Classical and Quantum Algorithms for the Characterization of Strongly Correlated Chemical Systems

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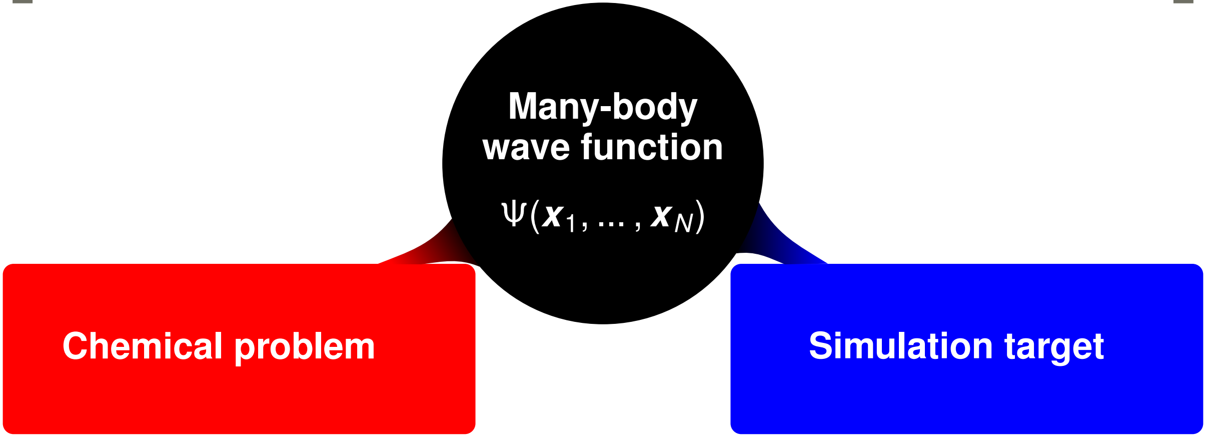
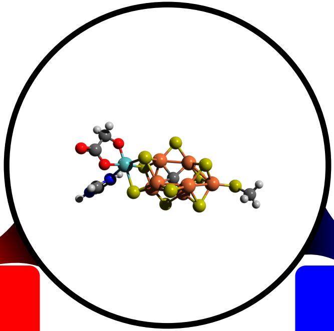


Many-body wave function

$\Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$

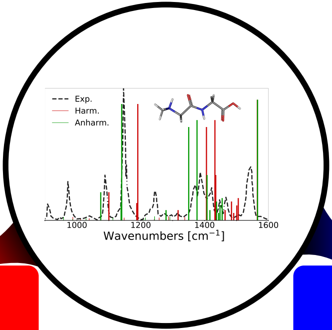
Chemical problem

Simulation target



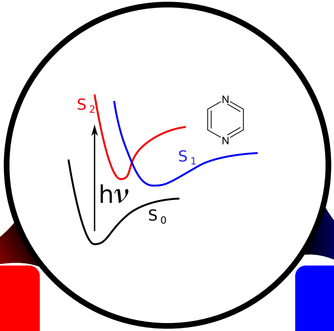
$$\mathcal{T}_{\text{ele}} + \sum_{i<j} \frac{1}{r_{ij}} - \sum_{\alpha,i} \frac{Z_\alpha}{|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|^2} + \sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha,\beta}}$$

$$\mathcal{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$$



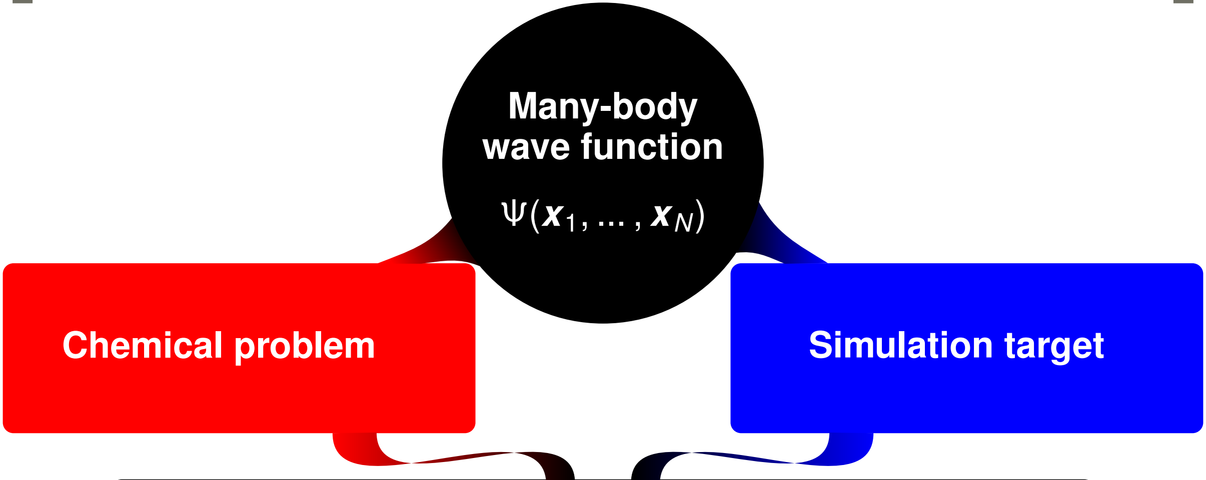
$$\mathcal{H}_v(\boldsymbol{q}) = \mathcal{T}(\boldsymbol{q}) + \sum_i \mathcal{V}^{[i]}(q_i) + \sum_{i<j} \mathcal{V}^{[i,j]}(q_i, q_j)$$

$$\mathcal{H} | \Psi_n \rangle = E_n | \Psi_n \rangle$$



$$\mathcal{H}_{ve} = \sum_{i} |\alpha_i\rangle\langle\alpha_i|\, \mathcal{H}_v^{(i)}(\boldsymbol{q}) + \sum_{i,j} |\alpha_i\rangle\langle\alpha_i|\, \mathcal{V}^{(i,j)}(\boldsymbol{q})$$

$$\mathcal{H}\left|\Psi(t)\right\rangle = \mathrm{i}\frac{\partial}{\partial t}\left|\Psi(t)\right\rangle$$



Many-body wave function

$\Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$

Chemical problem

Simulation target

Full CI: many-body problem ↔ one-particle basis functions.

$$\Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \sum_{i_1 \cdots i_N} C_{i_1 \cdots i_N} \mathcal{S} \left(\phi_{i_1}(\boldsymbol{x}_1) \cdots \phi_{i_N}(\boldsymbol{x}_N) \right)$$

The strong correlation problem: classical approaches

- Full CI-type wave function size grows **exponentially** with the system size.
- **Strongly correlated systems**: wave function expansion not dominated by a single configuration.
- Conventional approaches can target $\approx$ 24 particles/basis functions.

Modern CI methods

- **FCIQMC**: wave function optimized by stochastic imaginary time evolution.
- **Selected CI**: diagonalization algorithms leveraging the sparsity of the $\boldsymbol{C}$ tensor.
- **DMRG**: wave function compressed with **tensor factorization algorithms**.

FCIQMC: G. Booth, A. Thom, A. Alavi, *J. Chem. Theory Comput.* 131, 054106 (**2009**)
Selected CI: A. Holmes, N. Tubman, C. Umrigar, *J. Chem. Theory Comput.* 12, 3674 (**2016**), Y. Garniron *et al. J. Chem. Theory Comput.* 15, 3591 (**2019**), N. Tubman *et al.*, *J. Chem. Theory Comput.* 16, 2139 (**2020**)
DMRG: S. White, *Phys. Rev. Lett.* 69, 2863 (**1992**)

The strong correlation problem: quantum approaches

- **Curse of dimensionality** ↔ exponential requirements both to **store** and **optimize** a full-CI wave function.
- **Compact** representation of many-body wave functions on quantum computer.
- **Exponential** cost of the optimization reduced to linear when encoding the full CI wave function on a quantum hardware.

→ **Identify** systems/problems for which quantum computing would bring a **key** advantage compared to classical algorithms.

→ **Estimate** the requirements for observing **quantum supremacy** in quantum-chemical calculations.

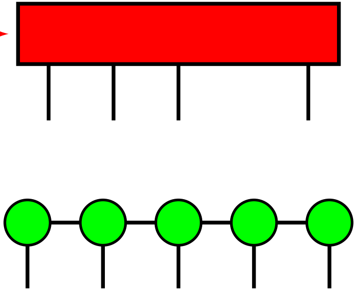
Y. Cao *et al.*, *Chem. Rev.* 119, 10856 (**2019**)
B. Bauer, S. Bravyi, M. Motta, G. K.-L. Chan, *Chem. Rev.* 120, 12685 (**2020**)
H. Liu, G. H. Low, D. S. Steiger, T.Häner, M. Reiher, M. Troyer, *Arxiv* 2102.10081 (**2021**)

The Density Matrix Renormalization Group

$$|\Psi\rangle = \sum_{\sigma_1\cdots\sigma_L} C_{\sigma_1\cdots\sigma_L} |\sigma_1\cdots\sigma_L\rangle$$

Tensor factorization

$$\sum_{\sigma_1,\ldots,\sigma_L}\ \sum_{m_1,\ldots,m_{L-1}} M^{\sigma_1}_{1,m_1} M^{\sigma_2}_{m_1,m_2}\cdots M^{\sigma_L}_{m_{L-1},1}|\boldsymbol{\sigma}\rangle$$



- **Mathematical** perspective: **compression** of the full-CI wave function with the tensor train factorization.
- **Physics** perspective: efficiency ensured for **nearest-neighbor** Hamiltonians.
- **Pragmatic** perspective: compression tuned by a single parameter (**bond dimension** *m*), cost scales **polynomially** with *m*.

A. Baiardi, M. Reiher, *J. Chem. Phys.* 152, 040903 (**2020**)

DMRG for molecular vibrations

- **Strong correlation** plays a key role beyond electronic-structure calculations.
- **Challenge**: design generic methods not tailored to a specific application field.

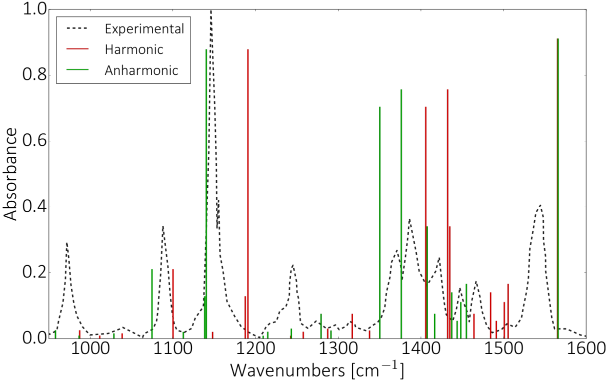
Vibrational DMRG

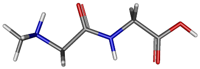
$$\mathcal{H}_{\text{vib}} = \sum_{i=1}^{L} \mathcal{T}\left(\mathbf{Q}_i\right) + \sum_{i=1}^{L} \mathcal{V}^{[i]}\left(\mathbf{Q}_i\right) + \sum_{i<j}^{L} \mathcal{V}^{[i,j]}\left(\mathbf{Q}_i, \mathbf{Q}_j\right) + \sum_{i<j<k}^{L} \mathcal{V}^{[i,j,k]}\left(\mathbf{Q}_i, \mathbf{Q}_j, \mathbf{Q}_k\right) + \ldots$$

- **Bose-Einstein** statistics, arbitrary occupation number.
- $\mathcal{V}\left(\mathbf{Q}\right)$ must be approximated with power series and/or fitting schemes.
- **High-order** many-body coupling terms are relevant.
- Choice for the coordinate set **Q influences** the extent of correlation effects.

A. Baiardi, C.J. Stein, V. Barone, M. Reiher, *J. Chem. Theory Comput.*, 13, 3764 (**2017**)
N. Glaser, A. Baiardi, M. Reiher, *Arxiv*:2109.08961 (**2021**)

DMRG for molecular vibrations: application





- Full anharmonic vibrational spectra → (many) strongly-correlated excited states.
- Molecular vibrations key to reaction rates, thermodynamic properties ...

A. Baiardi, C.J. Stein, V. Barone, M. Reiher, *J. Chem. Theory Comput.*, 13, 3764 (**2017**)

Pre-Born-Oppenheimer Hamiltonians

- Full molecular Hamiltonian for N_t particle types, with $N_{\mathrm{p}}^{(i)}$ particles for type i.

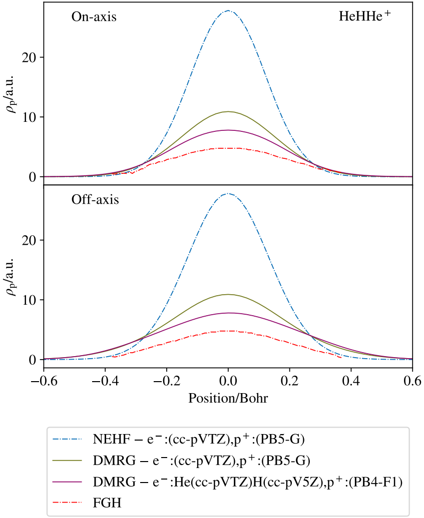
$$\mathcal{H} = -\sum_{i=1}^{N_t} \sum_{\mu_i=1}^{N_{\mathrm{p}}^{(i)}} \frac{1}{2m_{\mu_i}} \boldsymbol{\nabla}_{\mu_i}^2 + \sum_{i}^{N_t} \sum_{\mu_i<\nu_i} \frac{q_{\mu_i} q_{\nu_i}}{|\mathbf{r}_{\mu_i} - \mathbf{r}_{\nu_i}|} + \sum_{i<j}^{N_t} \sum_{\mu_i,\nu_j} \frac{q_{\mu_i} q_{\nu_j}}{|\mathbf{r}_{\mu_i} - \mathbf{r}_{\nu_j}|}$$

- Calculate molecular properties **without** invoking the Born–Oppenheimer approximation.
- Second-quantization form derived in terms of spinful **fermionic** and **bosonic** second-quantization operators.

A. Muolo, A. Baiardi, R. Feldmann, M. Reiher, *J. Chem. Phys.*, 152, 204103 (**2020**)
R. Feldmann, A. Muolo, A. Baiardi, M. Reiher, *Arxiv*:2109.05377 (**2021**)

Pre-Born-Oppenheimer Hamiltonians: applications

- **Example**: proton density for the model hydrogen-transfer system $[\mathrm{HeHHe}]^+$.
- **Reference**: full-CI vibrational calculation on CCSD(T) Born-Oppenheimer PES.
- **Challenge**: slower convergence to the complete basis set limit, many-body correlation effects may be more relevant than for electronic problems.



R. Feldmann, A. Muolo, A. Baiardi, M. Reiher, *Arxiv*:2109.05377 (**2021**)

The excited states challenge

- Full CI-based methods rely on the **variational principle**.
- Extension towards (potentially high-energy) excited-states **non-trivial**.
- **Algorithmic challenge**: design excited-state methods that are as **robust** as the ground-state one.
- **Conceptual challenge**: extent of many-particle correlation may increase for excited-states.

A. Baiardi, C.J. Stein, V. Barone, M. Reiher, *J. Chem. Phys.*, 150, 094113 (**2019**)

[2] A. Baiardi, A. K. Kelemen, *Arxiv*, 2110.00092 (**2021**)

Correlation effects in quantum dynamics

- Quantum dynamics methods: solution of the **time-dependent Schrödinger equation**.

$$\mathcal{H}|\,\Psi\,\rangle = \mathrm{i}\hbar\partial_t|\,\Psi\,\rangle$$

  1. static spectra *via* the correlation function formalism.
  2. non-equilibrium processes happening on short (femto/attosecond) time-scales.

- Many methods for **nuclear dynamics** (MCTDH, ML-MCTDH, Ehrenfest, surface hopping...)
- **Real-time electronic structure methods** for non-equilibrium electron dynamics (RT-TD-DFT, RT-CC ...).

Time-dependent DMRG approaches

- **Many variants available**: Time-Evolving Block Decimation Time-Step Targeted DMRG, Krylov-based methods ...
- Not tailored to the inherent **complexity** of molecular Hamiltonians.
- Our solution: **Tangent-space TD-DMRG**: support arbitrarily complex Hamiltonians and support stable propagation algorithms.
- **Challenge**: extent of many-particle correlation **increases** with time (**entanglement barrier** effect), MPS representation of the time-evolving wave function may become **increasingly less accurate** as the propagation proceeds.

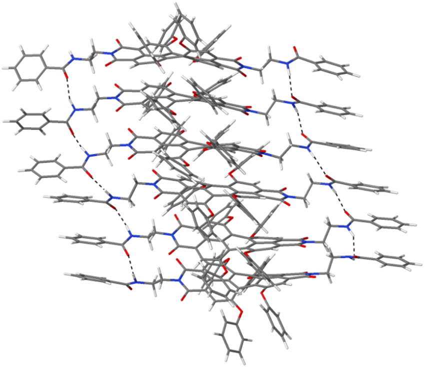
A. Baiardi, M. Reiher, *J. Chem. Theory Comput.*, 15, 3481 (**2019**)
A. Baiardi, *J. Chem. Theory Comput.*, 17, 3320 (**2021**)

Vibronic dynamics with TD-DMRG

- Monomer: $\approx$ 400 modes, not treatable with full quantum dynamics.
- Vibronic Hamiltonian within the excitonic approximation.

$$\mathcal{V}_{\text{coupl}}^{S_{\alpha_i}} = \mathcal{V}_{\text{coupl}}^{S_{\alpha_i}}\left(\boldsymbol{q}_{\text{eq}}\right) + \frac{1}{\sqrt{2}} \sum_{j=1}^{N_{\text{vib}}} \frac{\partial \mathcal{V}_i^{\alpha}}{\partial q_j} \left(b_j^{+} + b_j\right)$$

- 10 modes for each monomer, S_0 and S_1 electronic states.

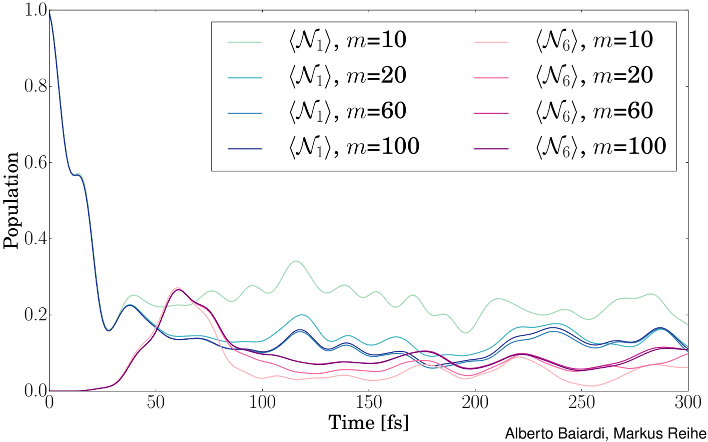


M. Schröter, S. Ivanov, J. Schulze, S.P. Polyutov, Y. Yan, T. Pullerits, O. Kühn, *Phys. Rep.* 567, 1 (**2015**)

Population dynamics

$$\langle \mathcal{N}_i \rangle = \langle \Psi \mid a^\dagger_{S_1^{(i)}} a_{S_1^{(i)}} \mid \Psi \rangle$$

- Simulation of the **excitation energy transfer** process.
- Molecule 1 initially excited, excitation transferred via vibronic coupling.



The dynamical correlation challenge

- DMRG can target up to $\approx$ 100 orbitals.
- DMRG can capture **strong correlation effects**, but more effective strategies exist for the **weakly correlated** part (dynamical correlation).
- **Challenge**: design **efficient** methods to include **dynamical correlation** effect in DMRG calculations.

Solutions

1. Methods based on **second-order perturbation theory**.
2. Integration with **Coupled Cluster** or **Density Functional Theory**.
3. Include dynamical correlation effects in the wave function *via* **explicitly-correlated schemes**.

The transcorrelated DMRG method

- Wave function ansatz: product of a **correlation factor** and a **CI**-type expansion.[1]

$$| \Psi \rangle = \exp\left(\sum_{i<j} f(r_{ij}) \right) | \Psi_{\text{MPS}} \rangle$$

- Correlator **revolved** into the Hamiltonian by **similarity transformation**.

$$\mathcal{H}_{\text{ele}} e^{\tau} \Phi = E_{TC} e^{\tau} \Phi \longrightarrow \left(e^{-\tau} \mathcal{H}_{\text{ele}} e^{\tau} \right) \Phi = E_{\text{TC}} \Phi$$

- **Non-Hermitian Hamiltonian**, optimization challenging with variational methods, straightforward with **imaginary time evolution**.[2,3]
- Faster convergence to the complete basis set limit, reduces the extent of correlation effects.

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[1] S. Boys, N. Handy *Proc. R. Soc. A Math. Phys. Eng. Sci.* 310, 43 (**1969**)

[2] K. Guther, A. J. Cohen, H. Luo, A. Alavi *J. Chem. Phys.* 155, 011102 (**2021**)

[3] A. Baiardi, M. Reiher *J. Chem. Phys.* 153, 164115 (**2020**)

Transcorrelated DMRG: the Fermi-Hubbard model

U/t	N_α	N_β	m	TI-DMRG	tcDMRG	Ref.[1]
4	12	12	500	-1.1500	-1.1804	-1.1853
2	18	18	500	-1.1345	-1.1530	-1.1516
4	18	18	500	-0.8206	-0.8596	-0.8574
4	18	18	1000	-0.8307	-0.8580	-0.8574

$$\mathcal{H}^{(\mathrm{m})}_{\mathrm{tcFH}} = \mathcal{H}^{1b} + \mathcal{H}^{2b}$$

$$+ 2t\frac{\cosh(J) - 1}{W^2 H^2} \sum_{\boldsymbol{p},\boldsymbol{q},\boldsymbol{s},\boldsymbol{k},\boldsymbol{k}',\sigma} \epsilon_{\boldsymbol{p}-\boldsymbol{k}+\boldsymbol{k}'} c^{\dagger}_{\boldsymbol{p}-\boldsymbol{k},\sigma} c^{\dagger}_{\boldsymbol{q}+\boldsymbol{k}',\bar{\sigma}} c^{\dagger}_{\boldsymbol{s}+\boldsymbol{k}-\boldsymbol{k}',\bar{\sigma}} c_{\boldsymbol{s},\bar{\sigma}} c_{\boldsymbol{q},\bar{\sigma}} c_{\boldsymbol{p},\sigma}$$

- **Faster** *m* convergence, DMRG **more efficient**.
- More compact MPS wave function representation.
- Complex three-body operator.

---

[1] A. Baiardi, M. Reiher *J. Chem. Phys.* 153, 164115 (**2020**)

The strong correlation challenge in classical simulations

1. Design methods that are **general** with respect to the problems they can target.
2. Efficient and reliable methods for **excited states**.
3. Many-body correlations more relevant for **non-equilibrium processes**.
4. Effectively combine methods tailored for **strongly-correlated** problems and cost-effective strategies to include **dynamical correlation** effects.

$\Rightarrow$ **Quantum computing** as a solution?

Quantum computing for molecular vibrations

- **Born-Oppenheimer** vibrational Hamiltonian → L **distinguishable**, **bosonic** particles coupled by a **arbitrary high-order** potential.

$$\left(\sum_{i=1}^{L} \mathcal{T}(Q_i) + \sum_{i=1}^{L} \mathcal{V}^{[i]}(Q_i) + \sum_{i<j}^{L} \mathcal{V}^{[i,j]}(Q_i, Q_i) + ... \right) \Psi(Q_1, ... , Q_L) = E_{\text{vib}} \Psi(Q_1, ... , Q_L)$$

- Finite basis $\chi_j^{[i]}(Q_i)$ introduced **per mode** → vibrational CI wave function.

$$|\Psi_{\text{VCI}}\rangle = \sum_{i_1=1}^{N_1} ... \sum_{i_L=1}^{N_L} C_{i_1,...,i_L} |i_1 \cdots i_L\rangle$$

- **Second quantization** for of the Hamiltonian obtained with the n-mode formalism.[1]

$$\mathcal{V}_{\text{SQ}} = \sum_{i=1}^{L} \sum_{k_i,h_i}^{N_i} \langle k_i | \mathcal{H}_i(Q_i) | h_i \rangle a^+_{k_i} a_{h_i} + \sum_{i<j}^{L} \sum_{k_i,h_i}^{N_i} \sum_{k_j,h_j}^{N_j} \langle k_i k_j | \mathcal{V}_{ij}(Q_i, Q_j) | h_i h_j \rangle a^+_{k_i} a^+_{k_j} a_{h_j} a_{h_i} + ...$$

- Efficient mapping to the qubit space → no need for the **Jordan-Wigner transformation**.[2]

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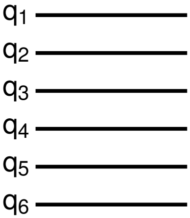
[1] O. Christiansen, *J. Chem. Phys.* 120, 2140 (**2004**)

[2] P. J. Ollitrault, A. Baiardi, M. Reiher, I. Tavernelli, *Chem. Sci.* 11, 6842 (**2020**)

Quantum computing beyond electronic problems

Example: 2-mode Hamiltonian, 3 basis functions per mode.



- **Equivalent** to conventional mapping of **electronic** problems.
- **Many** states of the qubit space do not represent physically acceptable basis functions.
- More **compact** mapping, based on binary representation, possible[1] → wave function ansatz design less trivial.

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[1] N. P. D. Sawaya, T. Menke, T. H. Kyaw, S. Johri, A. Aspuru-Guzik, *npj Quantum Inf.* 6, 1 (**2020**)

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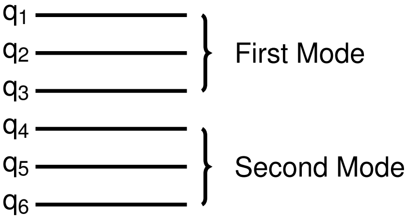

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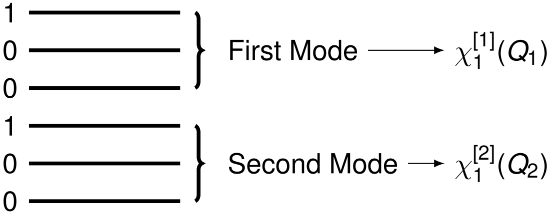

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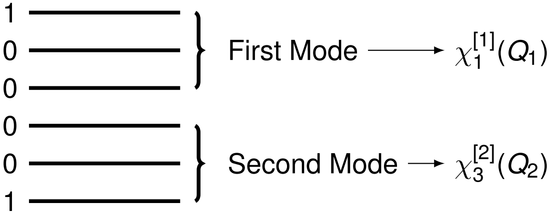

First Mode $\longrightarrow \chi_1^{[1]}(Q_1)$

Second Mode $\rightarrow \chi_3^{[2]}(Q_2)$

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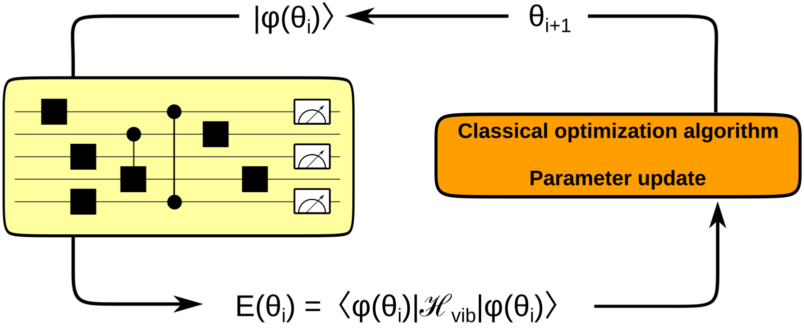
[1] N. P. D. Sawaya, T. Menke, T. H. Kyaw, S. Johri, A. Aspuru-Guzik, *npj Quantum Inf.* 6, 1 (**2020**)

The vibrational VQE

- **Quantum Phase Estimation**: Returns the full-CI energy but requires very deep circuits.
- **Variational Quantum Eigensolver**: optimize **classically** the energy for a given a wave function ansatz by evaluating the expectation value on a quantum computer.



$|\varphi(\theta_i)\rangle$

θ_{i+1}

Classical optimization algorithm

Parameter update

$$E(\theta_i) = \langle \varphi(\theta_i) | \mathscr{H}_{\text{vib}} | \varphi(\theta_i) \rangle$$

A. Peruzzo *et al.*, *Nat. Commun.* 5, 4213 (**2014**)

Wave function ansätze for vibrational problems

1. **Unitary vibrational Coupled Cluster**, exponential wave function ansatz.

$$| \Psi_{\mathrm{UVCC}} \rangle = e^{\mathcal{T}-\mathcal{T}^\dagger} | \Psi_{\mathrm{HF}} \rangle \qquad \mathcal{T} = \sum_{i=1}^{L} \sum_{k_i,h_i}^{N_i} \theta^{[i]}_{k_i,h_i} a^\dagger_{k_i} a_{h_i} + \sum_{i<j}^{L} \sum_{k_i,h_i}^{N_i} \sum_{k_j,h_j}^{N_j} \theta^{[i,j]}_{k_i k_j,h_i h_j} a^\dagger_{k_i} a_{h_i} a^\dagger_{k_j} a_{h_j}$$

2. Hardware efficient **SwapRZ** heuristic circuit, entangling blocks + Rz rotations.

$$| \Psi_{\mathrm{SwapRZ}} \rangle = e^{\mathrm{i}\mathcal{T}} | \Psi_{\mathrm{HF}} \rangle \qquad \mathcal{T} = \sum_{i<j}^{N_{\mathrm{qubits}}} \theta_{i,j} \left(X_i X_j + Y_i Y_j \right)$$

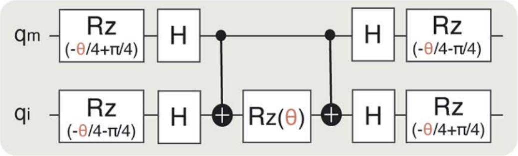
3. Low-depth approximation of the UVCC circuit → **Compact Heuristic Circuit** (CHC) for chemistry.

A. Kandala, A. Mezzacapo, K. Temme, M. Takita, M. Brink, J. Chow, J. Gambetta, *Nature* 549, 242 (**2017**)
P. J. Ollitrault, A. Baiardi, M. Reiher, I. Tavernelli, *Chem. Sci.* 11, 6842 (**2020**)

CHC wave function ansatz

- Single-excitation can be reproduced with the exponential of a product of X gates.

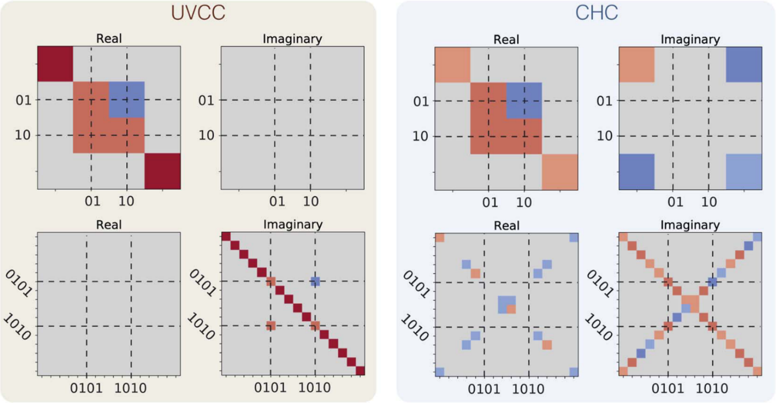
$$\left|\langle a_i^\dagger a_m \Psi_{\mathrm{HF}} | e^{\mathrm{i}\theta_{im} X_i X_m} | \Psi_{\mathrm{HF}} \rangle\right|^2 = \left|\langle a_i^\dagger a_m \Psi_{\mathrm{HF}} | e^{\theta_{im}(\sigma_i^+ \sigma_m^- - h.c.)} | \Psi_{\mathrm{HF}} \rangle\right|^2$$



- Relative **phase** not correctly reproduced → rotation angle θ optimized to reproduce the UVCC circuit when applied onto the reference determinant.
- Can be extended to **double excitations**.

P. J. Ollitrault, A. Baiardi, M. Reiher, I. Tavernelli, *Chem. Sci.* 11, 6842 (**2020**)

CHC wave function ansatz



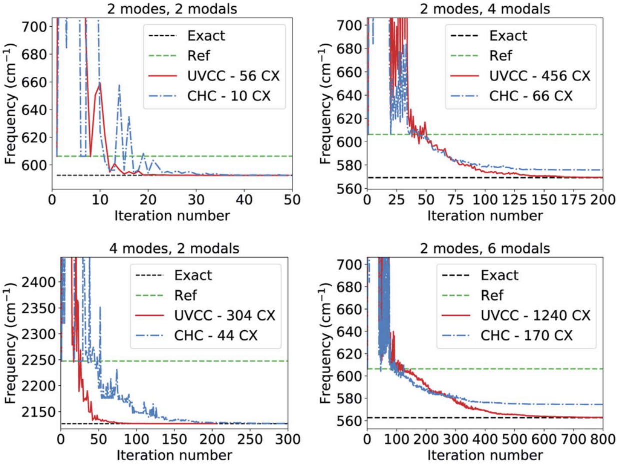
- CHC and UVCC equivalent only when applied onto the **HF state**.

→ Accuracy may deteriorate for **strong correlation**.

P. J. Ollitrault, A. Baiardi, M. Reiher, I. Tavernelli, *Chem. Sci.* 11, 6842 (**2020**)

Vibrational spectra on quantum computers: simulations

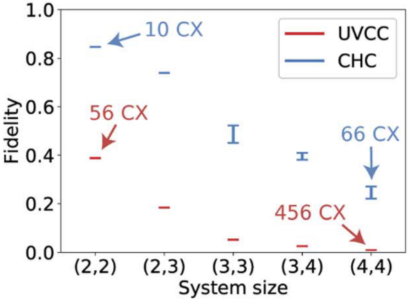
- **System**: CO_2, anharmonic quartic force field, vibrational ground state.
- **Optimizer**: COBYLA, no noise.
- Optimization of the **ground state** energy.
- CHC error **increases** with the size of the modal basis.

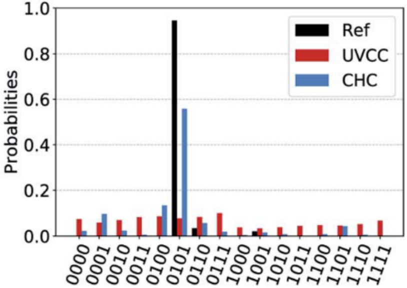


P. J. Ollitrault, A. Baiardi, M. Reiher, I. Tavernelli, *Chem. Sci.* 11, 6842 (**2020**)

Vibrational spectra on quantum computers: results

System: CO_2, anharmonic quartic force field, vibrational ground state, 2 modes/2 modals.



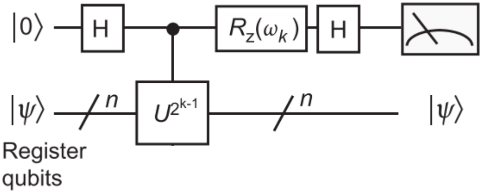


- UVCC large depth, noisy simulations on real quantum hardware.
- CHC more shallow, enables reliable optimization for the smallest Hamiltonian.

P. J. Ollitrault, A. Baiardi, M. Reiher, I. Tavernelli, *Chem. Sci.* 11, 6842 (**2020**)

Accurate quantum-chemical calculations with the QPE

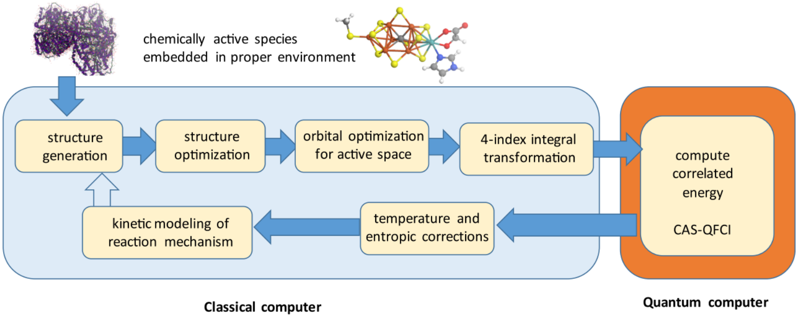
- **VQE** key for applications on near-term quantum devices.
- However, limited by the stability of the **classical optimization algorithm** and by the need of restricting the **wave function ansatz**.
- **Quantum phase estimation** do not suffer from these limitations → long-term solution.



B. P. Lanyon *et al.*, *Nat. Chem.* 2, 106 (**2010**)

Large-scale quantum simulation of molecules [work by M. Reiher & Microsoft Research]

- **Long-term goal**: **accurate** and **error-controllable** calculation of electronic energy for active spaces with more than ≈ 100 orbitals.
- **Quantum algorithms** for electronic energies, **classical** algorithms for geometry optimization (DFT), thermodynamic corrections, missing dynamical correlation.



chemically active species embedded in proper environment

structure generation

structure optimization

orbital optimization for active space

4-index integral transformation

compute correlated energy

CAS-QFCI

temperature and entropic corrections

kinetic modeling of reaction mechanism

Classical computer

Quantum computer

M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, *Proc. Natl. Acad. Sci.* 114, 7555 (**2017**)

FeMoCo nitrogenase: cost estimate [work by M. Reiher & Microsoft Research]

- Iron-molybdenum FeMoCo cofactor of nitrogenase: a challenging test-case for classical wave function algorithms.
- Singlet, triply positive charge state [CAS(54,54)], neutral triplet [CAS(65,57)].

		Qubits	Δt [10 ns/T]	Δt [100 ns/T]
Singlet	Serial	111	12 days	39 months
	Nested	135	1.4 days	14 days
Triplet	Serial	117	22 days	7.2 months
	Nested	142	2.5 days	25 days

- **Bottleneck**: non-Clifford T gate arising from the **single-qubit rotation**.
- **Nested**: operations acting on different qubits run **in parallel**.
- Δt execution time for T gate: 100 ns **optimistic**, 10 ns **very optimistic**.

M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, *Proc. Natl. Acad. Sci.* 114, 7555 (**2017**)

FeMoCo nitrogenase: noise [work by M. Reiher & Microsoft Research]

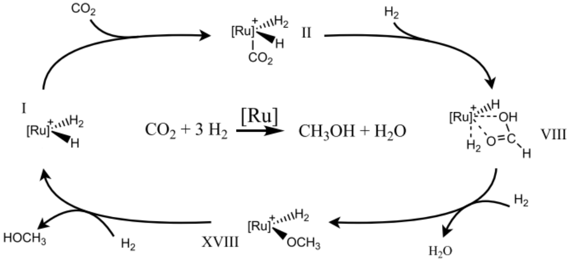
	Error rate	Serial	Nested
Num. qubits	10^{-3}	$1.8 * 10^{8}$	$1.8 * 10^{11}$
	10^{-6}	$1.2 * 10^{6}$	$3.1 * 10^{9}$
	10^{-9}	$2.3 * 10^{5}$	$1.5 * 10^{8}$

- Multiple **physical qubits** required to represent a **logical qubit** in fault-tolerant computation.
- Number of required physical qubits increases with the error rate.
- Hardware requirement increases **drastically**.
- Computational time **reasonable** for an error rate of 10^{-3}, but number of qubits is **prohibitive**, reduced with an error rate of 10^{-6}.

M. Reiher, N. Wiebe, K. M. Svore, D. Wecker, M. Troyer, *Proc. Natl. Acad. Sci.* 114, 7555 (**2017**)

Quantum computing enhanced computational catalysis [work by V. von Burg, M. Reiher & Microsoft Research]

- Ru-based catalyst for transforming CO_2 into methanol.
- Kinetic analysis → energetic of all the steps of a **reaction network**.
- Multi-configurational calculations on DFT-optimized geometries.



S. Wesselbaum *et al.*, *Chem. Sci.* 6, 693 (**2015**)

V. von Burg, G. H. Low, T. Häner, D. S. Steiger, M. Reiher, M. Roetteler, M. Troyer, *Phys. Rev. Res.* 3, 033055 (**2021**)

Enhancing the simulation efficiency [work by V. von Burg, M. Reiher & Microsoft Research]

- QPE efficiency enhanced via **qubitization** Propagator $e^{-\mathrm{i}\mathcal{H}/\alpha}$ replaced by $e^{-\mathrm{i}\,\mathrm{arcsin}(\mathcal{H}/\alpha)}$, can be encoded **exactly**.
- Size of the Hamiltonian reduced based on the **double factorized form** of the two-electron integral.

$$(pr|qs) = \sum_{Q}^{N_{\mathrm{rank}}} L_{pr}^{Q} L_{qs}^{Q} \qquad \rightarrow \qquad \mathcal{H}^{(2)} = \frac{1}{2} \sum_{Q}^{N_{\mathrm{rank}}} L_{pr}^{Q} \left(\sum_{pr}^{L} L_{pr}^{Q} a_p^{\dagger} a_r \right) \left(\sum_{qs}^{L} L_{qs}^{Q} a_q^{\dagger} a_s \right)$$

$$= \frac{1}{2} \sum_{Q}^{N_{\mathrm{rank}}} \left(\sum_{x}^{N_Q} \sum_{\sigma} s_x^Q n_x^Q \right) \left(\sum_{y}^{N_Q} \sum_{\sigma'} s_y^Q n_y^Q \right)$$

- **Simpler** Hamiltonian, **more** elementary operators.

V. von Burg, G. H. Low, T. Häner, D. S. Steiger, M. Reiher, M. Roetteler, M. Troyer, *Phys. Rev. Res.* 3, 033055 (**2021**)

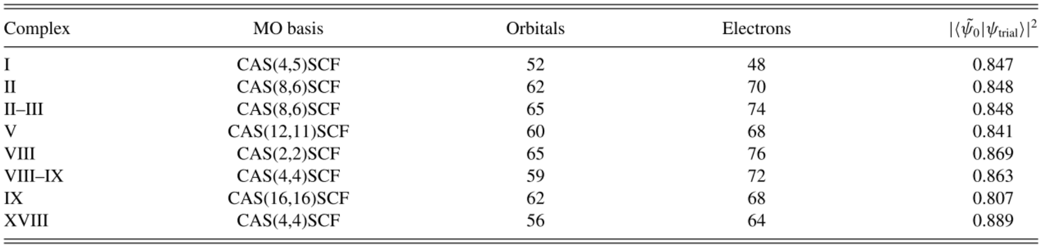
New cost estimate [work by V. Von Burg M. Reiher & Microsoft Research]

	Toffoli gates	Qubits	
FeMoCo	$2.3 * 10^{10}$	3600	Qubitization + Truncation=1 mHa
	$1.22 * 10^{10}$	3600	Qubitization + Truncation=73 mHa
	$1.5 * 10^{14}$	142	Trotterization
Ru	$4.6 * 10^{10}$	4600	Qubitization + Truncation=1 mHa
	$9.3 * 10^{11}$	11000	Qubitization

- **Strong** reduction of the number of gates compared to the previous estimate.
- **Larger** number of qubits required.

V. von Burg, G. H. Low, T. Häner, D. S. Steiger, M. Reiher, M. Roetteler, M. Troyer, *Phys. Rev. Res.* 3, 033055 (**2021**)

Initial state preparation [work by V. Von Burg M. Reiher & Microsoft Research]



Complex	MO basis	Orbitals	Electrons	$\|\langle\tilde{\psi}_0\|\psi_{\text{trial}}\rangle\|^2$
I	CAS(4,5)SCF	52	48	0.847
II	CAS(8,6)SCF	62	70	0.848
II–III	CAS(8,6)SCF	65	74	0.848
V	CAS(12,11)SCF	60	68	0.841
VIII	CAS(2,2)SCF	65	76	0.869
VIII–IX	CAS(4,4)SCF	59	72	0.863
IX	CAS(16,16)SCF	62	68	0.807
XVIII	CAS(4,4)SCF	56	64	0.889

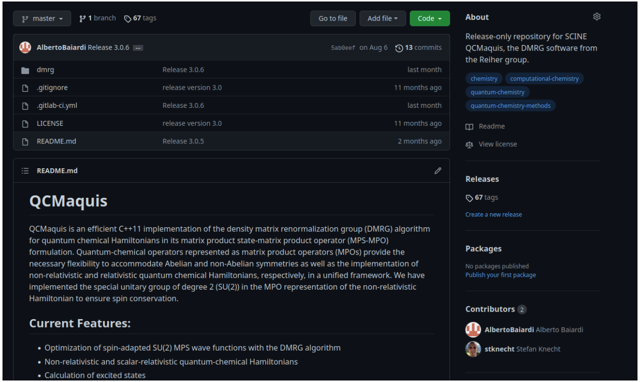
- Initial state prepared: **Hartree Fock** determinant.
- Weakly correlated system, single determinant is a **good approximation**.
- Becomes **less trivial** for strongly correlated molecules and/or excited states.

V. von Burg, G. H. Low, T. Häner, D. S. Steiger, M. Reiher, M. Roetteler, M. Troyer, *Phys. Rev. Res.* 3, 033055 (**2021**)

Conclusions and perspective

- **DMRG** can largely extend the application range of full CI-based methods.
- **Many** challenge remain, especially for **excited-states** and **non-equilibrium properties**.
- Quantum computing methods based on the QPE algorithm may further push the boundaries of modern CI schemes.
- Need for constantly assessing the cost of new quantum algorithms on challenging quantum-chemical problems.
- Although approximated, algorithms based on the VQE needed for algorithms to be run on near-term quantum computers.

The `QCMaquis` project



AlbertoBaiardi Release 3.0.6 … 5ab0eef on Aug 6 **13** commits

dmrg	Release 3.0.6	last month
.gitignore	release version 3.0	11 months ago
.gitlab-ci.yml	Release 3.0.6	last month
LICENSE	release version 3.0	11 months ago
README.md	Release 3.0.5	2 months ago

README.md

QCMaquis

QCMaquis is an efficient C++11 implementation of the density matrix renormalization group (DMRG) algorithm for quantum chemical Hamiltonians in its matrix product state-matrix product operator (MPS-MPO) formulation. Quantum-chemical operators represented as matrix product operators (MPOs) provide the necessary flexibility to accommodate Abelian and non-Abelian symmetries as well as the implementation of non-relativistic and relativistic quantum chemical Hamiltonians, respectively, in a unified framework. We have implemented the special unitary group of degree 2 (SU(2)) in the MPO representation of the non-relativistic Hamiltonian to ensure spin conservation.

Current Features:

- Optimization of spin-adapted SU(2) MPS wave functions with the DMRG algorithm
- Non-relativistic and scalar-relativistic quantum-chemical Hamiltonians
- Calculation of excited states

About

Release-only repository for SCINE QCMaquis, the DMRG software from the Reiher group.

Releases

67 tags

Create a new release

Packages

No packages published
Publish your first package

Contributors 2

AlbertoBaiardi Alberto Baiardi
stknecht Stefan Knecht

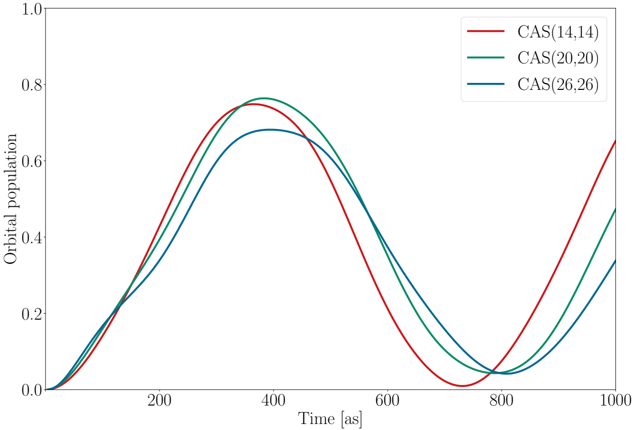
- Interfaced with `OpenMOLCAS` for electronic-structure problems (with Dr. Leon Freitag).
- **New features available**: NEAP-DMRG (3.0.6, by Robin Feldmann), electron dynamics (3.1.0).
- **To come**: explicitly-correlated DMRG (with Dr. Michał Lesiuk), vibrational/vibronic (TD-)DMRG (with Nina Glaser), massively parallel DMRG (with PD Dr. Stefan Knecht).

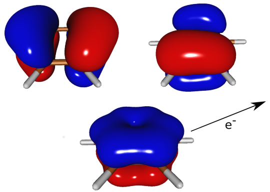
`https://github.com/qcscine/qcmaquis`

Acknowledgment

- Pauline Ollitrault and Dr. Ivano Tavernelli (IBM Zürich).
- Vera von Burg, Microsoft Research team led by Prof. Matthias Troyer.
- Reiher group.

Non-equilibrium electron dynamics with DMRG





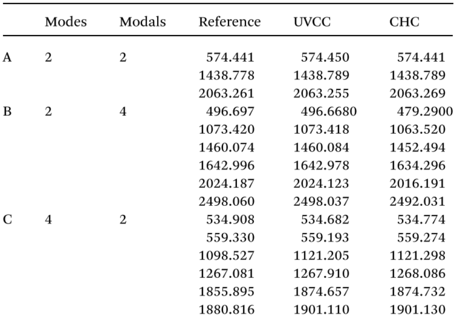
- Selected CI/CAS(8,8) ≈ 700 as, TD-ADC(3) ≈ 900 as.
- **Approximations**: **sudden** ionization, **instantaneous** ionization pulse, **orbitals relaxation** neglected.

ADC(3): V. Despré *et al.*, *J. Phys. Chem. Lett.*, 6, 426 (**2015**)
Selected CI: J. Schriber, F. Evangelista, *J. Chem. Phys.*, 151, 171102 (**2019**)
A. Baiardi, *J. Chem. Theory Comput.*, 17, 3320 (**2021**)

Vibrational excitation energies

- VQE returns the vibrational **ground state** energy.
- Excited states can be calculated with the quantum EOM algorithm.

→ Diagonalize **classically** the RPA matrix, by calculating the matrix elements on a **quantum computer**.

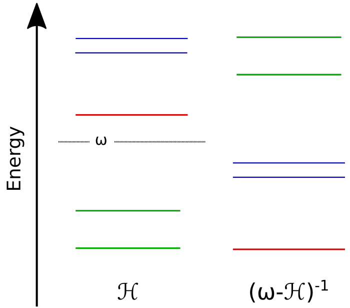


	Modes	Modals	Reference	UVCC	CHC
A	2	2	574.441	574.450	574.441
			1438.778	1438.789	1438.789
			2063.261	2063.255	2063.269
B	2	4	496.697	496.6680	479.2900
			1073.420	1073.418	1063.520
			1460.074	1460.084	1452.494
			1642.996	1642.978	1634.296
			2024.187	2024.123	2016.191
			2498.060	2498.037	2492.031
C	4	2	534.908	534.682	534.774
			559.330	559.193	559.274
			1098.527	1121.205	1121.298
			1267.081	1267.910	1268.086
			1855.895	1874.657	1874.732
			1880.816	1901.110	1901.130

P. J. Ollitrault, A. Baiardi, M. Reiher, I. Tavernelli, *Chem. Sci.* 11, 6842 (**2020**)

The excited states challenge

- Full CI-based methods rely on the **variational principle**.
- Extension towards (potentially high-energy) excited-states **non-trivial**.
- Extent of many-particle correlation may increase for excited-states.
- **Challenge**: design excited-state methods that are as **robust** as the ground-state one.



- **Spectral transformation** to map a target excited state to the ground state.

$$\Omega_{\omega}^{\text{S\&I}} = (\omega - \mathcal{H})^{-1} \qquad \Omega_{\omega}^{\text{Folded}} = (\omega - \mathcal{H})^{2}$$

A. Baiardi, C.J. Stein, V. Barone, M. Reiher, *J. Chem. Phys.*, 150, 094113 (**2019**)

The excited states challenge

- Full CI-based methods rely on the **variational principle**.
- Extension towards (potentially high-energy) excited-states **non-trivial**.
- Extent of many-particle correlation may increase for excited-states.
- **Challenge**: design excited-state methods that are as **robust** as the ground-state one.

- **Projective** approach: based on the **power method**, do not rely on the **variational principle**.

$$(\mathcal{H} - \sigma\mathcal{I}) \mid \tilde{\Psi}^{(i+1)} \rangle = \mid \Psi^{(i)} \rangle$$

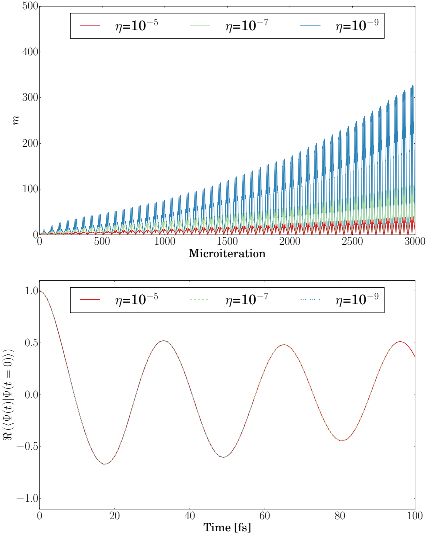
- Either **higher computational cost** or **smaller numerical stability**.
- **FEAST**: projective method, yields stable and efficient optimizations for multiple energy ranges.

---

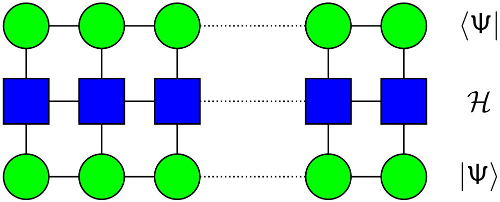
[2] A. Baiardi, A. K. Kelemen, *Arxiv*, 2110.00092 (**2021**)

The entanglement barrier challenge

- Target accuracy η fixed, MPS dimension adapted consequently.
- **Constant** increase of the MPS dimension with time → increase of correlation effects (**entanglement barrier effect**).
- **Challenge**: many-particle correlation more relevant for non-equilibrium processes.



The Density Matrix Renormalization Group - 2



- Factorization of the Hamiltonian $\mathcal{H}$ → **matrix product operator**.
- **Variational**, **iterative** optimization of the tensor → **sweep-based optimization** (equivalent to the alternating least squares method).
- **Efficient** optimization scheme + **compact** wave function representation.
- Can target $\approx$ 100 particles/basis functions.