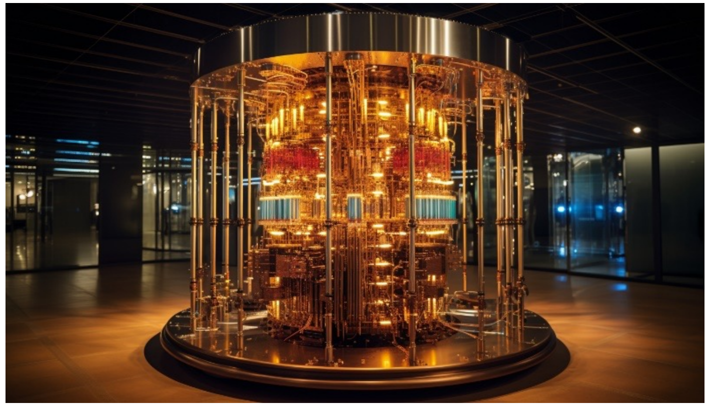
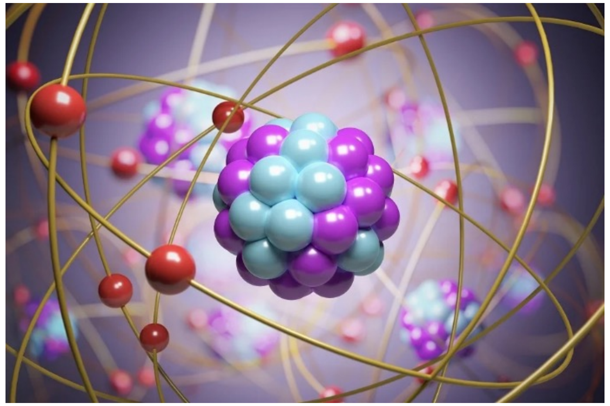
Quantum computing for quantum chemistry



Christian Schilling

6th October 2025



partly based on lectures/tutorials/articles by
- Artur Izmaylov (Youtube)
- Stefan Knecht (ESQC)
- Cheng-Lin Hong (MQV)
- Garnet Chan (Faraday discuss. 24)

Electron correlation problem

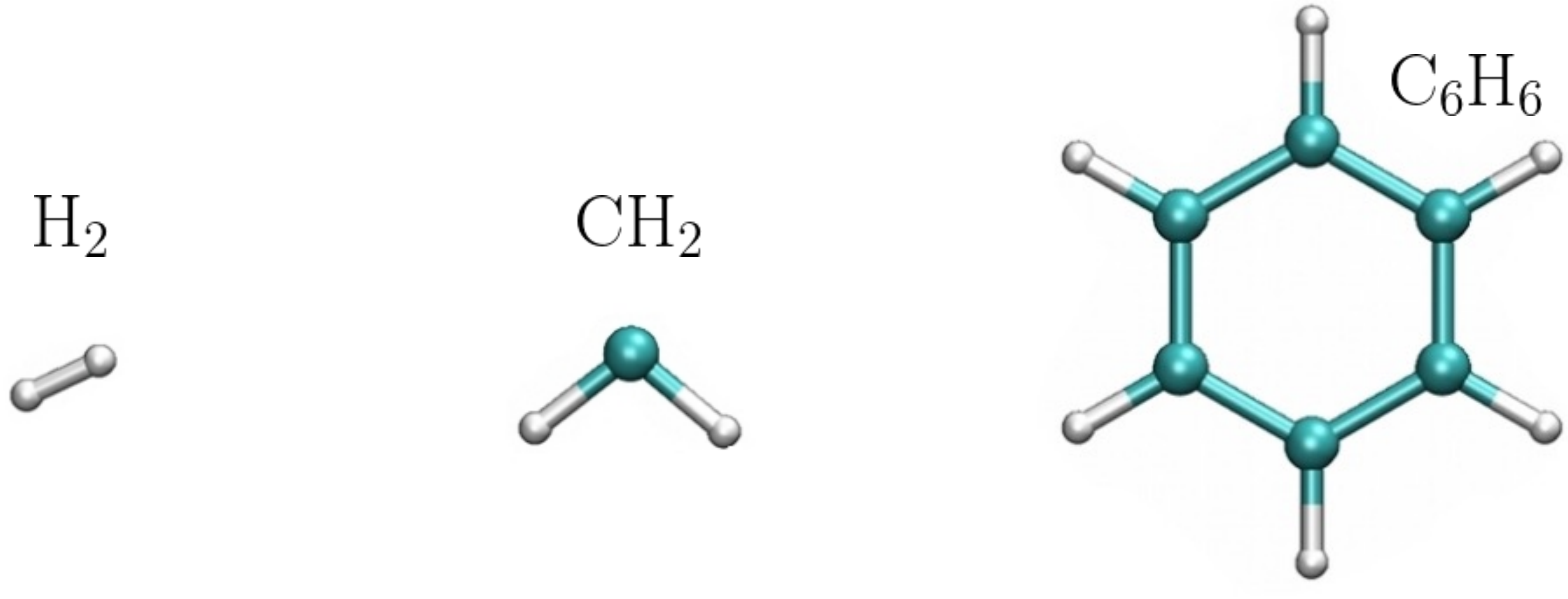
N interacting fermions

$$E_0 = \min_{|\Psi_N\rangle \in \mathcal{H}_N} \langle \Psi_N | \hat{H} | \Psi_N \rangle$$

N-fermion Hilbert space
exponentially large

$\Rightarrow$ hopeless !?

exponential wall/scaling



	H_2	CH_2	C_6H_6
N	2	8	42
$\dim(\mathcal{H}_N)$	100	10^7	10^{46}

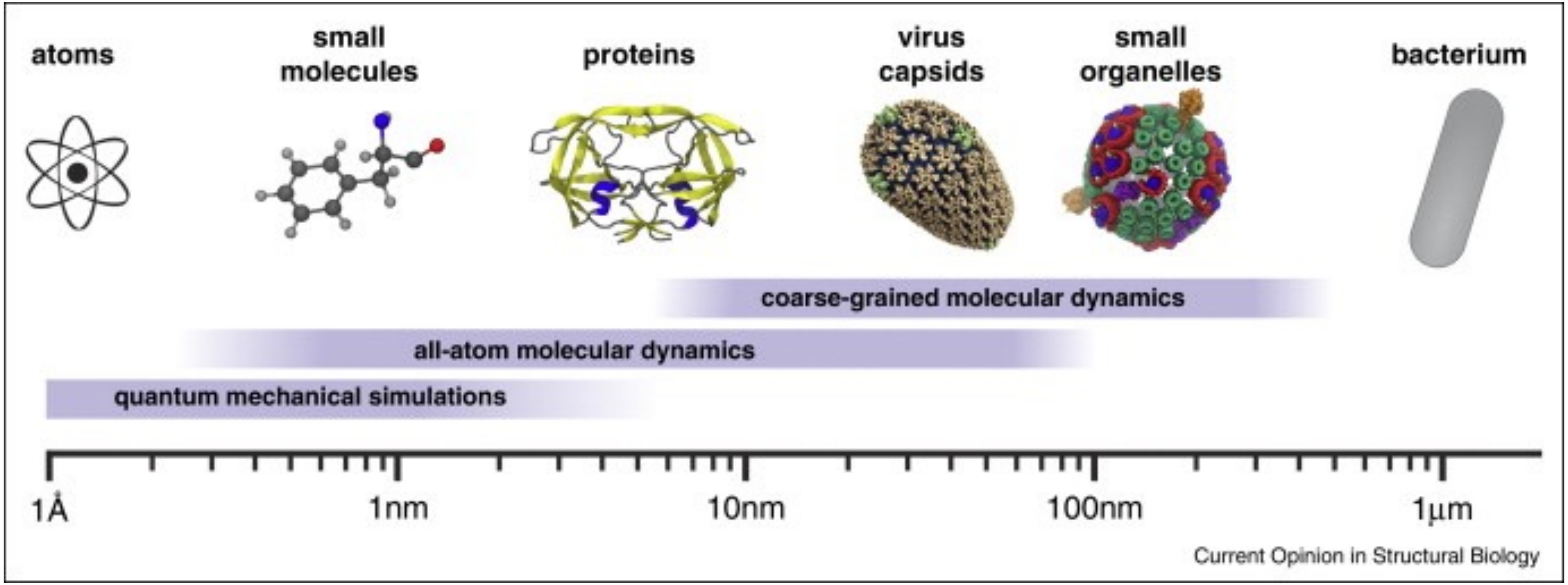
[L.Veiss, Juelich Correl21]

Significance of interacting particle systems?

Which systems?

Why to simulate them on a computer?

Systems

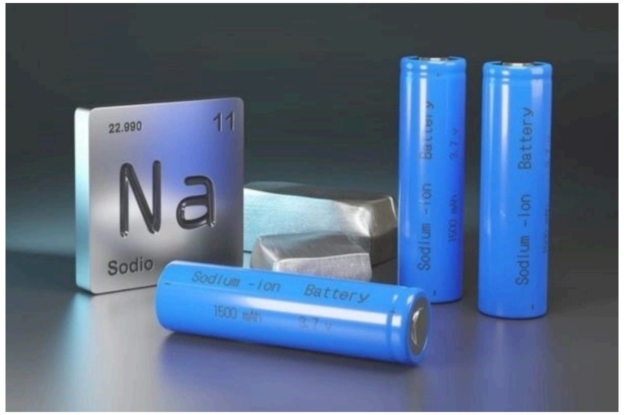


Current Opinion in Structural Biology

Significance

pharmaceuticals

industrial catalysis



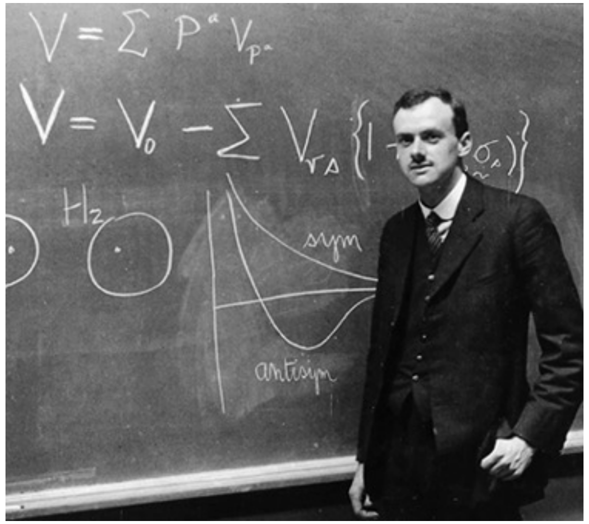
battery materials

screens & processors

Simulation (on a computer)?

- accelerating drug discovery by modelling reaction mechanisms
- reducing cost and waste of expensive materials (Pt, Ir, Li, Co)
- avoiding toxic, radioactive, or explosive substances (uranium oxides and plutonium compounds, nerve agents)
- exploring systems that cannot be manipulated in the lab (Astrochemistry, ultrafast reactions)

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.



It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.” (Paul A. M. Dirac,1929)

hope: two simplifying structures

particle picture (1st Q.)

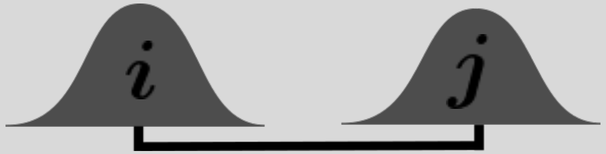
only pairwise interaction

$$\hat{W} = \sum_{1\leq i<j\leq N} \hat{W}_{ij}^{(2)}$$

orbital/mode picture (2nd Q.)

spatial decay

$$\hat{W}_{ij}^{(2)} \to 0$$



as $|\vec{x}_i - \vec{x}_j| \to \infty$

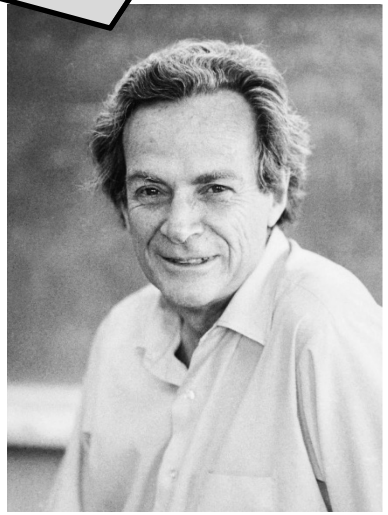
consequences

solution of electron correlation problem

classical computer
or
quantum computer?

[...] nature isn't classical,
dammit, and if you want to make a simulation of
nature, you'd better make it quantum mechanical,
and by golly it's a wonderful problem, because
it doesn't look so easy.

Yurin Manin
"Computable and
uncomputable" (1980)



Richard Feynman
"Simulating Physics with
computers" (1982)

Quantum versus classical: An estimation

Ideal gas:

$$\lambda_{\text{th}} = \sqrt{\frac{2\pi\hbar^2}{mk_BT}} \quad \overset{?}{\longleftrightarrow} \quad \left(\frac{V}{N}\right)^{1/3}$$

electrons
& nuclei:
(T=298K)

$$\lambda_{\text{th}}^{(\text{e})} \approx 10^{-9}\text{m} \quad > \quad 10^{-10}\text{m}$$

$$\lambda_{\text{th}}^{(\text{n})} \approx 10^{-10}-10^{-12}\text{m} \quad \leq \quad \text{atomic scale}$$

$\Rightarrow$

$$\boxed{\begin{array}{c}\text{electrons: quantum}\\ \text{nuclei: classical}\end{array}}$$

Outline

1) Notation & concepts
2) Variational principles
3) Classical methods in Quantum Chemistry
4) Fermion-to-qubit mapping
5) Estimating energy expectation values
6) Variational quantum eigensolver

1) Notation & concepts

Conventions

- use of Hartree atomic units: $\hbar \equiv m_e \equiv e \equiv 4\pi\varepsilon_0 \equiv 1$

  ⇨ length in units of Bohr radius, energies in Hartrees

- energy (gaps) with chemical accuracy: $\Delta E \leq 1.6\,\mathrm{mHa}$

  ⇨ leading order of reaction rates correct (Eyring)

- Pauli matrices/operators: $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

  or $\sigma_1, \sigma_2, \sigma_3$

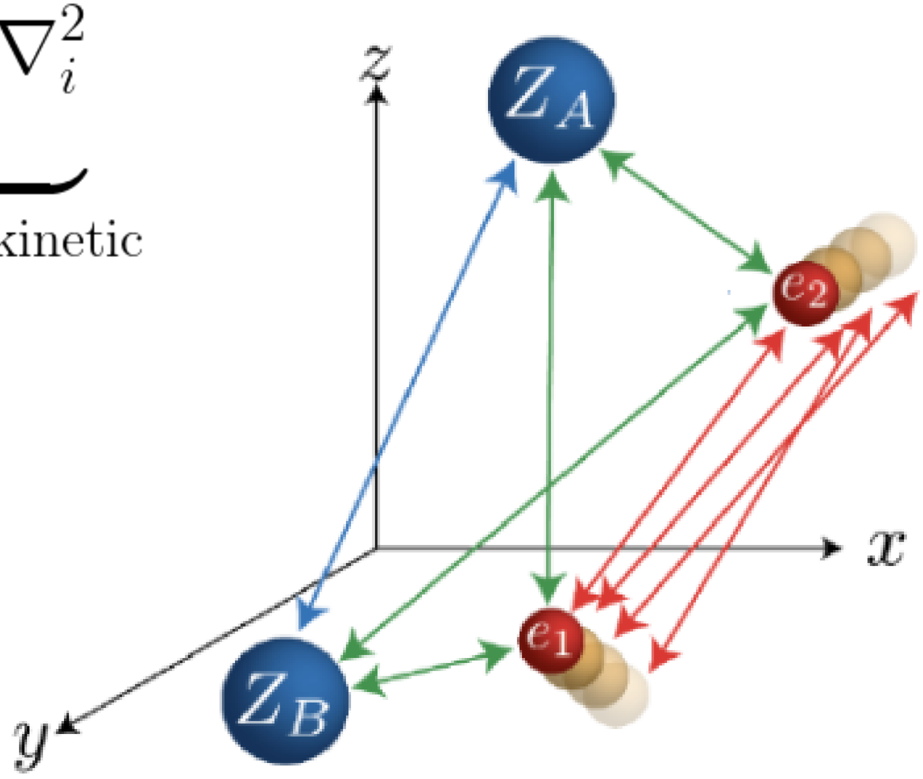
  or X, Y, Z

molecular Hamiltonian

$$\hat{H}_{\text{mol}} = \underbrace{-\sum_{A=1}^{N_n} \frac{1}{2M_A}\nabla_A^2}_{\text{nuclear kinetic}} + \underbrace{\sum_{A<B}^{N_n} \frac{Z_A Z_B}{R_{AB}}}_{\text{nucleus nucleus}} - \underbrace{\frac{1}{2}\sum_{i=1}^{N_e} \nabla_i^2}_{\text{electronic kinetic}}$$

$$- \underbrace{\sum_{i=1}^{N_e}\sum_{A=1}^{N_n} \frac{Z_A}{r_{iA}}}_{\text{electron nucleus}} + \underbrace{\sum_{i<j}^{N_e} \frac{1}{r_{ij}}}_{\text{electron electron}}$$

$$\equiv \hat{T}_{\text{n}} + \hat{V}_{\text{nn}} + \hat{T}_{\text{e}} + \hat{V}_{\text{en}} + \hat{V}_{\text{ee}}$$



Born-Oppenheimer approximation

$M_A \gg m_e \equiv 1$ ⇒ “nuclei move slower than electrons”

⇒ separation of nuclear and electronic degrees:

$$\Psi(\mathbf{r},\mathbf{R}) \;\approx\; \psi_e(\mathbf{r};\mathbf{R})\,\chi(\mathbf{R})$$

$$\boxed{(\hat{T}_e+\hat{V}_{en}+\hat{V}_{ee}+V_{nn})\,\psi_e(\mathbf{r};\mathbf{R}) = E_e(\mathbf{R})\,\psi_e(\mathbf{r};\mathbf{R})}$$

Hilbert spaces & truncations

- 1-particle Hilbert space:

$$\mathcal{H}^{(1)} = L^2(\mathbb{R}^3 \times \mathbb{Z}_2) = L^2(\mathbb{R}^3) \otimes \mathbb{C}^2 \equiv \mathcal{H}_l^{(1)} \otimes \mathcal{H}_s^{(1)}$$

truncation $\Big\Downarrow$ by choosing finite basis set of atomic orbitals

$$\mathcal{H}^{(1)}_{\text{trunc}} = \mathcal{H}^{(1)}_{l,\text{trunc}} \otimes \mathcal{H}_s^{(1)} \cong \mathbb{C}^L \otimes \mathbb{C}^2$$

with dimension $d = 2L$

- N-fermion Hilbert space

$$\mathcal{H}^{(N)} \equiv \wedge^N[\mathcal{H}^{(1)}] = \mathcal{A}_N\left[\mathcal{H}^{(1)}\right]^{\otimes N}$$

with dimension $\binom{d}{N}$

- Fock space

$$\mathcal{F}(\mathcal{H}_1) = \bigoplus_{N=0}^{d} \wedge^N[\mathcal{H}^{(1)}]$$

with dimension 2^d

- 2nd quantization (w.r.t. orthonormal basis for $\mathcal{H}^{(1)}$):

$$|n_1, n_2, \ldots, n_d\rangle \;\equiv\; (f_1^\dagger)^{n_1}(f_2^\dagger)^{n_2}\cdots(f_d^\dagger)^{n_d}|\Omega\rangle$$

$$n_i \in \{0,1\},\ \forall i = 1, \ldots, d$$

$$\{f_i^{(\dagger)}, f_j^{(\dagger)}\} = 0, \qquad \{f_i^\dagger, f_j\} = \delta_{ij}$$

$$\Downarrow$$

$$f_i\,|n_1, \ldots, 1_i, \ldots, n_d\rangle = (-1)^{\sum_{j<i} n_j}\,|n_1, \ldots, 0_i, \ldots, n_d\rangle$$

$$f_i^\dagger\,|n_1, \ldots, 0_i, \ldots, n_d\rangle = (-1)^{\sum_{j<i} n_j}\,|n_1, \ldots, 1_i, \ldots, n_d\rangle$$

Hamiltonian in 2nd quantization

$$\hat{H}_e = \sum_{p,q} h_{pq} f_p^\dagger f_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs} f_p^\dagger f_q^\dagger f_r f_s$$

where (according to Slater-Condon rules):

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

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

$\Rightarrow$ time: $\mathcal{O}(L^4)$

2) Variational principles

Rayleigh-Ritz

given Hamiltonian $\hat{H}$ with $\hat{H} = \sum_{j \geq 1} E_j |\Psi_j\rangle\langle\Psi_j|$

$$E_1 = \min_{|\Psi\rangle \in \mathcal{H}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad \& \ |\Psi_1\rangle$$

ground state

$$\Downarrow$$

$$E_2 = \min_{\substack{|\Psi\rangle \in \mathcal{H} \\ |\Psi\rangle \perp |\Psi_1\rangle}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad \& \ |\Psi_2\rangle$$

1^{st} excited state

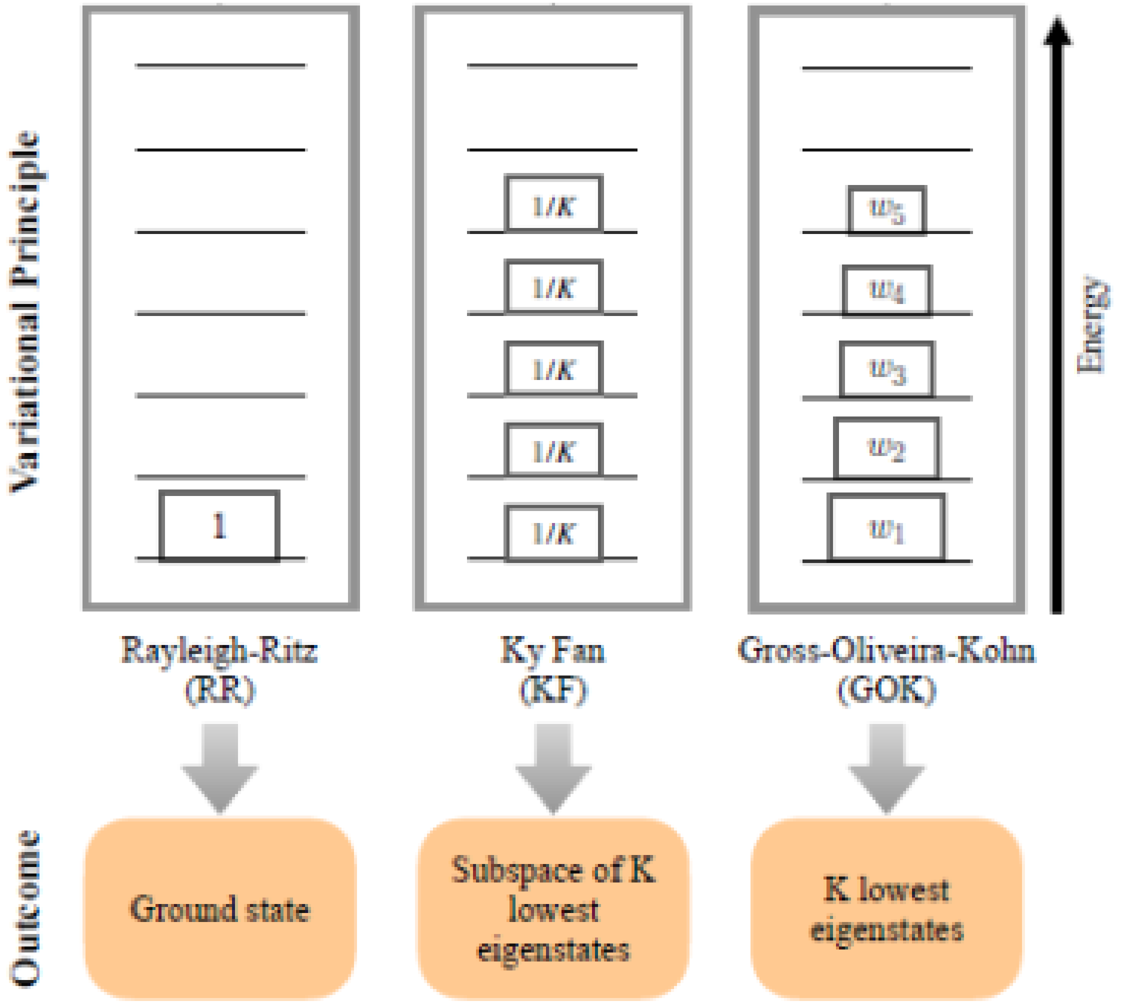
$$\Downarrow$$

$$\vdots$$

ensemble variational principle

$$\begin{aligned} E_{\boldsymbol{w}} &\equiv \sum_{j\geq 1} w_j E_j \\ &= \min_{\hat{\rho}\in\mathcal{D}(\boldsymbol{w})} \mathrm{Tr}[\hat{H}\hat{\rho}] \end{aligned}$$

$$\hat{\rho} \equiv \sum_{j\geq 1} w_j |\Phi_j\rangle\langle\Phi_j|$$



[Gross, Oliveira, Kohn, Phys. Rev. A, 37, 2805 (1988)]

[Ding, Hong, Schilling, Quantum 8, 1525 (2024)]

3) Classical methods in Quantum Chemistry

Hartree-Fock ansatz

$$E_1 \leq \min_{|\Psi\rangle \in \mathcal{M}_{\mathrm{HF}}} \langle \Psi | \hat{H} | \Psi \rangle \quad \xRightarrow[\frac{\delta E}{\delta |\Psi\rangle} = 0]{} \quad \hat{F} |\varphi_i\rangle = \varepsilon_i |\varphi_i\rangle$$

$$\uparrow \qquad\qquad\qquad\qquad \nwarrow \hat{F} \equiv \hat{F}[\{|\varphi_j\rangle\}_{j=1}^{N}]$$

$$\begin{aligned} |\Psi\rangle &= |\varphi_1\rangle \wedge \ldots \wedge |\varphi_N\rangle \\ &= \mathcal{A}_N |\varphi_1\rangle \otimes \ldots \otimes |\varphi_N\rangle \end{aligned}$$

$$|\varphi_1\rangle \perp \ldots \perp |\varphi_N\rangle$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix}$$

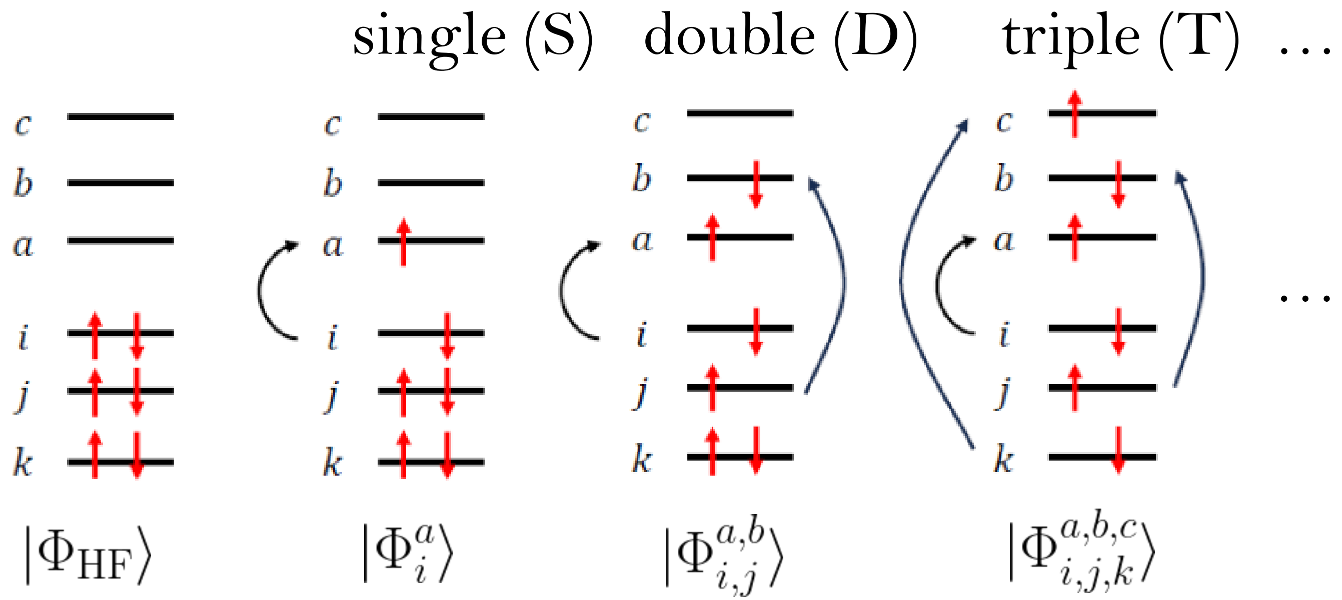
$$\Downarrow$$

Hartree-Fock
energies & orbitals

beyond Hartree-Fock: electron correlation

- correlation energy (Löwdin): $E_{\text{corr}} \equiv E_{\text{exact}} - E_{\text{HF}}$
- dynamic correlation:
  - instantaneous interactions with other electrons
  - perturbative
  - weakly correlated, but affects quantitative accuracy
- static correlation:
  - near-degenerate configurations
  - non-perturbative
  - strongly correlated, qualitatively important

Configuration Interaction (CI)

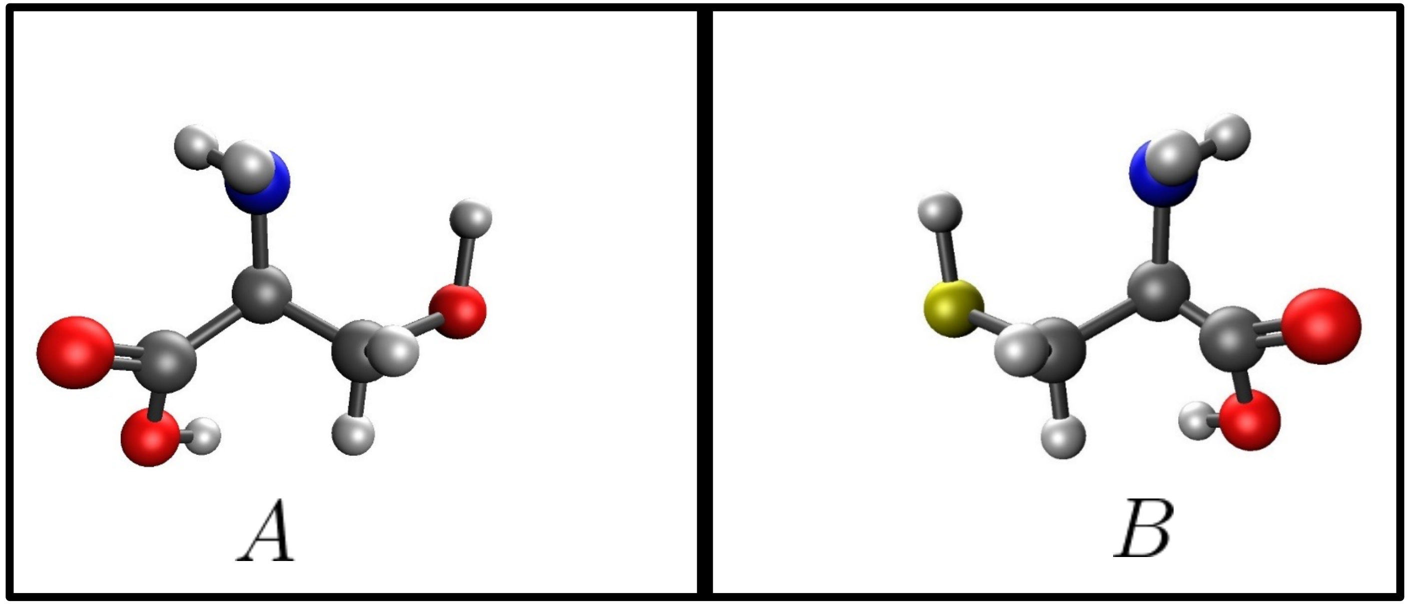


hierarchy of ansatzes:

CISD, CISDT, etc.

$$
\begin{aligned}
|\Psi_{\mathrm{CI}}\rangle &= |\Phi_{\mathrm{HF}}\rangle + \sum_{i,a} c_i^a |\Phi_i^a\rangle + \sum_{i,j,a,b} c_{i,j}^{a,b} |\Phi_{i,j}^{a,b}\rangle + \cdots \\
&= \Big(\mathbb{I} + \sum_{i,a} c_i^a f_a^\dagger f_i + \sum_{i,j,a,b} c_{i,j}^{a,b} f_a^\dagger f_b^\dagger f_i f_j + \cdots\Big) |\Phi_{\mathrm{HF}}\rangle
\end{aligned}
$$

Size conistency



Configuration Interaction is **not** size-consistent as

$$E_{\mathrm{CI}}(AB) \neq E_{\mathrm{CI}}(A) + E_{\mathrm{CI}}(B) \quad \Rightarrow \quad \text{very bad}$$

Coupled Cluster (CC)

$$
\begin{aligned}
|\Psi_{\mathrm{CC}}\rangle &= e^{\hat{T}}\,|\Phi_{\mathrm{HF}}\rangle, \qquad \hat{T} = \hat{T}_1 + \hat{T}_2\,(+\hat{T}_3 + \ldots) \\
&= \left(1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2 + \tfrac{1}{6}\hat{T}_1^3 + \ldots\right)|\Phi_{\mathrm{HF}}\rangle.
\end{aligned}
$$

$$
\hat{T}_1 = \sum_{i,a} t_{ia} f_a^\dagger f_i, \;\; \hat{T}_2 = \sum_{i,j,a,b} t_{ij}^{ab} f_a^\dagger f_b^\dagger f_i f_j, \;\; \ldots
$$

hierarchy of **size-extensive** ansatzes:

CCSD, CCSDT, etc.

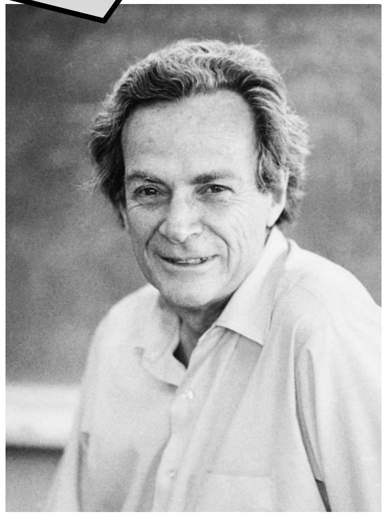
as $e^{\hat{T}_A + \hat{T}_B} = e^{\hat{T}_A} e^{\hat{T}_B}$

Summary (classical methods)

- mean-field theory provide foundation for most chemical intuition
- the ‘right’ methods work remarkably well, yet we have no formal theory of errors
- challenge for computational chemistry:
  How to treat strong correlation?

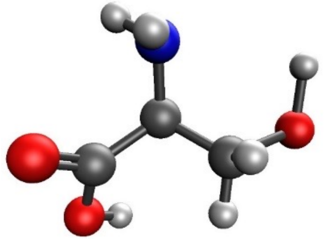
[...] nature isn’t classical,
dammit, and if you want to make a simulation
of nature, you’d better make it quantum
mechanical [. . .]

Yurin Manin
“Computable and
uncomputable” (1980)



Richard Feynman
“Simulating Physics with
computers” (1982)

Quantum computing workflow

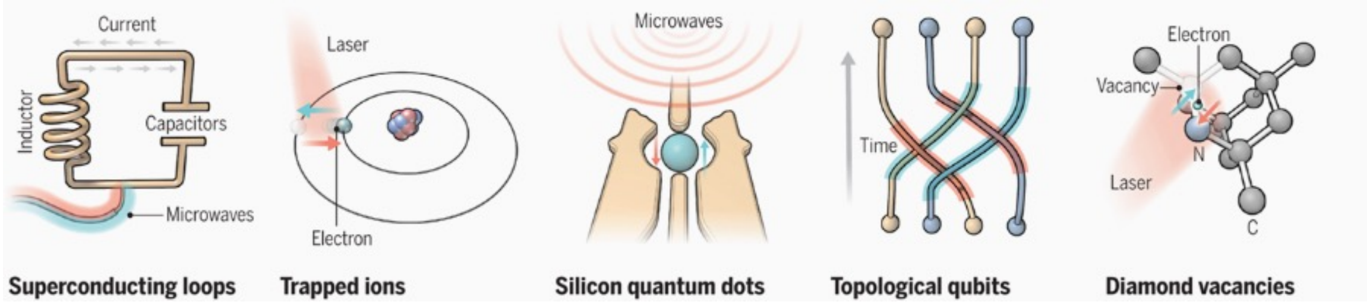


system & geometry

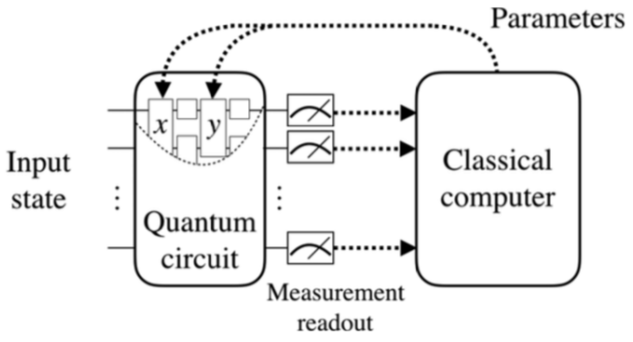
ab initio Hamiltonian

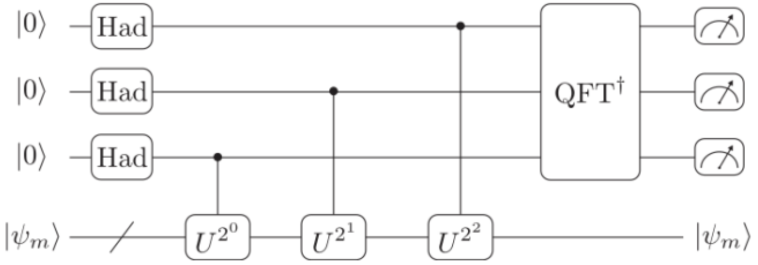
$$\hat{H} = \sum_{p,q} h_{pq}\, f_p^\dagger f_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs}\, f_p^\dagger f_q^\dagger f_r f_s$$

qubit platform

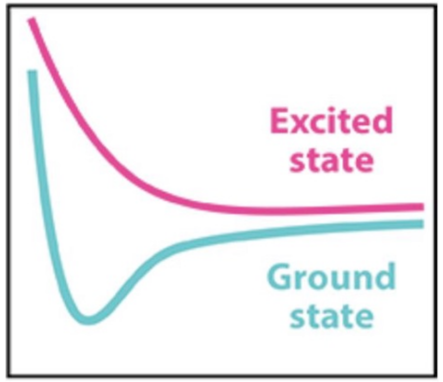


quantum algorithm





output



Quantum algorithms

- **Variational (NISQ-era) algorithms**
  - Variational Quantum Eigensolver (VQE)
  - Quantum Imaginary Time Evolution (QITE)

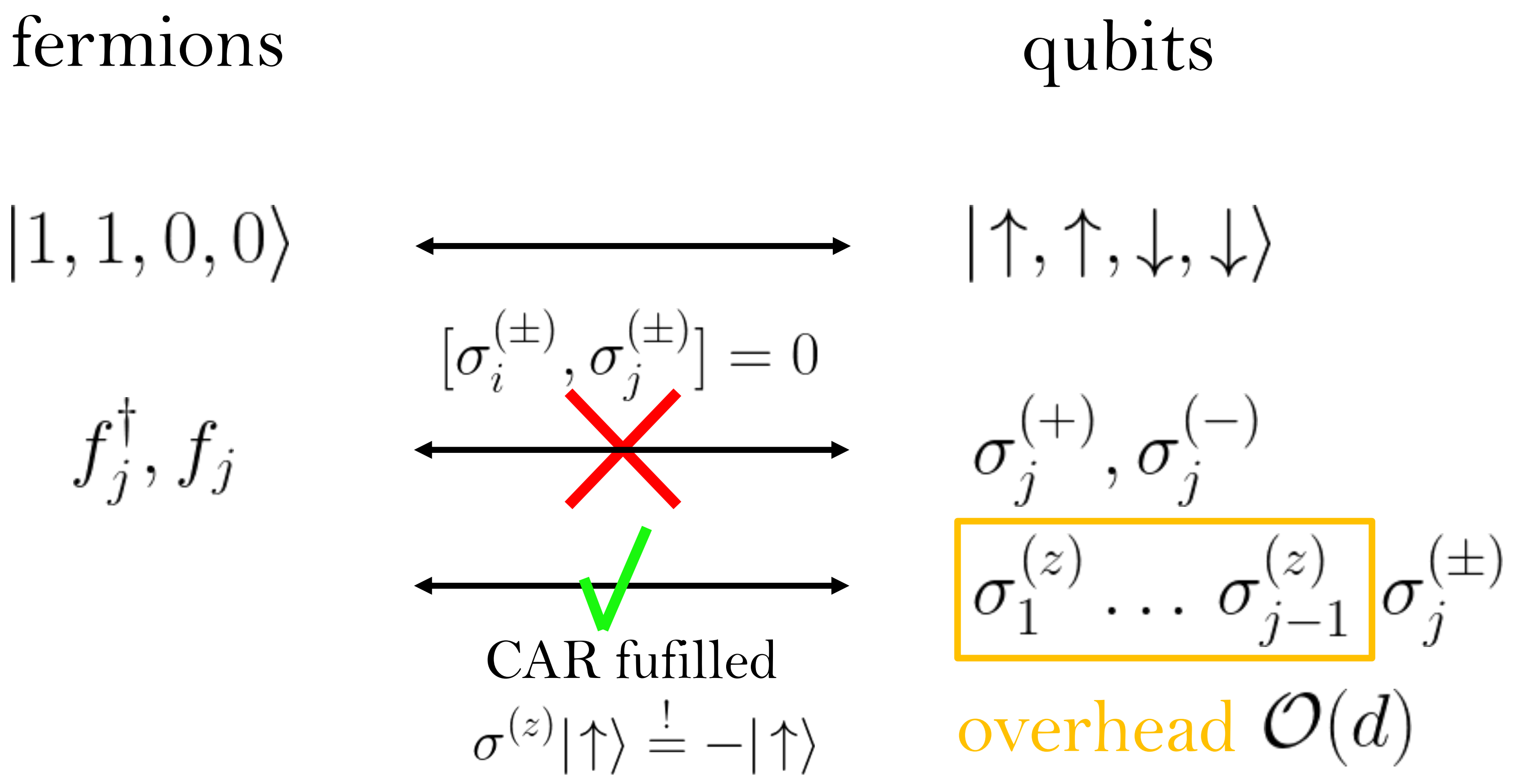
- **State preparation + phase estimation (fault-tolerant era)**
  - Quantum Phase Estimation (QPE) and related techniques

4) Fermion-to-qubit mapping

general setting/goal

$$\begin{tikzcd}
\text{fermions} & & \text{qubits} \\
\mathcal{F}[\mathbb{C}^d] \arrow[rr, shift left, "\text{isomorphism } J"] & & \left(\mathbb{C}^2\right)^{\otimes d} \arrow[ll, shift left, "J^{-1}"] \\
f_j^\dagger, f_j \arrow[rr, leftrightarrow] & & J f_j^\dagger J^{-1}, J f_j J^{-1}
\end{tikzcd}$$

Jordan-Wigner (1928)



fermions

qubits

$$|1,1,0,0\rangle \longleftrightarrow |\uparrow,\uparrow,\downarrow,\downarrow\rangle$$

$$[\sigma_i^{(\pm)},\sigma_j^{(\pm)}]=0$$

$$f_j^\dagger, f_j \longleftrightarrow \sigma_j^{(+)},\sigma_j^{(-)}$$

✗

$$\longleftrightarrow \boxed{\sigma_1^{(z)}\ \dots\ \sigma_{j-1}^{(z)}}\,\sigma_j^{(\pm)}$$

✓

CAR fufilled

$$\sigma^{(z)}|\uparrow\rangle \overset{!}{=} -|\uparrow\rangle$$

overhead $\mathcal{O}(d)$

effect on wavefunctions

fermions

qubits

$$|1,1,0,0\rangle = \hat{f}_1^\dagger \hat{f}_2^\dagger |0,0,0,0\rangle \longleftrightarrow |\uparrow,\uparrow,\downarrow,\downarrow\rangle = \hat{\sigma}_1^{(+)}\hat{\sigma}_1^{(z)}\hat{\sigma}_2^{(+)}|\downarrow,\downarrow,\downarrow,\downarrow\rangle$$

$$|\Psi\rangle = \sum_{\boldsymbol{n}} C_{\boldsymbol{n}}\,|n_1,n_2,\ldots,n_d\rangle, \quad n_i = \{0,1\} \longleftrightarrow |\Phi\rangle = \sum_{\boldsymbol{\sigma}} D_{\boldsymbol{\sigma}}\,|\sigma_1^{(z)},\sigma_2^{(z)},\ldots,\sigma_d^{(z)}\rangle, \quad \sigma_k^{(z)} = \{\uparrow,\downarrow\}$$

alternative mappings

- parity mapping $\Longrightarrow$ overhead $\mathcal{O}(d)$
- Bravyi-Kitaev mapping $\Longrightarrow$ overhead $\mathcal{O}(\log d)$
- references:

  [P. Jordan and E. Wigner, Z. Phys. 47, 631 (1928)]
  [S. Bravyi and A. Kitaev, Ann. Phys. 298, 210 (2002)]
  [F. Verstraete and J. I. Cirac, J. Stat. Mech.: Theory Exp., P09012 (2005)]
  [J. T. Seeley, M. J. Richard, and P. J. Love, J. Chem. Phys. 137, 224109 (2012)]

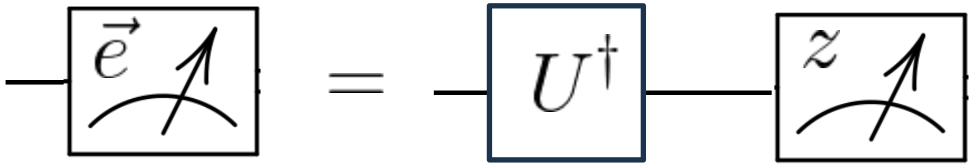
5) Estimating energy expectation values

measurement of single qubits

- given device : measurement of σ_z

- measurement of $\sigma_{\vec{e}} \equiv e_x\sigma_x + e_y\sigma_y + e_z\sigma_z$

$$\begin{aligned}\langle\sigma_{\vec{e}}\rangle_\Psi &= \langle\Psi|\sigma_{\vec{e}}|\Psi\rangle \\ &= \langle\Psi|U\sigma_z U^\dagger|\Psi\rangle\end{aligned} \qquad U:\ |\uparrow/\downarrow\rangle_z \mapsto |\uparrow/\downarrow\rangle_{\vec{e}}$$



measurement of Hamiltonian

- system of d qubits: cannot directly measure $\hat{H}$
- estimation of $\langle \hat{H} \rangle_{\Psi}$ by measuring fragments:

$$\hat{H} = \sum_{I} \hat{h}_I \overset{\text{e.g.}}{=} \sum_{j_1,\ldots,j_d=0}^{3} \eta_{\boldsymbol{j}}\, \hat{\sigma}_{j_1} \otimes \ldots \otimes \hat{\sigma}_{j_d}$$

however, 4^d Pauli strings to measure

⇓ quantum chemistry

\`only' d^4 Pauli strings to measure

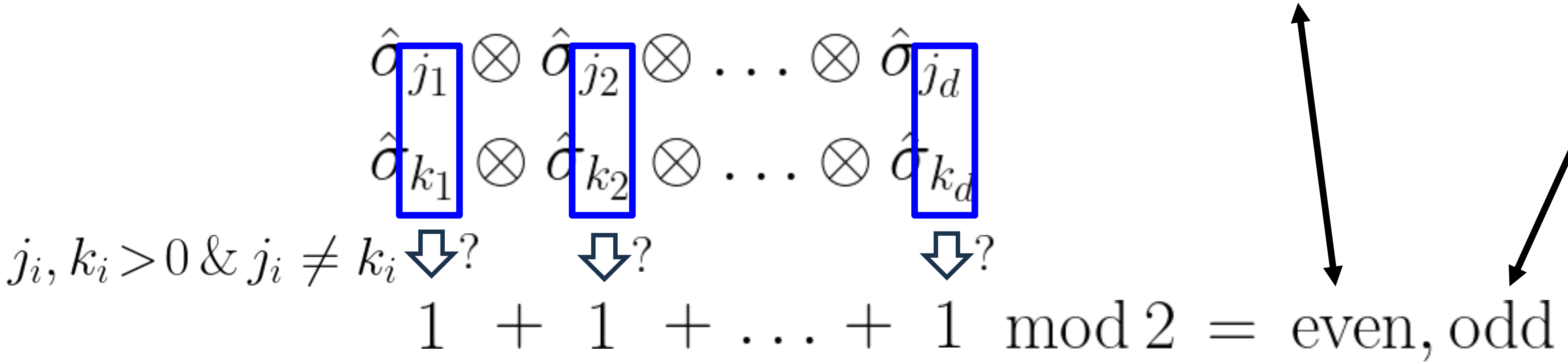
reduction of measurements

- idea: identify commuting Pauli strings

e.g. $\hat{\sigma}_x \otimes \hat{1},\ \hat{1} \otimes \hat{\sigma}_x,\ \hat{\sigma}_x \otimes \hat{\sigma}_x$

or $\hat{\sigma}_x \otimes \hat{\sigma}_x,\ \hat{\sigma}_y \otimes \hat{\sigma}_y,\ \hat{\sigma}_z \otimes \hat{\sigma}_z$

- in general: two Pauli strings either commute or anticommute



$$\hat{\sigma}_{\boxed{j_1}} \otimes \hat{\sigma}_{\boxed{j_2}} \otimes \ldots \otimes \hat{\sigma}_{\boxed{j_d}}$$

$$\hat{\sigma}_{\boxed{k_1}} \otimes \hat{\sigma}_{\boxed{k_2}} \otimes \ldots \otimes \hat{\sigma}_{\boxed{k_d}}$$

$j_i, k_i > 0 \,\&\, j_i \neq k_i \Downarrow ? \quad \Downarrow ? \quad \Downarrow ?$

$$1 + 1 + \ldots + 1 \mod 2 = \text{even}, \text{odd}$$

measurement process

- estimating $\langle \hat{A} \rangle_\Psi = \langle \Psi | \hat{A} | \Psi \rangle$ $\qquad \hat{A} = \sum_I \alpha_I |I\rangle\langle I|$

$$= \sum_I \alpha_I \left| \langle I | \Psi \rangle \right|^2$$

$$\equiv \sum_I \alpha_I \, p_I$$

- corresponds to sampling random variable $\mathcal{A} \sim (p_I, \alpha_I)$

- uncertainty: $\mathrm{Var}_{\vec{p}}(\mathcal{A}) = \mathrm{Var}_\Psi(\hat{A}) = \langle \Psi | \hat{A}^2 | \Psi \rangle - \langle \Psi | \hat{A} | \Psi \rangle^2$

Shot noise

- K times sampling $\mathcal{A} \;\widehat{=}\;$ sampling once $\bar{\mathcal{A}} \equiv (\mathcal{A}_1 + \ldots \mathcal{A}_K)/K$
- uncertainty: $\mathrm{Var}(\bar{\mathcal{A}}) = \mathrm{Var}_{\vec{p}}(\mathcal{A})/K$
- estimating $\langle \hat{H} \rangle_\Psi = \sum_{\boldsymbol{j}} \eta_{\boldsymbol{j}} \, \langle \hat{\sigma}_{\boldsymbol{j}} \rangle_\Psi$

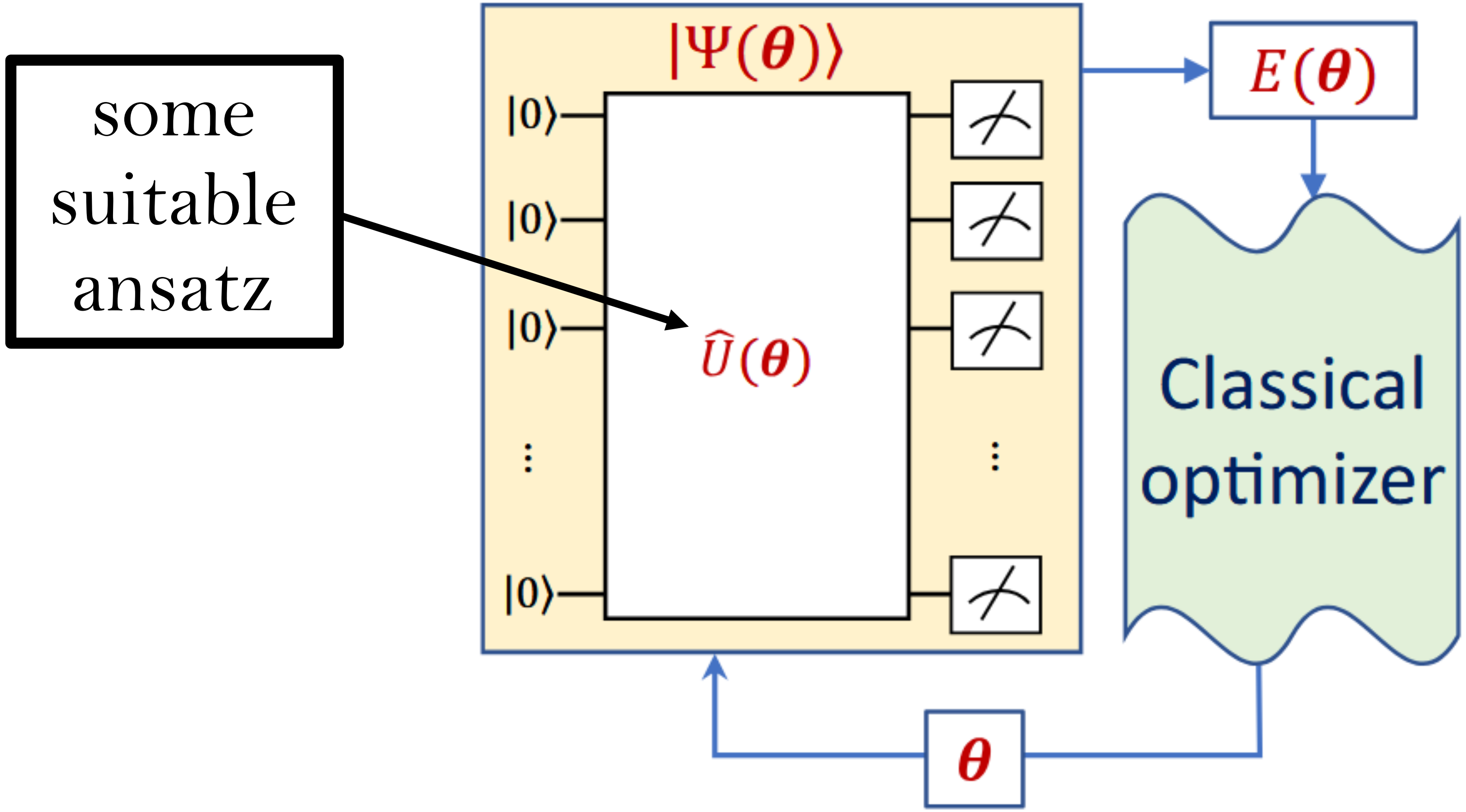
⇨ $\mathrm{Var}_\Psi(\hat{H}) = \sum_{\boldsymbol{j}} \eta_{\boldsymbol{j}}^2 \, \mathrm{Var}_\Psi(\hat{\sigma}_{\boldsymbol{j}})$

⇨ different sampling strategies:

[Arrasmith, Cincio, Somma, Coles, arXiv:2004.06252]

6) Variational quantum eigensolver

hybrid scheme



some suitable ansatz

[graphics from Commun. Physics 6, 4 (2023)]

Unitary Coupled Cluster

$$|\Psi_{\mathrm{UCC}}\rangle = e^{\hat{T}-\hat{T}^\dagger}\,|\Phi_{\mathrm{HF}}\rangle = e^{\sum_j t_j\,(\hat{\tau}_j-\hat{\tau}_j^\dagger)}\,|\Phi_{\mathrm{HF}}\rangle$$

Trotter decomposition

typically first order: $r = 1$ $\Downarrow$

$$|\Psi_{\mathrm{UCC}}\rangle \sim \left(\prod_j e^{\frac{t_j}{r}(\hat{\tau}_j-\hat{\tau}_j^\dagger)}\right)^r |\Phi_{\mathrm{HF}}\rangle$$

Fermion-qubit mapping

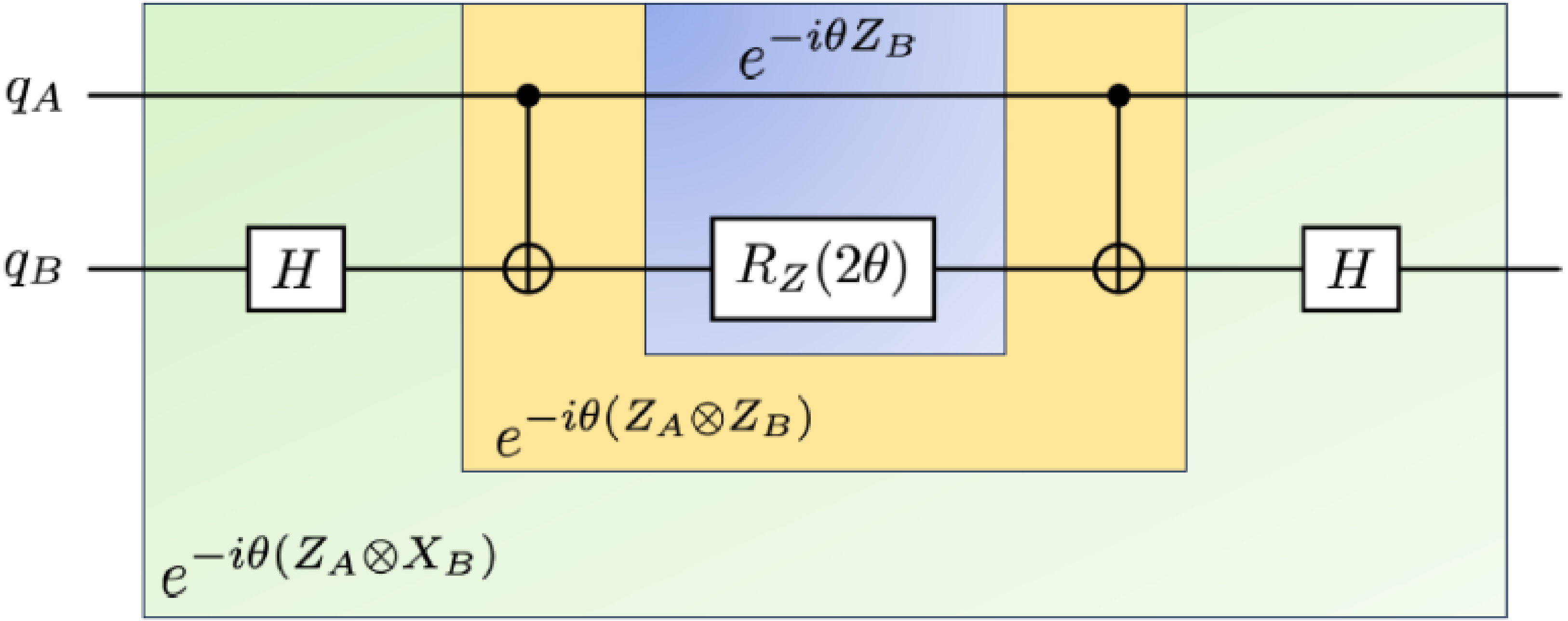
$(\hat{\tau}_j - \hat{\tau}_j^\dagger) \mapsto i\sum_k P_k^j$ $\Downarrow$

$$|\Psi_{\mathrm{UCC}}\rangle \sim \prod_j \exp\left\{it_j \sum_k P_k^j\right\}|\Phi_{\mathrm{HF}}\rangle = \prod_j \prod_k \exp\left\{it_j P_k^j\right\}|\Phi_{\mathrm{HF}}\rangle$$

[Babbush, McClean, Wecker, Aspuru-Guzik, Wiebe, Phys. Rev. A 91, 022311 (2015)]

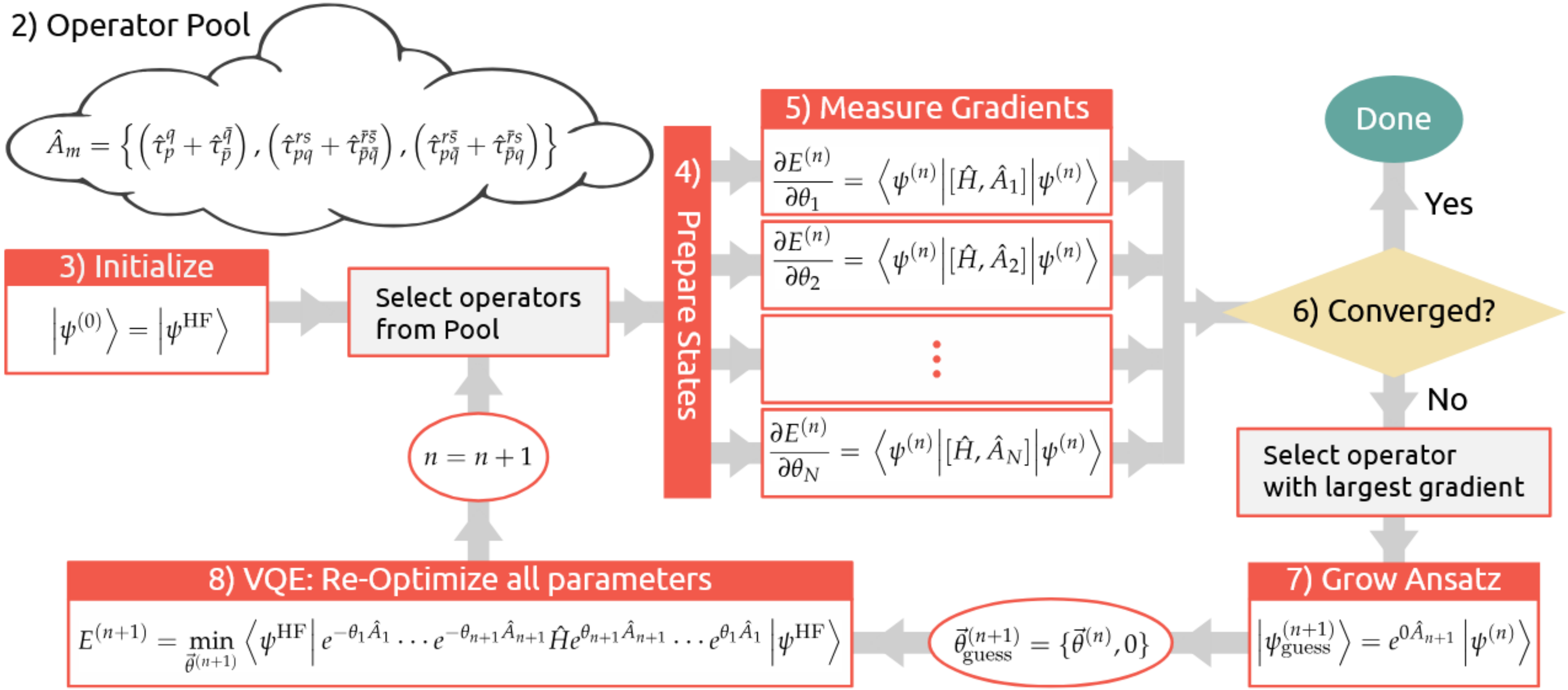
2-qubit building blocks

quantum circuit representation of exponentiated Paulis:
(Pauli gadget)



ADAPT VQE

ansatz of UCC too rigid + Trotter error ⟹ alternative approach



2) Operator Pool

$$\hat{A}_m = \left\{ \left(\hat{\tau}_p^q + \hat{\tau}_{\bar{p}}^{\bar{q}}\right), \left(\hat{\tau}_{pq}^{rs} + \hat{\tau}_{\bar{p}\bar{q}}^{\bar{r}\bar{s}}\right), \left(\hat{\tau}_{p\bar{q}}^{r\bar{s}} + \hat{\tau}_{\bar{p}q}^{\bar{r}s}\right) \right\}$$

3) Initialize

$$\left|\psi^{(0)}\right\rangle = \left|\psi^{\mathrm{HF}}\right\rangle$$

Select operators from Pool

$n = n + 1$

4) Prepare States

5) Measure Gradients

$$\frac{\partial E^{(n)}}{\partial \theta_1} = \left\langle \psi^{(n)} \middle| [\hat{H}, \hat{A}_1] \middle| \psi^{(n)} \right\rangle$$

$$\frac{\partial E^{(n)}}{\partial \theta_2} = \left\langle \psi^{(n)} \middle| [\hat{H}, \hat{A}_2] \middle| \psi^{(n)} \right\rangle$$

$$\vdots$$

$$\frac{\partial E^{(n)}}{\partial \theta_N} = \left\langle \psi^{(n)} \middle| [\hat{H}, \hat{A}_N] \middle| \psi^{(n)} \right\rangle$$

6) Converged?

Yes

Done

No

Select operator with largest gradient

7) Grow Ansatz

$$\left|\psi_{\mathrm{guess}}^{(n+1)}\right\rangle = e^{0\hat{A}_{n+1}} \left|\psi^{(n)}\right\rangle$$

$$\vec{\theta}_{\mathrm{guess}}^{(n+1)} = \{\vec{\theta}^{(n)}, 0\}$$

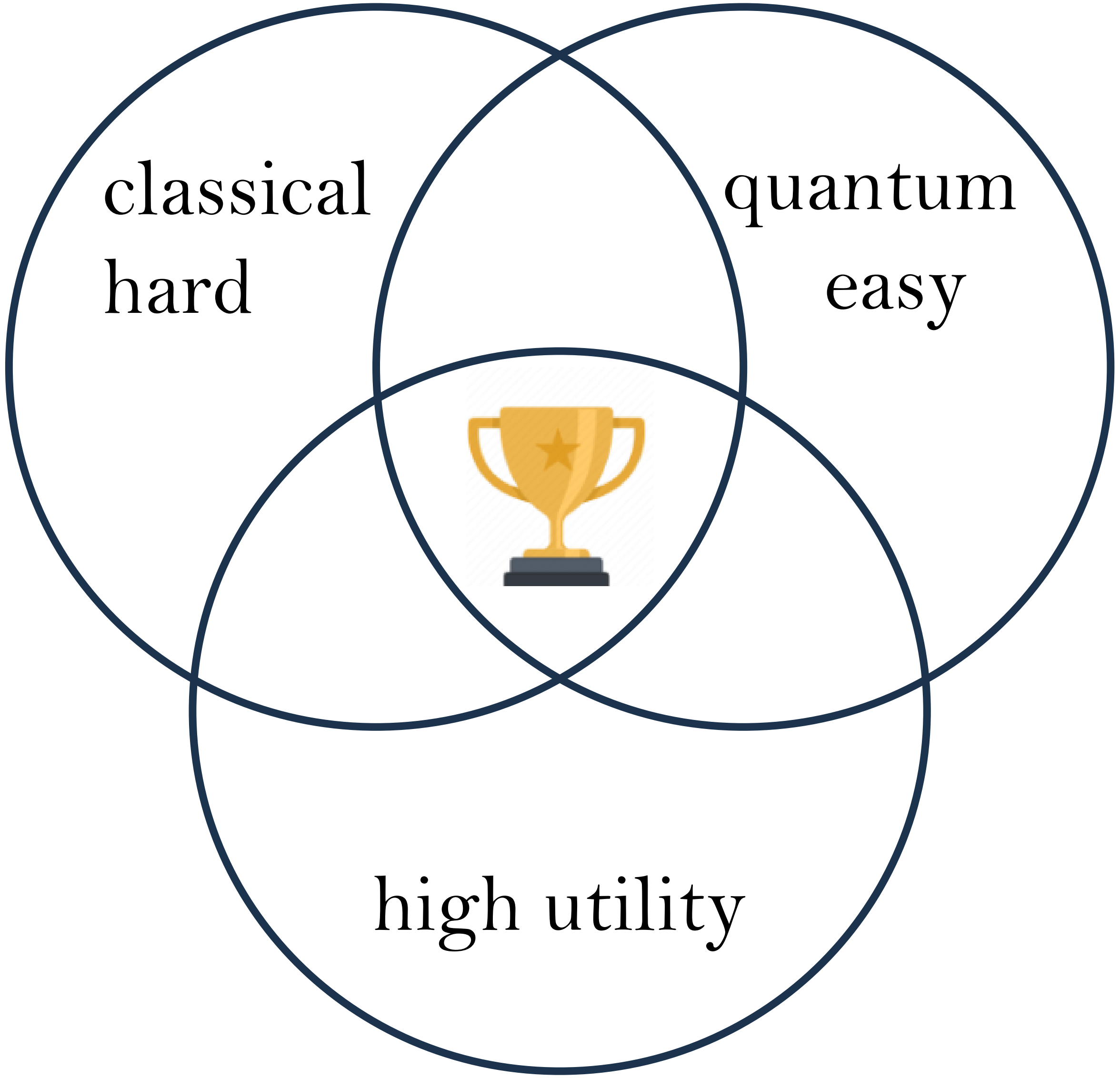
8) VQE: Re-Optimize all parameters

$$E^{(n+1)} = \min_{\vec{\theta}^{(n+1)}} \left\langle \psi^{\mathrm{HF}} \middle| e^{-\theta_1 \hat{A}_1} \cdots e^{-\theta_{n+1}\hat{A}_{n+1}} \hat{H} e^{\theta_{n+1}\hat{A}_{n+1}} \cdots e^{\theta_1 \hat{A}_1} \middle| \psi^{\mathrm{HF}} \right\rangle$$

[Grimsley, Economou, Barnes, Mayhall, Nature Commun. 10, 3007 (2019)]

Outlook

Quantum advantage in Quantum Chemistry (?)

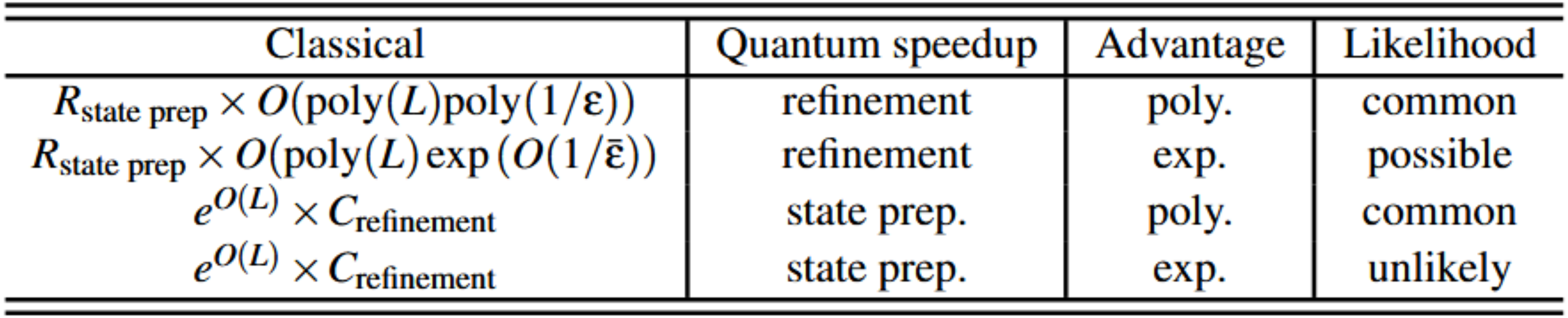


classical
hard

quantum
easy

high utility

expectation

- total cost/time: $C = R_{\text{state prep}} \times C_{\text{refinement}}$
- 

Classical	Quantum speedup	Advantage	Likelihood
$R_{\text{state prep}} \times O(\text{poly}(L)\text{poly}(1/\varepsilon))$	refinement	poly.	common
$R_{\text{state prep}} \times O(\text{poly}(L)\exp(O(1/\bar{\varepsilon}))$	refinement	exp.	possible
$e^{O(L)} \times C_{\text{refinement}}$	state prep.	poly.	common
$e^{O(L)} \times C_{\text{refinement}}$	state prep.	exp.	unlikely

$\bar{\varepsilon} \equiv \varepsilon/L$

- quantum advantage refers to $C_{\text{classical}} = f(C_{\text{quantum}})$

[Chan, Faraday Discuss., 254, 11 (2024)]

Thank you!

Any questions?