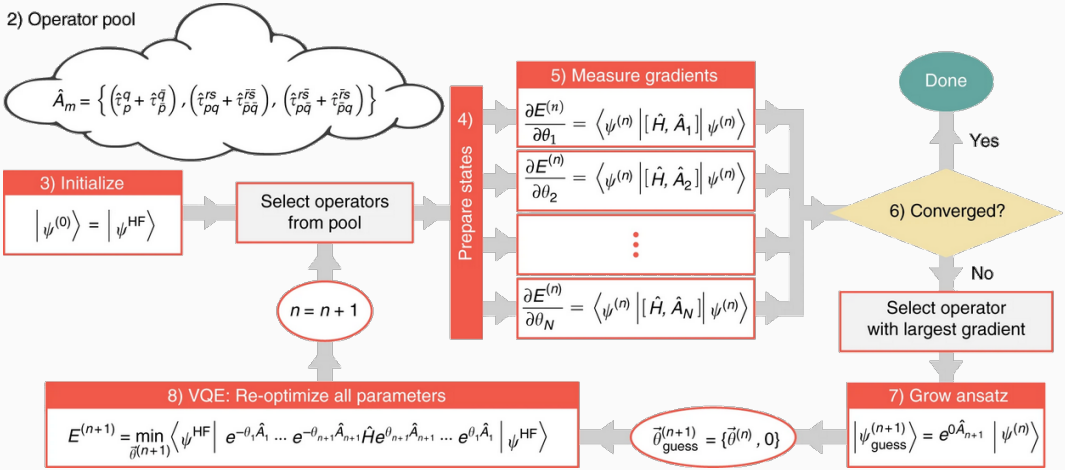




	H_2				LiH			
	qubits	R_e(Å)	D_0(eV)	ω_e(cm^{-1})	qubits	R_e(Å)	D_0(eV)	ω_e(cm^{-1})
no-TC	4	0.7330	3.67	4954	12	1.5422	2.66	1690
	8	0.7462	3.87	4297	22	1.6717	1.80	1283
	20	0.7609	4.19	4353	38	1.6154	2.17	1360
TC	**4**	**0.7428**	**4.69**	**4435**	**6**	**1.5998**	**2.47**	**1390**
Exp.		**0.7414**	**4.52**	**4401**		**1.5949**	**2.47**	**1406**

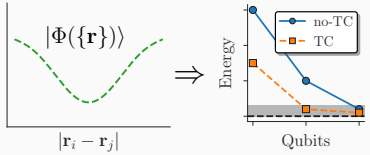
Adaptive Circuit Ansätze

Adaptive Circuit Ansätze

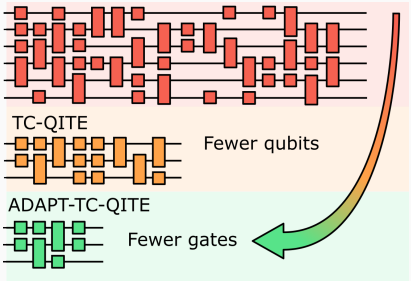


From: Grimsley et al. Nat Commun 10, 3007

Transcorrelation with Adaptive Circuit Ansätze



Smaller basis → fewer qubits



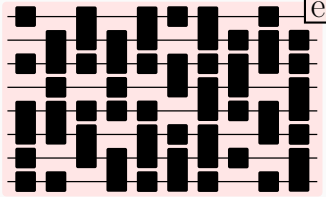
Full operator pool:

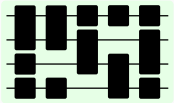
$\hat{U}_1, \hat{U}_2, \hat{U}_3, \hat{U}_4, \hat{U}_5, \hat{U}_6, \hat{U}_7, \hat{U}_8, \hat{U}_9, \hat{U}_{10}, \ldots$

ADAPT:

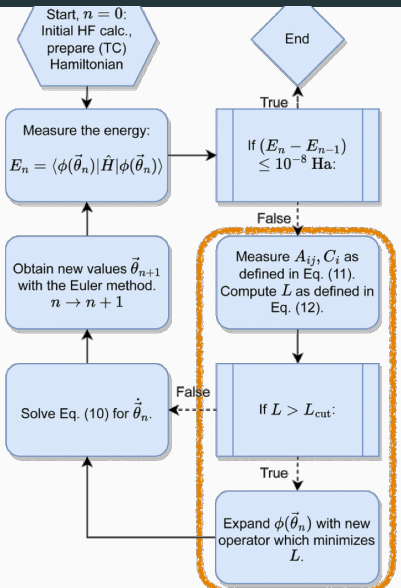
$\hat{U}'_1, \hat{U}'_2, \hat{U}'_3, \hat{U}'_4$

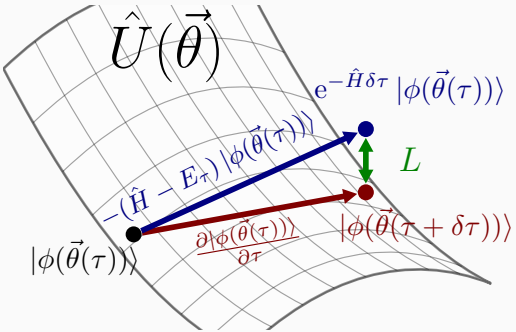
$e^{-\hat{J}} \hat{H} e^{\hat{J}}$





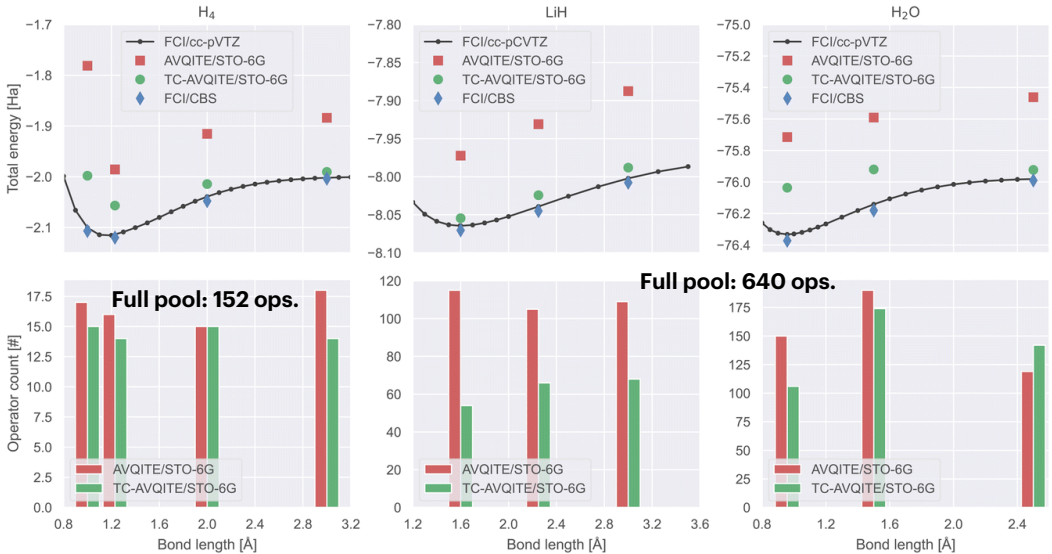
TC-Adaptive-VarQITE – Faraday Discuss., 254, 402





N. Gomes et al, Adv. Quantum Technol., 2021, 4, 2100114; Magnusson, Fitzpatrick, Knecht, Rahm and **WD**, Faraday Discuss., 254, 402 (2024)

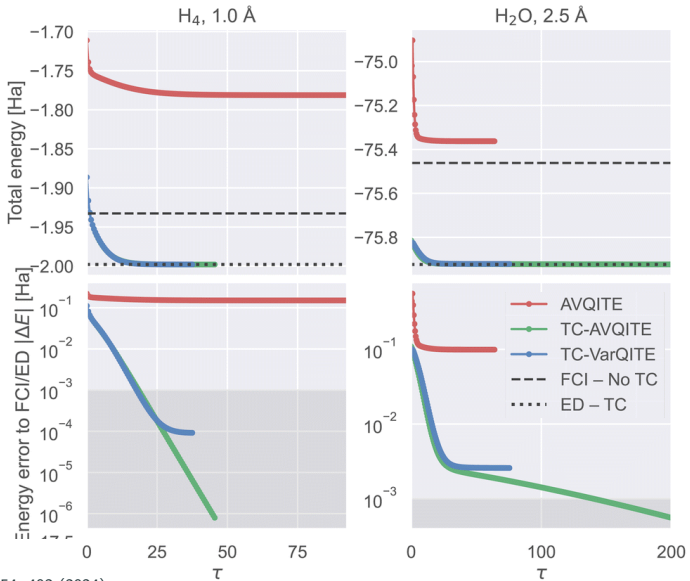
TC-AVQITE – Results – Qubit-ADAPT UCCSD Pool



Magnusson, Fitzpatrick, Knecht, Rahm and **WD**, Faraday Discuss., 254, 402 (2024)

TC-AVQITE – Improved Convergence

- More compact right eigenvector → shallower circuits
- Better convergence of TC calculations compared to non-TC results
- Additionally improved convergence compared to "full" UCCSD Ansätze.

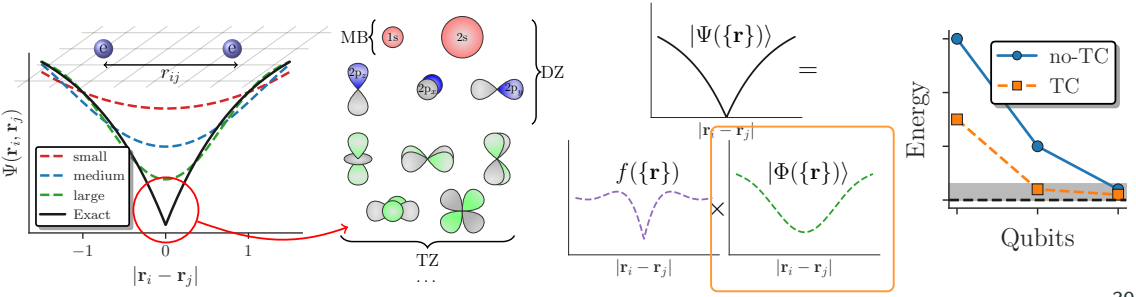


Magnusson, Fitzpatrick, Knecht, Rahm and **WD**, Faraday Discuss., 254, 402 (2024)

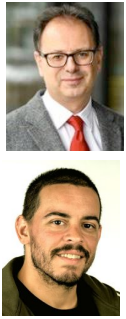
Conclusions

Conclusion – Transcorrelated Approach on Quantum Hardware

- The **TC method** partially transfers electronic correlations from the wavefunction into the Hamiltonian, **capturing the cusp condition**.
- **Reduce qubit requirements and circuit depth**, due to accurate results with a small basis sets and more compact (right) eigenvectors
- With efficient error mitigation techniques → **extends applicability of current and near-term quantum devices** to more relevant quantum chemistry problems.



Acknowledgments



Funding

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Funding and Acknowledgements

Bundesministerium für Bildung und Forschung

SACHSEN

DRESDEN concept

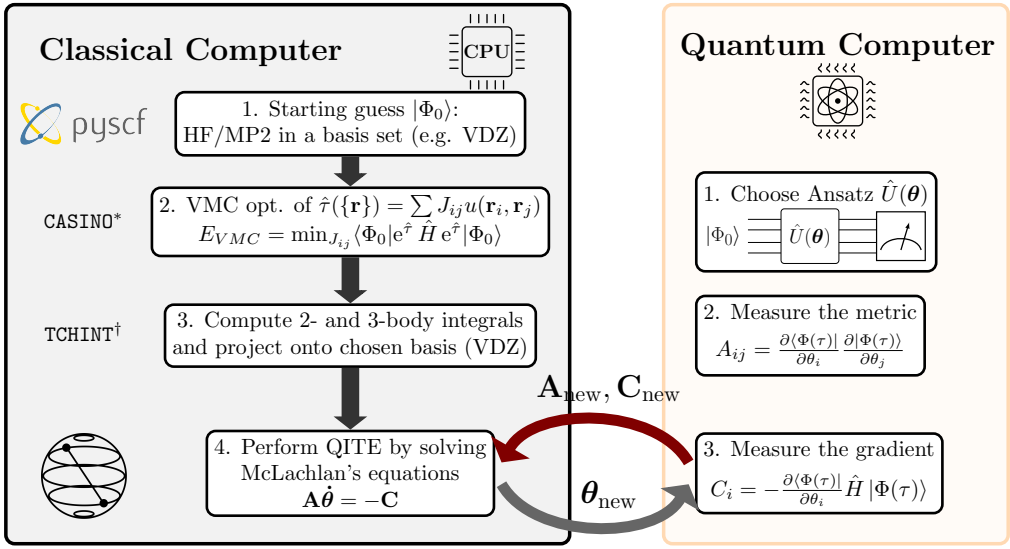
ScaDS.AI DRESDEN LEIPZIG

HELMHOLTZ HZDR

CASUS

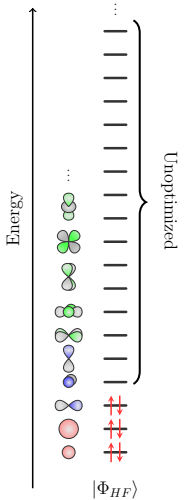
Thank you for your attention!

Workflow



*https://vallico.net/casinoqmc/ †https://gitlab.com/kguther/tchint ‡https://github.com/ghb24/NECI_STABLE

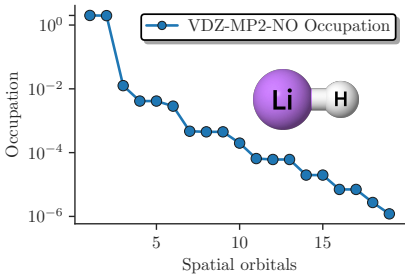
(Virtual) orbital optimization

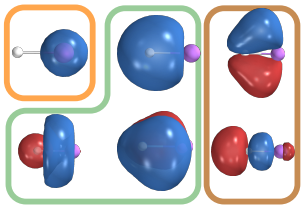


- "Standard basis sets" not optimized for the TC method

→ include effect of virtuals through orbital optimization / downfolding

→ e.g. natural orbitals (NO) from a "cheap" perturbation theory (MP2) calculation





FNO: Sosa *et al.*, Chem. Phys. Lett. **159** (2-3) 148 (1989); Taube and Bartlett Collect. Czech. Chem. Commun. **70**, 837 (2005); **NISQ:** Gonthier *et al.* arXiv:2012.04001; (2020); Verma *et al.* JCP **155**, 034110 (2021)

VarQITE

Three ingredients:

- Evolution of $|\Phi(\boldsymbol{\theta}(\tau))\rangle$ according to imaginary time Schrödinger equation, $|\Psi(\tau)\rangle = \mathrm{e}^{-\tau(\hat{H}-S_\tau)}\,|\Psi(0)\rangle$ for small $\delta\tau$: $\mathrm{e}^{-\delta\tau(\hat{H}-S_\tau)} \approx (1-\delta\tau(\hat{H}-S_\tau))$

$$|\Phi(\boldsymbol{\theta}(\tau+\delta\tau))\rangle \approx \Big[1-\delta\tau(\hat{H}-S_\tau)\Big]\,|\Phi(\boldsymbol{\theta}(\tau))\rangle \tag{1}$$

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

$$|\Phi(\boldsymbol{\theta}(\tau+\delta\tau))\rangle \approx |\Phi(\boldsymbol{\theta}(\tau))\rangle + \sum_j \frac{\partial\,|\Phi(\boldsymbol{\theta}(\tau))\rangle}{\partial\theta_j}\frac{\partial\theta_j}{\partial\tau}\delta\tau \tag{2}$$

Equate r.h.s. of Eqs. (1) and (2) $\Rightarrow$

McLachlan's variational principle

$$\implies \sum_j \frac{\partial \left|\Phi(\boldsymbol{\theta}(\tau))\right\rangle}{\partial \theta_j} \dot{\theta}_j \approx -(\hat{H} - S_\tau) \left|\Phi(\boldsymbol{\theta}(\tau))\right\rangle, \quad \text{with} \quad \dot{\theta}_j = \frac{\partial \theta_j}{\partial \tau} \tag{3}$$

3. McLachlan's variational principle to minimize the distance between l.h.s and r.h.s. of (3)

$$\delta \left|\left| \left(\frac{\partial}{\partial \tau} + \hat{H} - S_\tau \right) \left|\Phi(\boldsymbol{\theta}(\tau))\right\rangle \right|\right| = 0, \quad \text{with} \quad \left|\left| \left|\Phi\right\rangle \right|\right| = \sqrt{\langle \Phi \,|\, \Phi \rangle}.$$

After some calculations we find a formula to update the parameters $\boldsymbol{\theta}$ to emulate imaginary time evolution on quantum computers

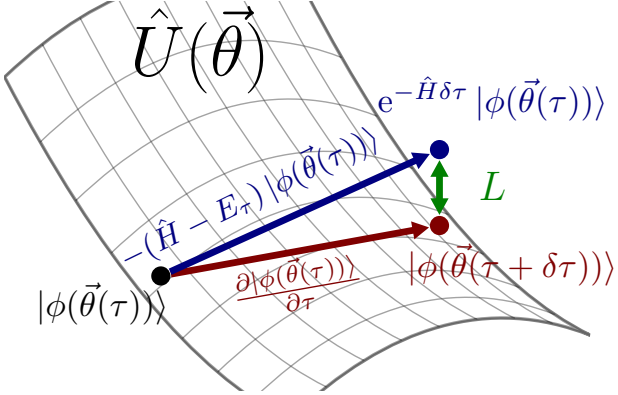
McLachlan, Molecular Physics, 8(1),39 (1964)

VarQITE

Simulate the imaginary-time (Wick-rotated) Schrödinger equation

$$\frac{\partial |\Psi(\tau)\rangle}{\partial \tau} = -(\hat{H} - E_\tau)|\Psi(\tau)\rangle \quad \rightarrow |\Psi(\tau)\rangle = \mathrm{e}^{-\delta\tau(\hat{H}-E_\tau)}|\Psi(0)\rangle$$

by mapping on time evolution of parameters $\boldsymbol{\theta}(\tau)$



- Ansatz $|\Phi(\boldsymbol{\theta}(\tau))\rangle = \hat{U}(\boldsymbol{\theta}(\tau))|0\rangle$
- McLachlan's variational principle

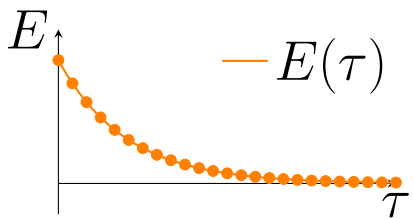
$$\delta \left| \left(\frac{\partial}{\partial \tau} + (\hat{H} - E_\tau) \right) |\Phi(\boldsymbol{\theta}(\tau))\rangle \right| = 0$$

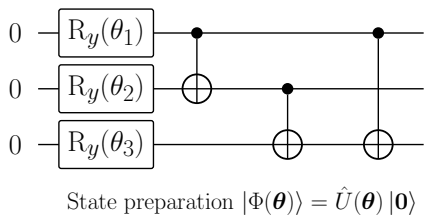
- Evolution of parameters $\mathbf{A} \cdot \dot{\boldsymbol{\theta}} = C$

$$A_{ij} = \frac{\partial \langle\Phi|}{\partial \theta_i} \frac{\partial |\Phi\rangle}{\partial \theta_j} \qquad C_i = -\frac{\partial \langle\Phi|}{\partial \theta_i} \hat{H} |\Phi\rangle$$

Quantum Imaginary Time Evolution

Imaginary-time evolution (ITE) applicable to efficiently solve for groundstate energy on quantum hardware





Quantum ITE: Map imaginary-time evolution of $|\Phi(\tau)\rangle$ to change of gate parameters $\boldsymbol{\theta}(\tau)$

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

with the metric (quantum Fisher information), $\mathbf{A}$, and the gradient of the cost function, $\mathbf{C}$.

primo.ai; pennylane.ai; McArdle *et al.*, npj Quantum, 5, 75 (2019); Yuan *et al.* Quantum 3, 191 (2019);

Connection to natural gradient

Equation for change in parameters $\boldsymbol{\theta}$ due to McLachlan's variational principle to enable Ansatz-based quantum imaginary time evolution:

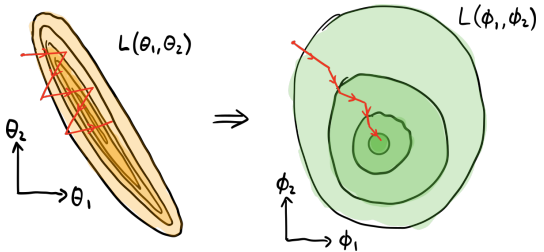
$$\sum_j A_{ij}\dot{\theta}_j = C_i, \quad \implies \dot{\boldsymbol{\theta}} = \mathbf{A}^{-1}\boldsymbol{C}$$

with the metric:

$$A_{ij} = \frac{\partial \langle\Phi|}{\partial\theta_i}\frac{\partial |\Phi\rangle}{\partial\theta_j}$$

and energy gradient:

$$C_i = -\frac{\partial \langle\Phi|}{\partial\theta_i}\hat{H}\,|\Phi\rangle$$

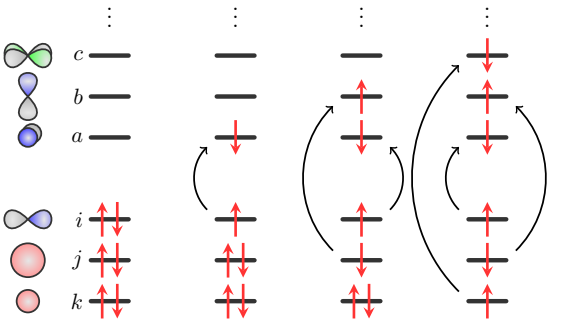


* Motta *et al.*, Nature Physics, 16, 205 (2020); pennylane.ai

Exponential scaling of Full Configuration Interaction

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

$$|\Psi\rangle = |\Phi_{HF}\rangle + \sum_i c_i |\Phi_i\rangle$$



All possible excitations from HF determinant

Number of possible states for given number of electrons, N, and orbitals, n, $\sim \binom{N}{n}$

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	$\sim 2 \cdot 10^9$

Variational Quantum Monte Carlo to optimize Jastrow factors

Minimize variational energy, by optimizing trial wavefunction parameters J_{ij}:

$$E_{VMC} = \min_{\hat{J}(J_{ij})} \frac{\langle \Phi_0 | \mathrm{e}^{\hat{J}} \hat{H} \, \mathrm{e}^{\hat{J}} | \Phi_0 \rangle}{\langle \Phi_0 | \mathrm{e}^{2\hat{J}} | \Phi_0 \rangle}, \quad |\Phi_T\rangle = \mathrm{e}^{\hat{J}} |\Phi_0\rangle$$

- The choice of trial wavefunction is critical in VMC calculations $\rightarrow$ accuracy limited by $|\Phi_T\rangle = \mathrm{e}^{\hat{J}} |\Phi_0\rangle$!
- Hartree-Fock state usually first starting point for $|\Phi_0\rangle$, but more elaborate/accurate states possible...
- Polynomial scaling $\sim N^3$
- Such a VMC calculations to optimize J_{ij} with a HF state $|\Phi_0\rangle = |\Phi_{HF}\rangle$ our **starting point** for the **transcorrelated method**

Jastrow s.t. Hamiltonian in 2nd quantised form

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

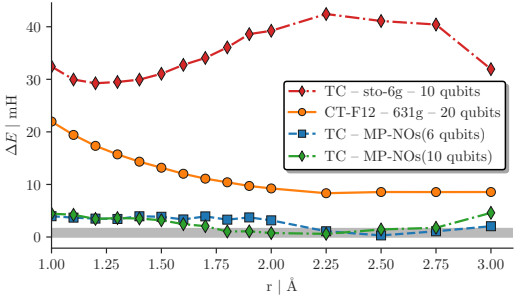
with

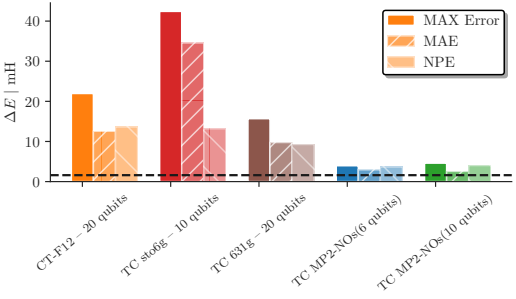
$$K_{rs}^{pq} = \langle \phi_p \phi_q | \hat{K} | \phi_r \phi_s \rangle$$
$$L_{stu}^{pqr} = \langle \phi_p \phi_q \phi_r | \hat{L} | \phi_s \phi_t \phi_u \rangle \quad \text{(48-fold symmetry in } L \text{ for real orbitals)}$$

Both integrals K and L are computed numerically using standard DFT grids over gaussian orbitals. The main problem is the storage of L. Current limit $\approx$ 80 orbitals

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

LiH


40
30
20
10
0
ΔE | mH
1.00
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
r | Å
TC – sto-6g – 10 qubits
CT-F12 – 631g – 20 qubits
TC – MP-NOs(6 qubits)
TC – MP-NOs(10 qubits)

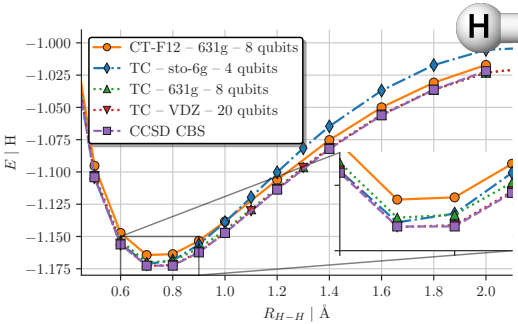

40
30
20
10
0
ΔE | mH
MAX Error
MAE
NPE
CT-F12 – 20 qubits
TC sto6g – 10 qubits
TC 631g – 20 qubits
TC MP2-NOs(6 qubits)
TC MP2-NOs(10 qubits)

Hydrogen molecule

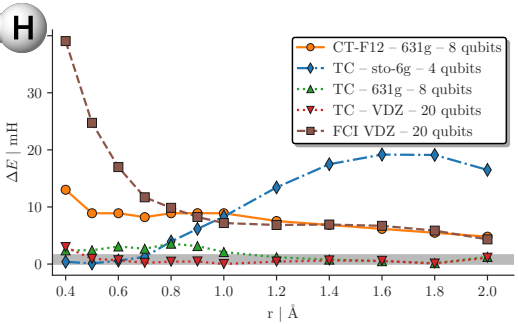
Favorite quantum chemistry test case: Hydrogen molecule – H_2

CT-F12 approximated explicitly correlated method, by Motta *et al.*[*]

Exact statevector simulation – UCCSD Ansatz



Energy vs. bond distance



Error wrt. CBS result vs. bond distance

[*] CT-F12: Motta *et al.*, Phys. Chem. Chem. Phys. **22**, 24270, 2020

Imaginary Time Evolution (ITE) – Normalization

$E_0 - S_\tau = 0$ would require knowledge of ground state. Alternative, and also to ensure proper normalization:

For small time-steps $\Delta\tau$ approximate exponential by first-order Taylor approximation* and obtain iterative solution:

$$\mathrm{e}^{-\Delta\tau(\hat{H}-S_\tau)} \approx 1 - \Delta\tau(\hat{H} - S_\tau) + \mathcal{O}(\Delta\tau^2) \quad \rightarrow \quad |\Psi(\tau+\Delta\tau)\rangle = \Big[1 - \Delta\tau(\hat{H} - S_\tau)\Big]\,|\Psi(\tau)\rangle \tag{4}$$

Assuming $\langle\Psi(\tau)\,|\,\Psi(\tau)\rangle = 1$:

$$\begin{aligned}\langle\Psi(\tau+\Delta\tau)\,|\,\Psi(\tau+\Delta\tau)\rangle &= \langle\Psi(\tau)|\Big[1 - \Delta\tau(\hat{H} - S_\tau)\Big]^2|\Psi(\tau)\rangle \stackrel{!}{=} 1 \\ &= \underbrace{\langle\Psi(\tau)\,|\,\Psi(\tau)\rangle}_{=1} - 2\Delta\tau \underbrace{\Big(\langle\Psi(\tau)|\hat{H}|\Psi(\tau)\rangle - S_\tau\Big)}_{\stackrel{!}{=}0} + \mathcal{O}(\Delta\tau^2)\end{aligned}$$

$\Longrightarrow S_\tau = \langle\Psi(\tau)|\hat{H}|\Psi(\tau)\rangle$ ensures normalization of $|\Psi(\tau)\rangle$ and allows ITE to converge to the groundstate

* for $\Delta\tau < 1/E_W$, with $E_W = E_{max} - E_0$ being the many-body spectral width, Trivedi and Ceperley, Phys. Rev. B, 41, 4552 (1990)

$$\langle\Phi|\Big(\partial/\partial\tau+\hat{H}-S_\tau\Big)^\dagger\Big(\partial/\partial\tau+\hat{H}-S_\tau\Big)|\Phi\rangle=\sum_{ij}\frac{\partial\langle\Phi|}{\partial\theta_i}\frac{\partial|\Phi\rangle}{\partial\theta_j}\dot{\theta}_i\dot{\theta}_j+\sum_i\frac{\partial\langle\Phi|}{\partial\theta_i}(\hat{H}-S_\tau)|\Phi\rangle\,\dot{\theta}_i$$

$$+\sum_i\langle\Phi|(\hat{H}-S_\tau)\frac{\partial|\Phi\rangle}{\partial\theta_i}\dot{\theta}_i+\langle\Phi|(\hat{H}-S_\tau)^2|\Phi\rangle \tag{5}$$

Variations in $\dot{\theta}_i \Longrightarrow$ and focusing on one term in $\dot{\theta}_i$:

$$\frac{\partial||(\partial/\partial\tau+\hat{H}-S_\tau)|\Phi\rangle||}{\partial\dot{\theta}_i}=\sum_j\left(\frac{\partial\langle\Phi|}{\partial\theta_i}\frac{\partial|\Phi\rangle}{\partial\theta_j}+\frac{\partial\langle\Phi|}{\partial\theta_j}\frac{\partial|\Phi\rangle}{\partial\theta_i}\right)\dot{\theta}_j$$

$$+\frac{\partial\langle\Phi|}{\partial\theta_i}\hat{H}|\Phi\rangle+\langle\Phi|\hat{H}\frac{\partial|\Phi\rangle}{\partial\theta_i}-S_\tau\left(\frac{\partial\langle\Phi|}{\partial\theta_i}|\Phi\rangle+\langle\Phi|\frac{\partial|\Phi\rangle}{\partial\theta_i}\right)$$

with

$$\langle\Phi\,|\,\Phi\rangle=1,\quad\rightarrow\quad\frac{\partial\langle\Phi\,|\,\Phi\rangle}{\partial\theta_i}=\frac{\partial\langle\Phi|}{\partial\theta_i}|\Phi\rangle+\langle\Phi|\frac{\partial|\Phi\rangle}{\partial\theta_i}=0$$

$$\Longrightarrow\frac{\partial||(\partial/\partial\tau+\hat{H}-S_\tau)|\Phi\rangle||}{\partial\dot{\theta}_i}=\sum_j A_{ij}\dot{\theta}_j-C_i\stackrel{!}{=}0$$

Monotonic energy convergence

$$\frac{dE(\tau)}{d\tau} = \langle\Phi(\tau)|\,\hat{H}\,\frac{d\,|\Phi(\tau)\rangle}{d\tau} = \sum_i \langle\Phi(\tau)|\,\hat{H}\,\frac{\partial\,|\Phi(\tau)\rangle}{\partial\theta_i}\dot{\theta}_i \tag{6}$$

$$= -\sum_i C_i\dot{\theta}_i = -\sum_i C_i A^{-1}_{ij} C_j \leq 0,$$

if $\mathbf{A}^{-1}$ is positive. For arbitrary $\mathbf{x} = (x_1, x_2, \ldots, x_N)^T$:

$$\mathbf{x}^\dagger \cdot \mathbf{A} \cdot \mathbf{x} = \sum_{ij} x_i^* A_{ij} x_j = \sum_{ij} x_i^* \left(\frac{\partial\,\langle\Phi(\tau)|}{\partial\theta_i}\frac{\partial\,|\Phi(\tau)\rangle}{\partial\theta_j} \right) x_j$$

with a general $|\zeta\rangle = \sum_i x_i \frac{\partial|\Phi(\tau)\rangle}{\partial\theta_i}$:

$$\sum_{ij} x_i^* \left(\frac{\partial\,\langle\Phi(\tau)|}{\partial\theta_i}\frac{\partial\,|\Phi(\tau)\rangle}{\partial\theta_j} \right) x_j = \langle\zeta|\zeta\rangle \geq 0.$$

And we only consider non-zero eigenvalues in case $\mathbf{A}^{-1}$ is singular

Linear combination of unitaries

Assuming: each unitary gate depends only on one parameter θ_i and each U_i is a rotation or controlled rotation gate.

$$\frac{\partial U_i(\theta_i)}{\partial \theta_i} = \sum_k f_{k,i} U_i(\theta_i) u_{k,i}, \quad \rightarrow \quad \frac{\partial \left|\Phi(\tau)\right\rangle}{\partial \theta_i} = \sum_k f_{k,i} V'_{k,i} \left|\mathbf{0}\right\rangle \tag{7}$$

with a unitary operator $u_{k,i}$, scalar parameter $f_{k,i}$ and:

$$V'_{k,i} = U_n(\theta_n) \dots U_i(\theta_i) u_{k,i} \dots U_1(\theta_1)$$

Evaluation $\mathbf{A}$ and C with Quantum Circuits

How do we measure the metric, $\mathbf{A}$, and the gradient, $\mathbf{C}$ on quantum hardware.

$$A_{ij} = \frac{\partial \langle \Phi |}{\partial \theta_i} \frac{\partial | \Phi \rangle}{\partial \theta_j}, \qquad C_i = -\frac{\partial \langle \Phi |}{\partial \theta_i} \hat{H} | \Phi \rangle$$

$|\Phi(\boldsymbol{\theta}(\tau))\rangle$ encoded by unitary gates acting on initial state: Ansatz $\hat{U}(\boldsymbol{\theta}(\tau))$

$$|\Phi(\boldsymbol{\theta}(\tau))\rangle = \hat{U}_n(\theta_n(\tau)) \cdots \hat{U}_i(\theta_i(\tau)) \cdots \hat{U}_1(\theta_1(\tau)) |\mathbf{0}\rangle = \hat{U}(\boldsymbol{\theta}(\tau)) |\mathbf{0}\rangle$$

- Numerical differentiation/approximation: $\frac{\partial \hat{U}_i(\theta_i)}{\partial \theta_i} \approx \frac{\hat{U}_i(\theta_i + \Delta\theta_i) - \hat{U}_i(\theta_i)}{\Delta \theta_i}$
- Parameter-shift rule* (for single qubit gates): $R_z(\theta_i) = \mathrm{e}^{-i\theta_i \sigma_z} \rightarrow \frac{\partial U_i(\theta_i)}{\partial \theta_i} = -i\sigma_z R_Z(\theta_i)$
- Linear combination of unitaries* (for general gates), see (7)ff for details

*Schuld *et al.*, Phys. Rev. A 99, 032331 (2019); Romero *et al.*, Quantum Science and Technology, 4, 1 (2019); Li and Benjamin, Phys. Rev. X 7, 021050 (2017);

Derivative Example

- $U_i(\theta_i)$ is a single qubit rotation: $R_Z(\theta_i) = \mathrm{e}^{-i\theta_i\sigma_z}$:

$$\frac{\partial U_i(\theta_i)}{\partial \theta_i} = -\frac{i}{2}\sigma_z R_Z(\theta_i)$$

  $\rightarrow$ add an extra σ_z gate with factor $-i/2$

- $U_i(\theta_i)$ a controlled rotation: $|0\rangle\langle 0| \otimes I + |1\rangle\langle 1| \otimes R_Z(\theta_i)$:

$$\frac{\partial U_i(\theta_i)}{\partial \theta_i} = |1\rangle\langle 1| \otimes \partial R_Z(\theta_i)/\partial\theta_i = -\frac{i}{2}|1\rangle\langle 1| \otimes \sigma_z R_Z(\theta_i)$$

  $\rightarrow$ realized with

$$u_{1,i} = I \otimes \sigma_z, f_{1,i} = -i/4,$$
$$u_{2,i} = \sigma_z \otimes \sigma_z, f_{2,i} = i/4$$

  in $\sum_k f_{k,i} U_i(\theta_i) u_{k,i}$ from previous slide

Evaluation $\mathbf{A}$ and $\mathbf{C}$ with Quantum Circuits – cont.

$$A_{ij} = \sum_{k,l} f^*_{k,i} f_{l,j} \langle \mathbf{0} | V^{\prime\dagger}_{k,i} V^{\prime}_{l,j} | \mathbf{0} \rangle, \qquad C_i = \sum_{k,l} f^*_{k,l} \lambda_l \langle \mathbf{0} | V^{\prime\dagger} h_l \hat{V} | \mathbf{0} \rangle \tag{8}$$

with $\hat{H} = \sum_l \lambda_l h_l$. Both $\mathbf{A}$ and $\boldsymbol{C}$ are of the form $a \cdot \mathrm{e}^{i\phi} \langle \mathbf{0} | \hat{U} | \mathbf{0} \rangle$ and can be evaluated on a quantum circuit.