Quantum non-orthogonal methods for calculation of electronic energies

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Molecular Hamiltonian for electrons and nuclei:

$$H = -\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I'} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

N electrons (*i*), finite number of nuclei (*I*)

Born Oppenheimer approximation

$$H = -\sum_i \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

second quantization

$$H = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

$$\{a_p, a_q^\dagger\}_+ = \delta_{pq}, \quad \{a_p, a_q\}_+ = 0$$

Hamiltonian matrix elements

$$h_{pq} = \int d\mathbf{x} \phi_p^*(\mathbf{x}) \left(-\frac{\nabla_i^2}{2} - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) \phi_q(\mathbf{x})$$

$$h_{pqrs} = \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\phi_p^*(\mathbf{x}_1)\, \phi_q^*(\mathbf{x}_2)\, \phi_s(\mathbf{x}_1)\, \phi_r(\mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|}$$

over Slater determinant basis generated by $\{\phi_i\}_{i=1}^M$.

M spin-space orbitals ('spin-orbitals')

Representation of molecular electronic states (MOs):

Determinantal wavefunctions:

$$\psi_N(x_0, x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_0(x_0) & \phi_1(x_0) & \cdots & \phi_{M-1}(x_0) \\ \phi_0(x_1) & \phi_1(x_1) & \cdots & \phi_{M-1}(x_1) \\ \vdots & \vdots & & \vdots \\ \phi_0(x_{N-1}) & \phi_1(x_{N-1}) & \cdots & \phi_{M-1}(x_{N-1}) \end{vmatrix}$$

Starting point for solutions: mean field (Hartree-Fock) solutions $E^{\mathrm{HF}} = \inf_{\Psi \in \mathcal{A}_N^0, \langle \Psi | \Psi \rangle = 1} \langle \Psi | H | \Psi \rangle$

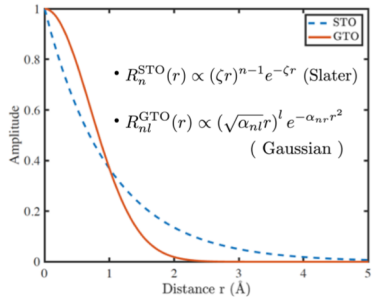
Diagonalize **Fock matrix** ("mean-field Hamiltonian") in an atomic orbital basis set $\{|\nu\rangle\}$:

$FC = SC\epsilon$

single electron MO coefficients

$S_{\nu\mu} = \langle \nu | \mu \rangle$
overlap matrix

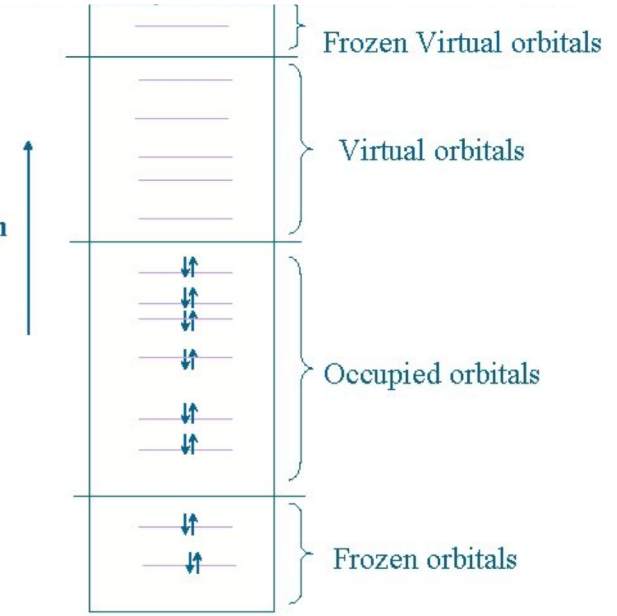
single electron energies



- **solve self-consistently**
- **efficient (typically O(M^3)) but neglects electron correlations (static, dynamic) – inaccurate for strongly correlated molecules**

Correlated electronic systems - classical:

- each determinant represents one electron configuration
- all possible configurations – FCI, scales $O(e^M)$



$$|\psi_{FCI}\rangle = \left(I + \sum_{pr} C_p^r a_r^\dagger a_p + \sum_{rasp} C_{pq}^{rs} a_r^\dagger a_s^\dagger a_p a_q + \dots\right) |\psi_{HF}\rangle$$

Full CI CIS CISD CISDT …

- coupled cluster expansion – not unitary or variational

$$|\psi_{CC}\rangle = e^T |\psi_{HF}\rangle, \quad T = \sum_i T_i$$

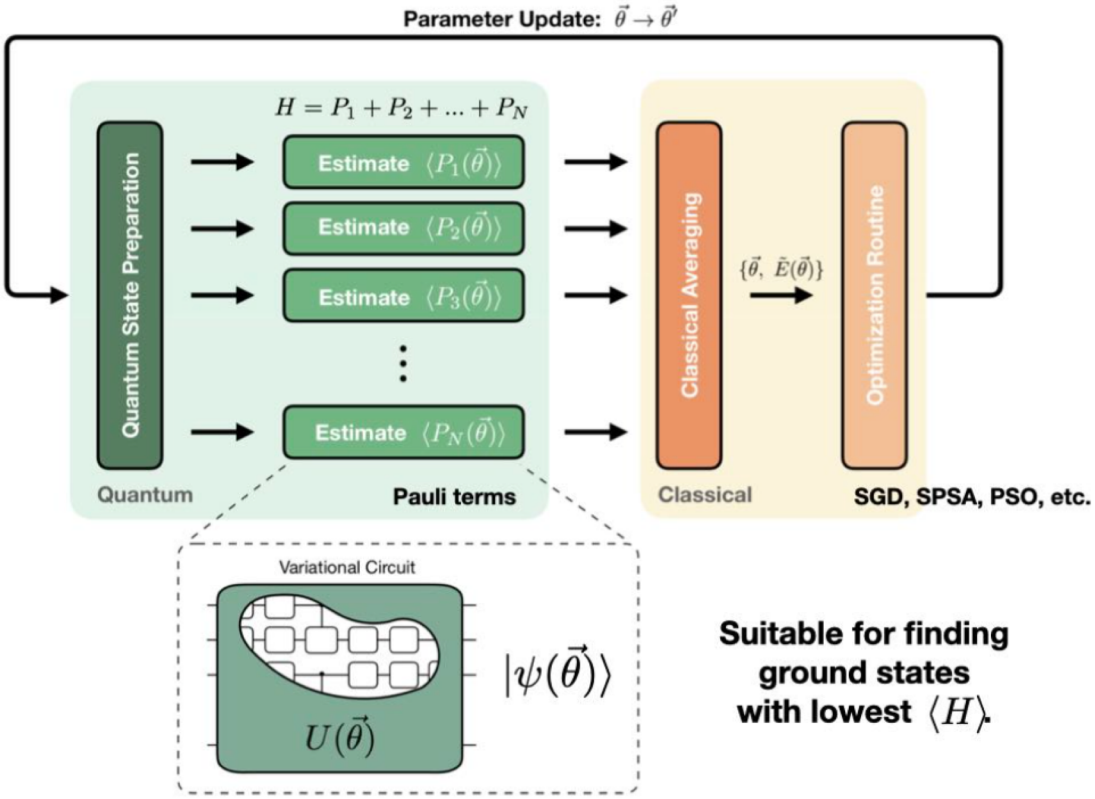
$$T_1 = \sum_{r\in virt, p\in occ} t_p^r a_r^\dagger a_p$$

$$T_2 = \sum_{r,s\in virt, p,q\in occ} t_{pq}^{rs} a_r^\dagger a_s^\dagger a_p a_q, \dots$$

- HF solutions can be restricted (same spatial orbitals for α, β spin), unrestricted (different s.o. for α, β), or general (mixed s.o. across α, β)
- typically one seeks chemical accuracy 1.6 x 10^{-3} Ha for energy gaps
- replace $|\psi_{HF}\rangle$ by $\sum_{i=1}^{m} c_i |\psi_{HF}^i\rangle$, better accuracy

→ non-orthogonal CI (NOCI), scales $O(e^M)$

Quantum computing for quantum chemistry – near term



Variational Quantum Eigensolver

- ansatz $\left|\psi(\vec{\theta})\right\rangle$ with circuit dependent parameters
- low depth quantum circuit to generate ansatz
- decompose Hamiltonian into Pauli operators
- measure Hamiltonian expectation value
- optimize parameters of quantum state preparation
- iterate to find lowest (variational) energy

Tradeoff – limited coherence vs repeated measurements

Two major challenges

- small, noisy devices do not allow for deep circuits because of restricted coherence times and gate fidelity
- VQE calculations require a large number of repeated circuit evaluations, for measurement and for optimization

These challenges reflect two different limitations on the runtime of NISQ algorithms:

- coherence time - limits quantum components
- total (wall clock) time – general limitation for iterative hybrid algorithms

Coherence time limitation:

- T_1 of qubits
- noisy quantum gates

resource cost metric - total two-qubit gate count

Total (wall clock) time limitation:

- iterative optimization overhead
- measurement costs at each iteration
- repetition of problem instances
- calibration drift etc.

resource cost metric – number of circuit repetitions required

Reduce these costs and enable additional tradeoffs

- reducing the number of two-qubit gates required, by design of new/improved ansatze, e.g., for electronic states

JCTC 15, 311 (2018)

- trading two-qubit qates for circuit repetitions, by using a linear combination of ansatz states → non-orthogonal VQE

New J. Physics 22, 073009 (2020)
1905.05118

- reducing the number of required circuit repetitions, by using changes of basis in which energy measurements are performed

npj Quantum Information **7,** 23 (2021)

Correlated electronic systems - quantum:

- map fermions to (distinguishable) qubits:

$$|f_0, f_1, \ldots, f_{M-1}\rangle \rightarrow |q_0, q_1, \ldots, q_{M-1}\rangle\,, q_p = f_p \in 0, 1$$

fermions → qubits

Jordan-Wigner transformation $a_p = Q_p \otimes Z_{p-1} \otimes \cdots \otimes Z_0, \;\; Q_p = \frac{1}{2}\left(X + iY\right) \equiv \sigma_p^-$

- Unitary coupled cluster (UCC) ansatze:

$$|\psi\rangle = e^{T - T^\dagger}\,|\psi_{ref}\rangle$$

many approximations/variants

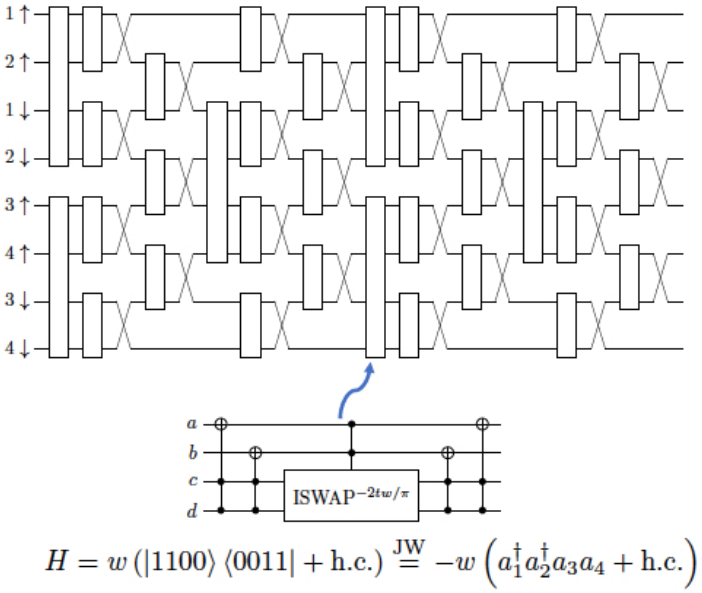
$$|\psi\rangle = \prod_{i=1}^{k}\left(e^{T(i) - T(i)^\dagger}\right)|\psi_{ref}\rangle$$

k-UpCCGSD: $T_1 = \sum_{q \in virt, p \in occ} t_p^q\left(a_{q\alpha}^\dagger a_{p\alpha} + a_{q\beta}^\dagger a_{p\beta}\right) \quad T_2 = \sum_{pq} t_{p_\alpha p_\beta}^{q_\alpha q_\beta} a_{q\alpha}^\dagger a_{q\beta}^\dagger a_{p\beta} a_{p\alpha}$

O(kN^2) amplitudes (compare with O(N^4) from UCCSD)

Quantum Circuit for k-UpCCGSD ansatz:

- use fermionic swap gates to reorder system modes → Trotter step in O(kM) depth using $O(kM^2)$ gates
  - require $\binom{M}{2}$ two-qubit gates together with $\binom{M/2}{2}$ four-qubit gates (need ≤ 40 2-qubit gates)
- compare 1 Trotter step for UCCSD ansatz, requires $O(M^4)$ gates
- ground state of the minimal basis H_4 example on 8 qubits is well described by 2-UpCCGSD circuit with 536 two-qubit gates

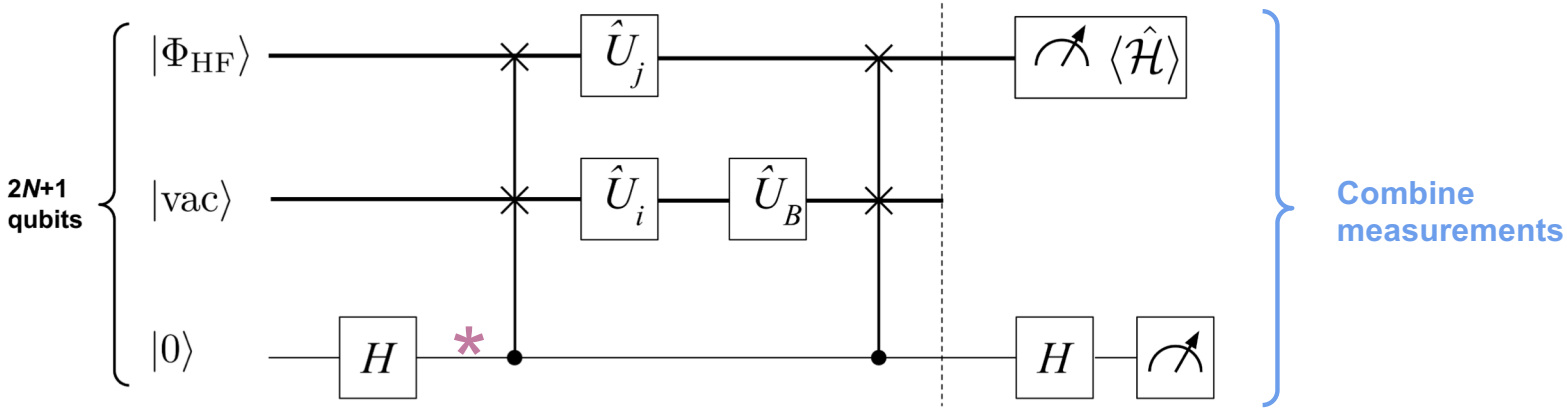


$$H = w\left(|1100\rangle\langle 0011| + \text{h.c.}\right) \overset{\text{JW}}{=} -w\left(a_1^\dagger a_2^\dagger a_3 a_4 + \text{h.c.}\right)$$

- single block of a k-UpCCGSD circuit on 4 spin-orbital system using fermionic swap gates
- boxes denote two and four qubit unitaries exponentiating individual terms from the cluster operator T, cf. example

Matrix Elements between non-orthogonal basis states:

- Circuit prepares building-block states *i* and *j* in parallel:



- *Hadamard test protocol* to evaluate the off-diagonal matrix elements:[1]

$$\mathrm{Re}(\mathcal{H}_{ij}) = \langle\hat{\mathcal{H}}\hat{Z}_{\mathrm{anc}}\rangle$$

$$\mathrm{Re}(\mathcal{S}_{ij}) = \langle\hat{Z}_{\mathrm{anc}}\rangle$$

Addition of *phase gate* to measure imaginary part:

$$* \begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix} \longrightarrow \begin{aligned} \mathrm{Im}(\mathcal{H}_{ij}) &= \langle\hat{\mathcal{H}}\hat{Z}_{\mathrm{anc}}\rangle \\ \mathrm{Im}(\mathcal{S}_{ij}) &= \langle\hat{Z}_{\mathrm{anc}}\rangle \end{aligned}$$

[1] W. J. Huggins, J. Lee, U. Baek, B. O'Gorman and K. B. Whaley, *New J. Phys.*, 2020, **22**, 073009.

- off-diagonal matrix elements of *H* and *S* – measurement requires overhead of only 2L controlled-SWAP gates + small cost for coupling to an ancilla qubit

generate logical ansatz from linear combination of L ansatz states

$$\left|\psi(\vec{c},\vec{\theta}_1,\ldots,\vec{\theta}_L)\right\rangle = \sum_{l=1}^{L} c_l \left|\phi_{ref}^{(l)}\right\rangle \qquad |\phi_l\rangle = e^{T_k - T_k^\dagger}\left|\phi_{ref}^{(l)}\right\rangle$$

solve generalized eigenvalue problem

$$Hc = ESc$$

classically – *exponential cost in M* for CC wavefunctions
quantum – *polynomial gate cost in M* for UCC wavefunctions

- non-orthogonal methods, efficient quantum implementation
- domain-specific ansatze informed by classical correlated states

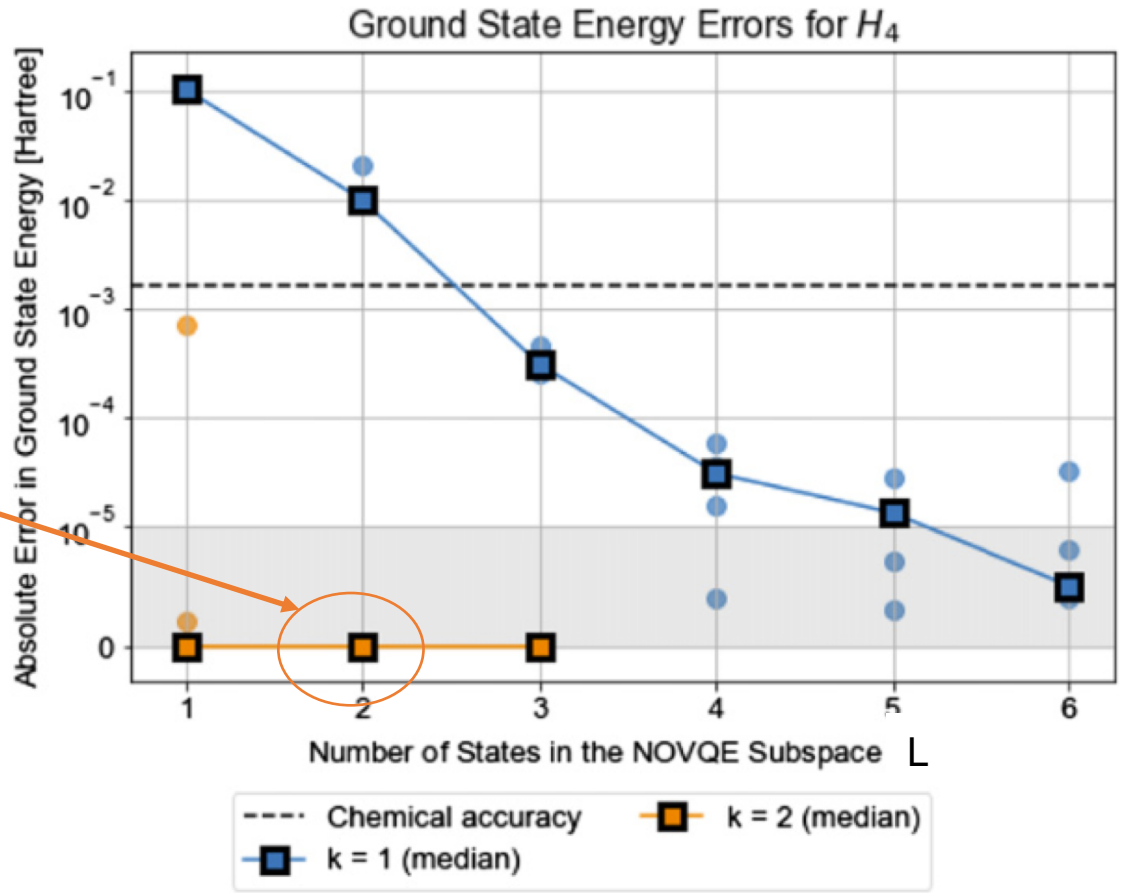
→ hybrid algorithmic approach taking advantage of ease of non-orthogonal calculations for quantum states

NOVQE example I : H_4

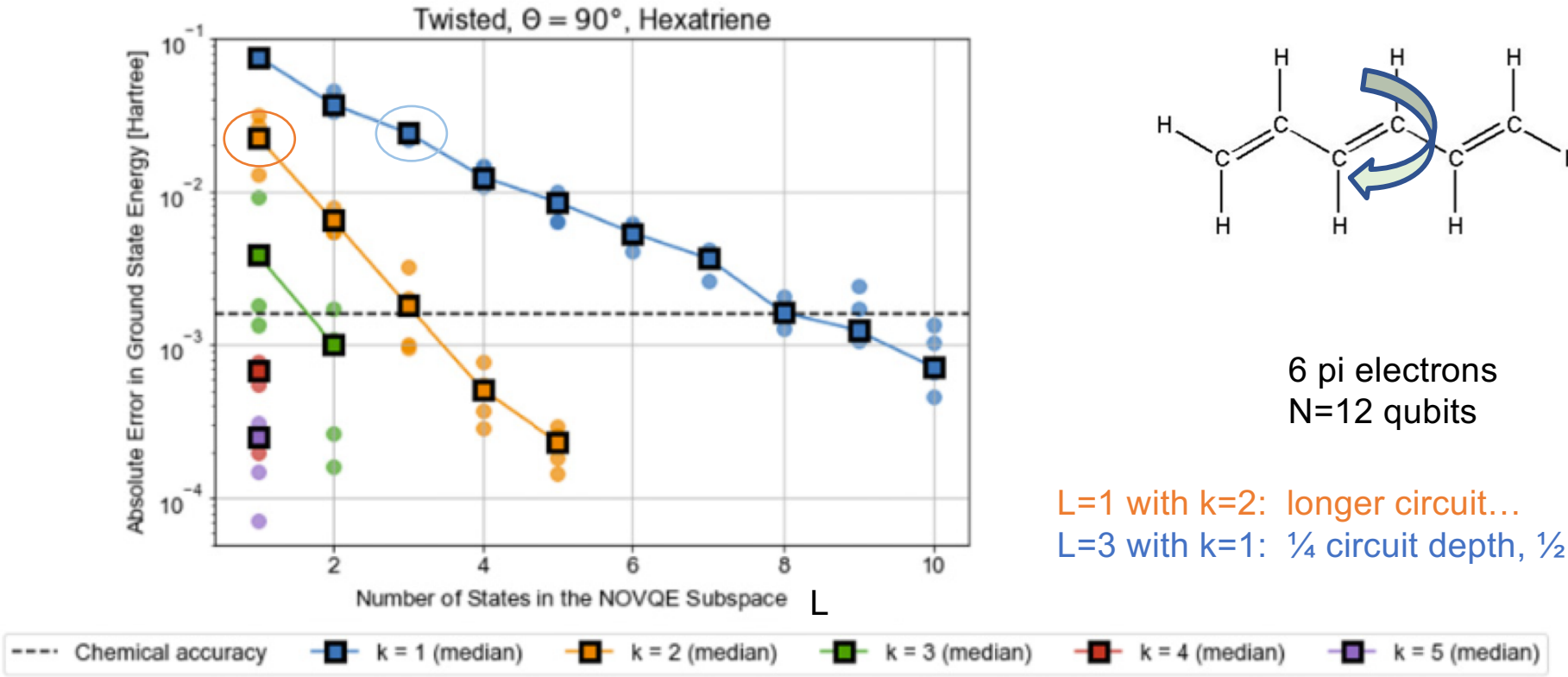
Square H_4, R=1.23 Angstrom

8 qubits:
2-UpCCGSD (k=2) circuit has
536 two-qubit gates

~2000 gradient evaluations
(finite difference)



NOVQE example II : twisted hexatriene



6 pi electrons
N=12 qubits

L=1 with k=2: longer circuit…
L=3 with k=1: ¼ circuit depth, ½ gates

NOVQE

advantages:

- non-orthogonal approach has efficient quantum implementation
- cost of measuring off-diagonal elements independent of K ⇒ can increase representational power of ansatz without requiring longer circuits
- domain-specific ansatze informed by classical correlated states

disadvantage:

- large overhead in measurements from repeated circuit evaluation for variational optimization - ~10^{10} for H_4, ~10^{12} for hexatriene

can we remove or at least significantly reduce the variational loop?

Non-orthogonal quantum eigensolver, NOQE

- remove variational optimization, significantly reduces measurement costs
- employ better ansatze
- low rank tensor decomposition of the two-body electron interaction terms[1,2]

$$\hat{T} = \sum_{pqrs=1}^{N} T_{ps,qr} \hat{a}_p^\dagger \hat{a}_s \hat{a}_q^\dagger \hat{a}_r$$

Takagi and SVD decompositions

$$e^{\hat{T}-\hat{T}^\dagger} \approx \prod_{l=1}^{L} \prod_{\mu=1}^{4} \mathcal{U}_B^{(l,\mu)\dagger} \exp(-i \sum_{ij=1}^{N} \rho_i^{(l,\mu)} \rho_j^{(l,\mu)} \hat{n}_i \hat{n}_j) \mathcal{U}_B^{(l,\mu)}$$

- reduce propagator to polynomially long product of basis rotations and number operators
- similar reduction for Hamiltonian further reduces measurement cost[3]

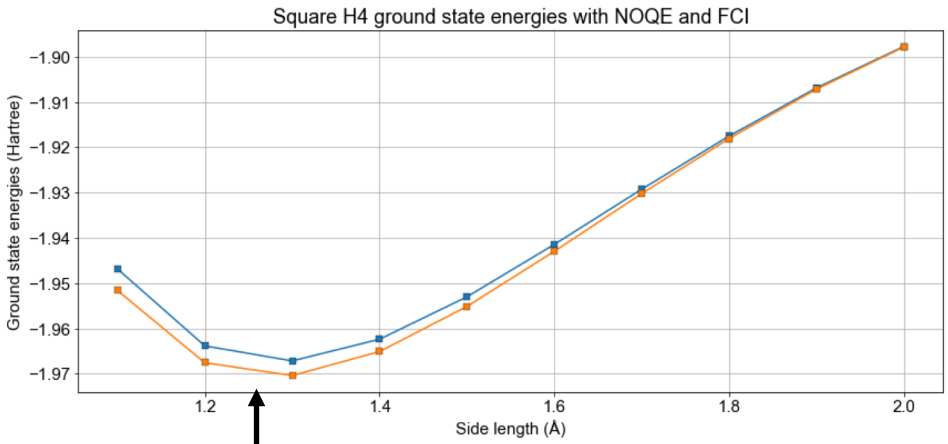
[1] M. Motta, et al., *npj Qu. Inf. 7, 83 (2021)*

[2] N. C. Rubin, et al., 2109.05010

[3] Huggins et al. npj Qu. Inf. **7,** 23 (2021)

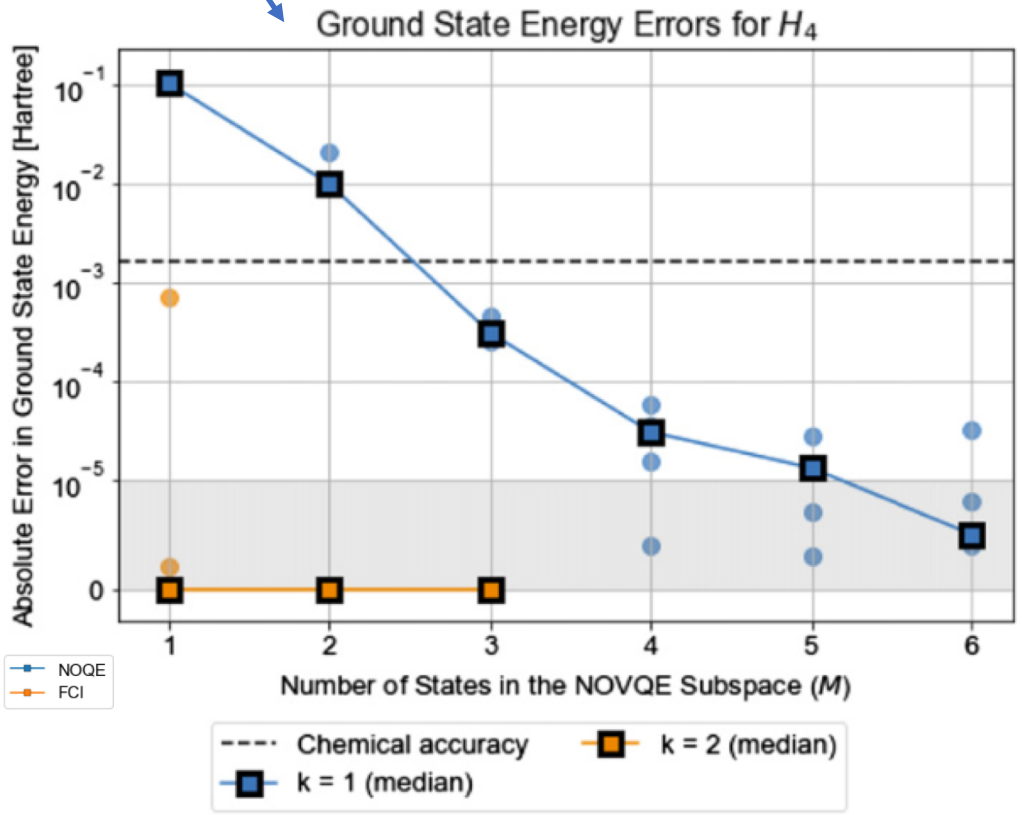
Comparison of NOQE with NOVQE

no gradient evaluations



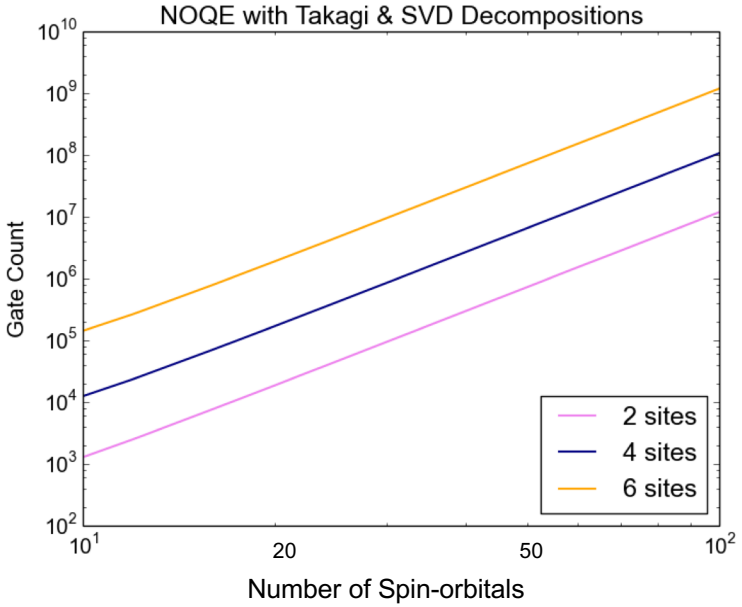
R=1.23 Angstrom
error ~4 mHa

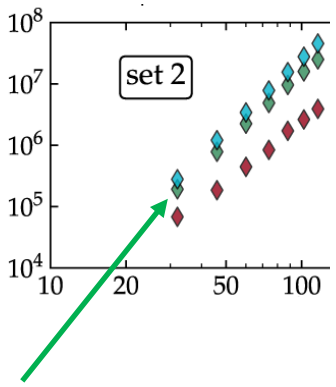
~2000 gradient evaluations



square H_4, R=1.23 Angstrom

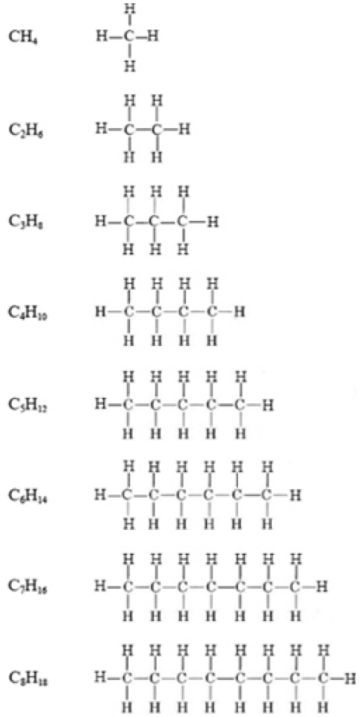
Resource estimates: total gate counts for ansatz state preparation



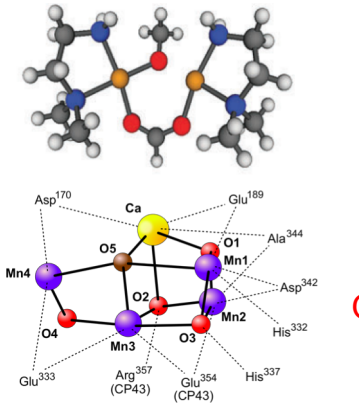


(green data) found to yield sub-mHa truncation errors as tested on alkane chains with double-SVD uCC ansatz

Motta *et al. npj Quantum Inf* **7**, 83 (2021)



- only a relatively mild increase in gate count as the number of radical sites increases
- with 2 sites, NOQE can rigorously describe the strong static correlation involved in single-bond breaking (e.g., H_2) and systems such as twisted hexatriene and di-copper molecules
- with hardware advances, NOQE is well-positioned to target relative spin-state energetics of polynuclear transition metal clusters in metalloenzymes and molecular magnets



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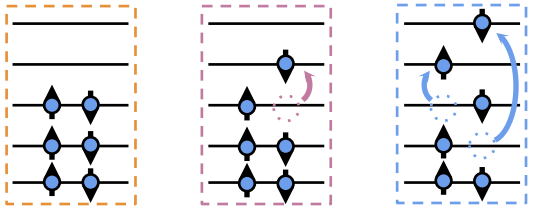
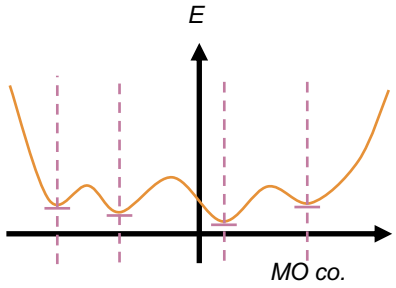
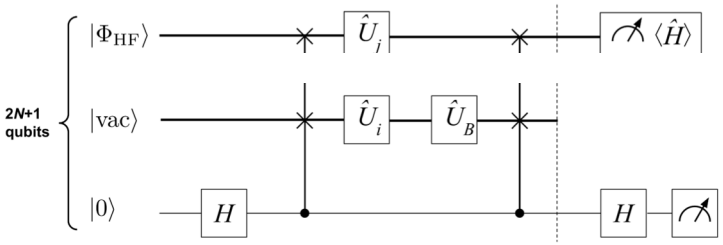
Summary

- molecular electronic energies: exact analysis of electron correlation scales exponentially with classical methods
- hybrid quantum-classical approach: makes use of limited quantum resources, e.g., VQE
- classical NOCI: superposition of non-orthogonal states captures *static correlation,* but scales exponentially
- UCC-NOVQE: efficient off-diagonal matrix element evaluation via *Hadamard test protocol*
- High quality UCC ansatze: capture also *dynamic correlation* without the high measurement overhead from a variational loop







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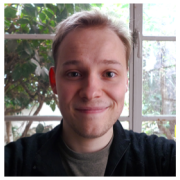

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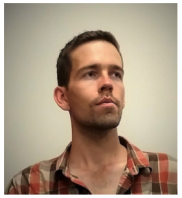

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