Multiconfigurational methods: past, present and the road ahead

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Content of the lectures

- Concepts

Past

- CASCI
- MCSCF/CASSCF
- MR Dynamical Correlation Approaches

Present: “Sample” CI coefficients using an advanced optimisation algorithm

- Density Matrix Renormalisation Group

Road ahead: Beyond “classical quantum chemistry”

- Quantum Chemistry on Quantum Computers

The Present …

Second example: the Cr_2 puzzle resolved

H. R. Larsson, H. Zhai, C. J. Umrigar, G. K.-L. Chan, JACS, 144, 15932 (2022)

Cr_2 potential energy curse...

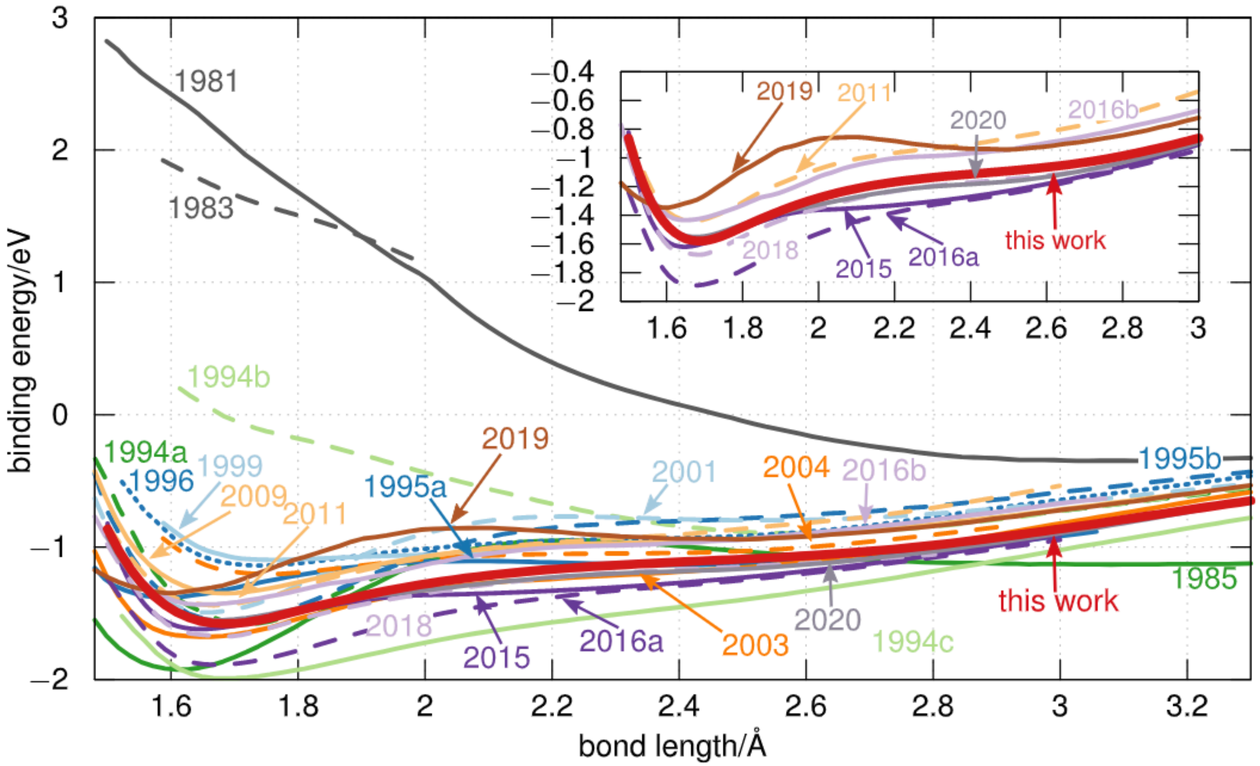


FIG. 1. Some of the simulated potential energy curves (PECs) of the chromium dimer that are available in the literature. The PECs are labeled by the study's year. The red curve marks the PEC from this work. The inset shows selected PECs from 2011 onwards. (List of references in SI).

Short and weak bond with a narrow minimum around 1.68 Å & extended shelf at around 2.5 Å.
→ Cr 4s and 3d AOs different in size, with the minimum corresponding mostly to 3d orbital interactions and the shelf to 4s orbital interactions.

A unique bonding and its consequences

- Complex electronic structure arises from interplay of two types of electron correlation
  - type I — “static correlation”: spin-coupling of the 12 valence electrons (3*d* + 4*s* shells)

energy-driven degeneracy

  - type II — "spatial correlation / dynamic correlation”: need for a large basis to capture excitations involving non-valence orbitals

overlap-driven degeneracy

—> formation of 3*d*-3*d* bonds requires the 3*p* electrons to move out of the same spatial region by exciting to higher lying orbitals

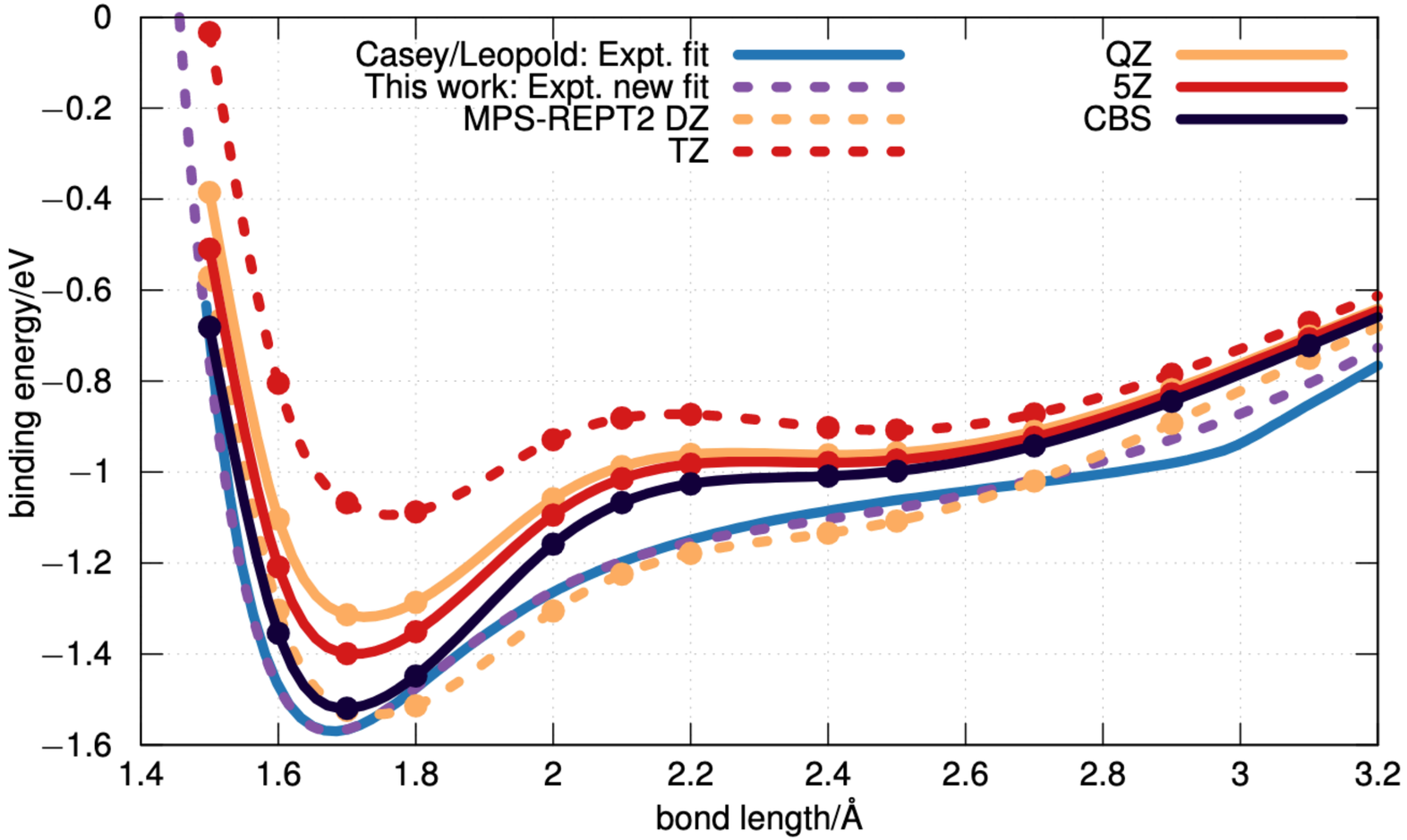
- **Challenge:**
  “The problem is computationally challenging because **both the static and dynamic correlation** must be computed sufficiently well even for a qualitatively reasonable description.”

Computational approach I

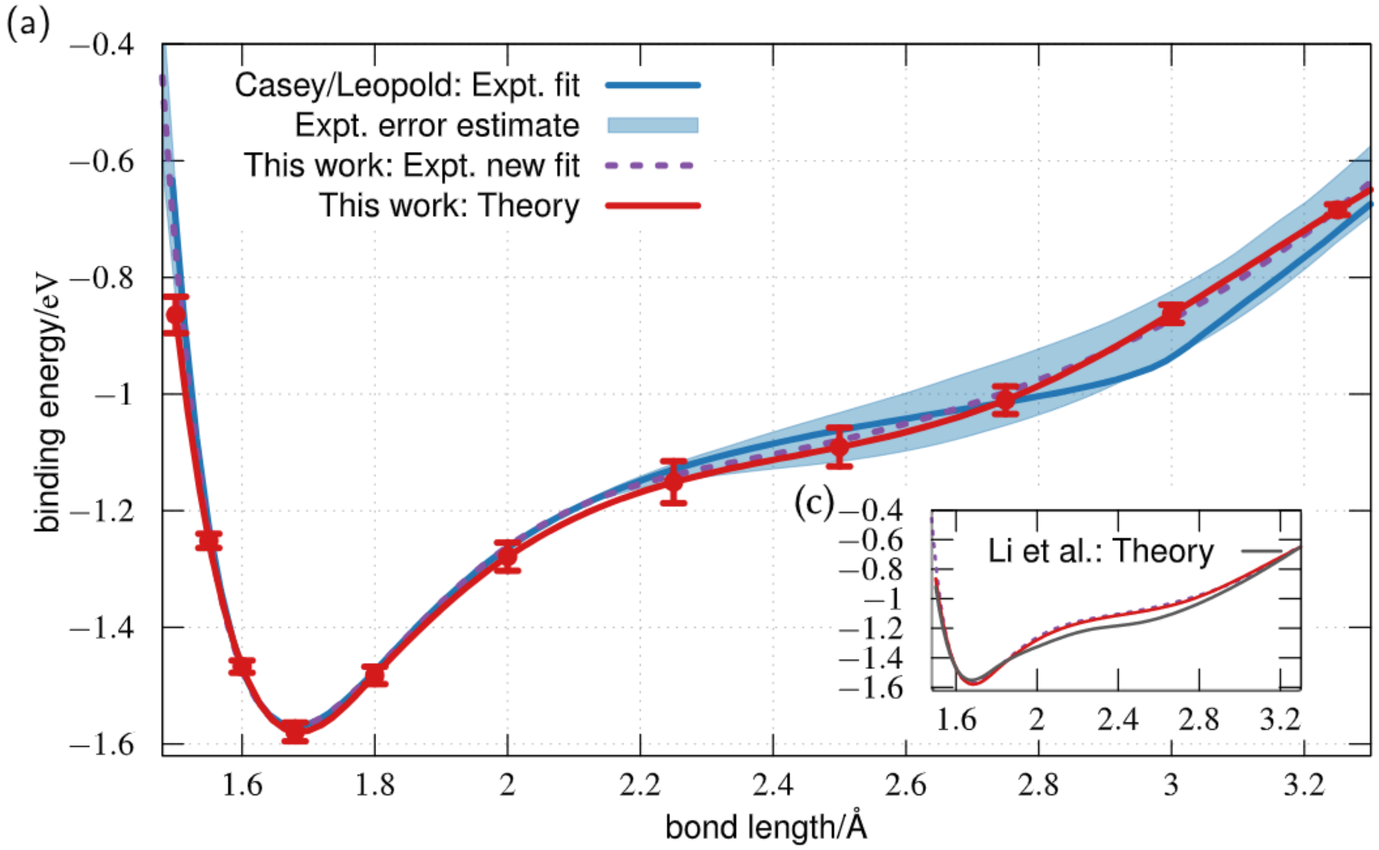
$$\Delta E = \Delta E_{\mathrm{PDZ}}(\text{“exact”}) + \Delta E_{\mathrm{CBS}}(\text{MPS-REPT2}) - \Delta E_{\mathrm{DZ}}(\text{MPS-REPT2})$$

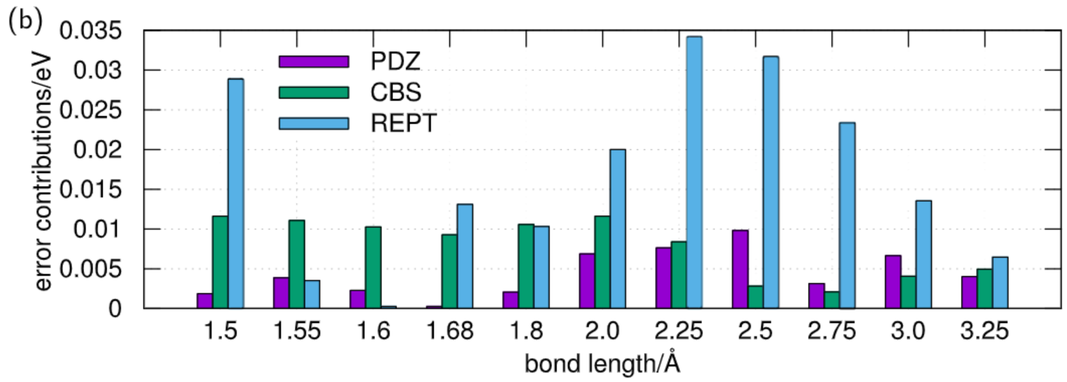
- Static electron correlation: CAS(28e,76o)/cc-pVDZ-DK
  - Heat-Bath CI (selective CI)
  - DMRG (with huge bond dimension!)
- Dynamic electron correlation: CAS(12,12)/MRPT2
  - PT2 correlation of 3*s* and 3*p* inner-valence shells
  - all secondary shells considered
- Basis set: MRPT2 with cc-pv*N*Z-DK (*N*=2,3,4,5) with extrapolation to CBS limit

Computational approach II



New state-of-the-art





$$\epsilon = \sqrt{\epsilon_{\mathrm{PDZ}}^2 + \epsilon_{\mathrm{CBS}}^2 + \epsilon_{\mathrm{REPT}}^2},$$

with the individual error contributions as defined above,

$$\epsilon_{\mathrm{PDZ}} = |\Delta E(\mathrm{SHCI}) - \Delta E(\mathrm{DMRG})|/2,$$
$$\epsilon_{\mathrm{CBS}} = \sigma_{\mathrm{CBS}},$$
$$\epsilon_{\mathrm{REPT}} = |\Delta E(\mathrm{MPS\text{-}REPT2}) - \Delta E[\mathrm{UCCSD(T)}]|/2.$$

Thinking outside the box

Standard CI approach

- CI-type diagonalization for a **preselected** set of many-particle basis states

$$|\Psi\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} |k_1\rangle \otimes |k_2\rangle \otimes \ldots \otimes |k_L\rangle$$

- Could we do better or, say, something else?

Thinking outside the box

Standard CI approach

- CI-type diagonalization for a **preselected** set of many-particle basis states

$$\left|\Psi\right\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} \left|k_1\right\rangle \otimes \left|k_2\right\rangle \otimes \ldots \otimes \left|k_L\right\rangle$$

- Could we do better or, say, something else?
  - select many-particle basis sets / configurations / etc. based on some energy/weighting criteria:
    → selected CI approaches
    → difference dedicated CI,
    → many-body expansion FCI
    → ...
  - find “best” many-particle basis set based on correlations among orbitals → **DMRG**

Thinking outside the box

Standard CI approach

- CI-type diagonalization for a **preselected** set of many-particle basis states

$$\left|\Psi\right\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} \left|k_1\right\rangle \otimes \left|k_2\right\rangle \otimes \ldots \otimes \left|k_L\right\rangle$$

DMRG

- **Determine** CI coefficients from correlations among orbitals

$$\left|\Psi\right\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} \left|k_1\right\rangle \otimes \left|k_2\right\rangle \otimes \ldots \otimes \left|k_L\right\rangle$$

- Local space k_l of l-th spatial orbital is of dimension $d = 4$:

$$k_l = \{\left|\uparrow\downarrow\right\rangle \left|\uparrow\right\rangle, \left|\downarrow\right\rangle, \left|0\right\rangle\}$$

From a CI wave function to Matrix Product States (MPS): Optimising an MPS with the DMRG algorithm

Optimising an MPS wave function with the DMRG algorithm

- Optimisation algorithm
- Parameters that determine DMRG accuracy

U. Schollwöck, The density-matrix renormalization group in the age of matrix product states, Annals of Physics, 326 (2011) 96–192.

Some reviews on about 20 years of DMRG in quantum chemistry

- Ö. Legeza *et al.*, Lect. Notes Phys., 739, 653 (2008)
- G. K.-L. Chan *et al.*, Prog. Theor. Chem. and Phys., 18, 49 (2008)
- D. Zgid and G. K.-L. Chan, Ann. Rep. Comp. Chem., 5, 149, (2009)
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- K. Marti and M. Reiher, Phys. Chem. Chem. Phys., 13, 6750 (2011)
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- Y. Kurashige, Mol. Phys., 112, 1485 (2013)
- S. Wouters and D. van Neck, Eur. Phys. J. D, 68, 272 (2014)
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- T. Yanai *et al.*, Int. J. Quantum Chem., 115, 283 (2015)
- G. K.-L. Chan et al., J. Chem. Phys., 145, 014102 (2016)
- A. Baiardi and M. Reiher, J. Chem. Phys. 152, 040903 (2020)

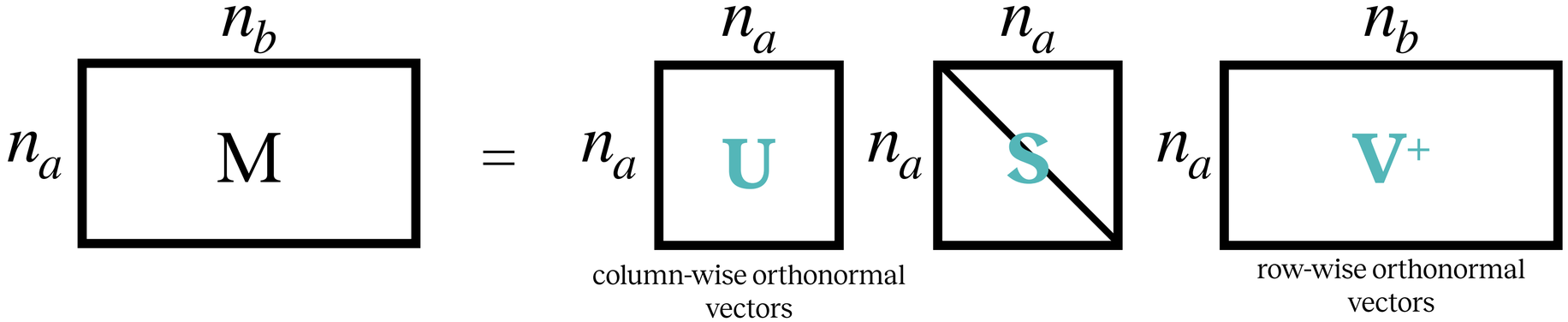
Intermission: singular value decomposition

- Singular value decomposition (SVD) of a matrix $\mathbf{M}$ $(n_a \times n_b)$

Remember?

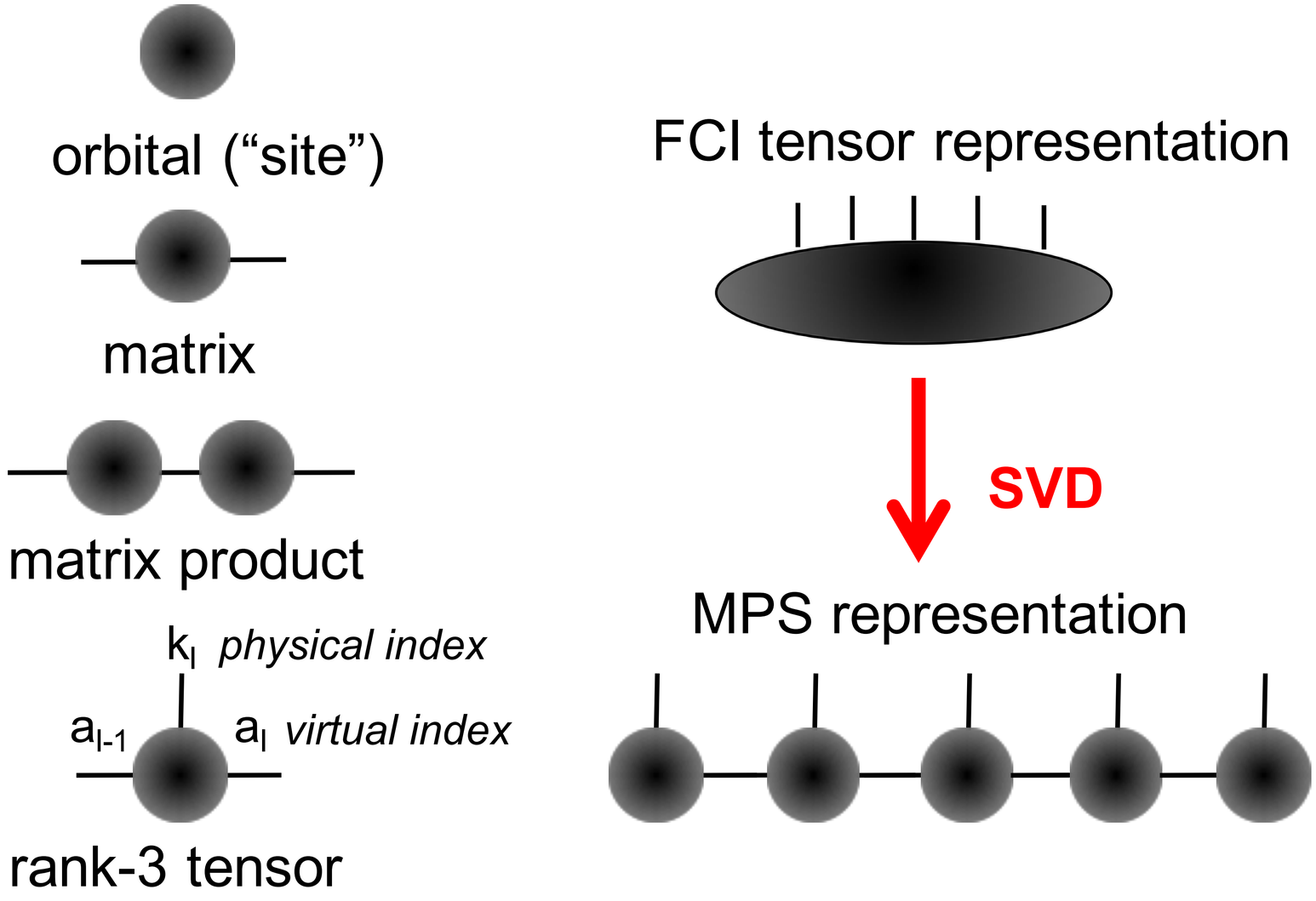
yields:

  - Left-singular matrix $\mathbf{U}$ $(n_a \times \min(n_a, n_b))$ with $\mathbf{U}^\dagger\mathbf{U} = 1$
  - Right-singular matrix $\mathbf{V}$ $(\min(n_a, n_b) \times n_b)$ with $\mathbf{V}^\dagger\mathbf{V} = 1$
  - Diagonal singular value matrix $\mathbf{S}$ $(\min(n_a, n_b) \times \min(n_a, n_b))$ with r nonzero singular values $\rightarrow$ r is the (Schmidt) rank of $\mathbf{M}$



From a CI to an MPS parametrisation I

- Successive application of SVD to CI tensor → MPS wave function



From a CI to an MPS parametrisation II

- Reshape coefficient tensor $c_{k_1,k_2,\ldots,k_L}$ into a $d \times d^{L-1}$ matrix $\mathbf{\Gamma}$

$$\Gamma_{k_1,(k_2,\ldots,k_L)} = c_{k_1,k_2,\ldots,k_L}$$

- SVD of $\Gamma_{k_1,(k2,\ldots,k_L)}$ yields

$$\Gamma_{k_1,(k_2,\ldots,k_L)} = \sum_{a_1}^{r_1} U_{k_1,a_1} S_{a_1,a_1} (V^\dagger)_{a_1,(k_2,\ldots,k_L)}$$

$$\equiv \sum_{a_1}^{r_1} A^{k_1}_{1,a_1} c_{a_1,(k_2,\ldots,k_L)}$$

with

  - $\mathbf{S}$ and $\mathbf{V}^\dagger$ multiplied and reshaped into coefficient tensor $c_{a_1,(k_2,\ldots,k_L)}$
  - $r_1 \leq d$
  - collection of $d(=4)$ row vectors A^{k_1} with entries $A^{k_1}_{1,a_1} = U_{k_1,a_1}$

From a CI to an MPS parametrisation III

- Reshape coefficient tensor $c_{a_1,(k_2,\ldots,k_L)}$ into a $r_1 d \times d^{L-2}$ matrix $\mathbf{\Gamma}$

$$c_{k_1,k_2,\ldots,k_L} = \sum_{a_1}^{r_1} A^{k_1}_{1,a_1} \Gamma_{(a_1 k_2),(k_3,\ldots,k_L)}$$

$$\overset{\text{SVD}}{=} \sum_{a_1}^{r_1} \sum_{a_2}^{r_2} A^{k_1}_{1,a_1} U_{(a_1 k_2),a_2} S_{a_2,a_2} (V^\dagger)_{a_2,(k_3,\ldots,k_L)}$$

$$\overset{\text{reshape}}{\equiv} \sum_{a_1}^{r_1} \sum_{a_2}^{r_2} A^{k_1}_{1,a_1} A^{k_2}_{a_1,a_2} \Gamma_{(a_2 k_3),(k_4,\ldots,k_L)}$$

with

  - $\mathbf{S}$ and $\mathbf{V}^\dagger$ multiplied and reshaped into coefficient tensor $c_{a_1,(k_2,\ldots,k_L)}$
  - $r_2 \leq r_1 d \leq d^2$
  - collection of d matrices A^{k_2} with entries $A^{k_2}_{a_1,a_2} = U_{(a_1 k_2),a_2}$

From a CI to an MPS parametrisation IV

- Continue with SVDs until last site which then gives

$$c_{k_1,k_2,\ldots,k_L} = \sum_{a_1,a_2,\ldots,a_L-1} A^{k_1}_{1,a_1} A^{k_2}_{a_1,a_2} \cdots A^{k_{L-1}}_{a_{L-2,L-1}} A^{k_L}_{a_{L-1},1}$$
$$\equiv A^{k_1} A^{k_2} \cdots A^{k_{L-1}} A^{k_L}$$

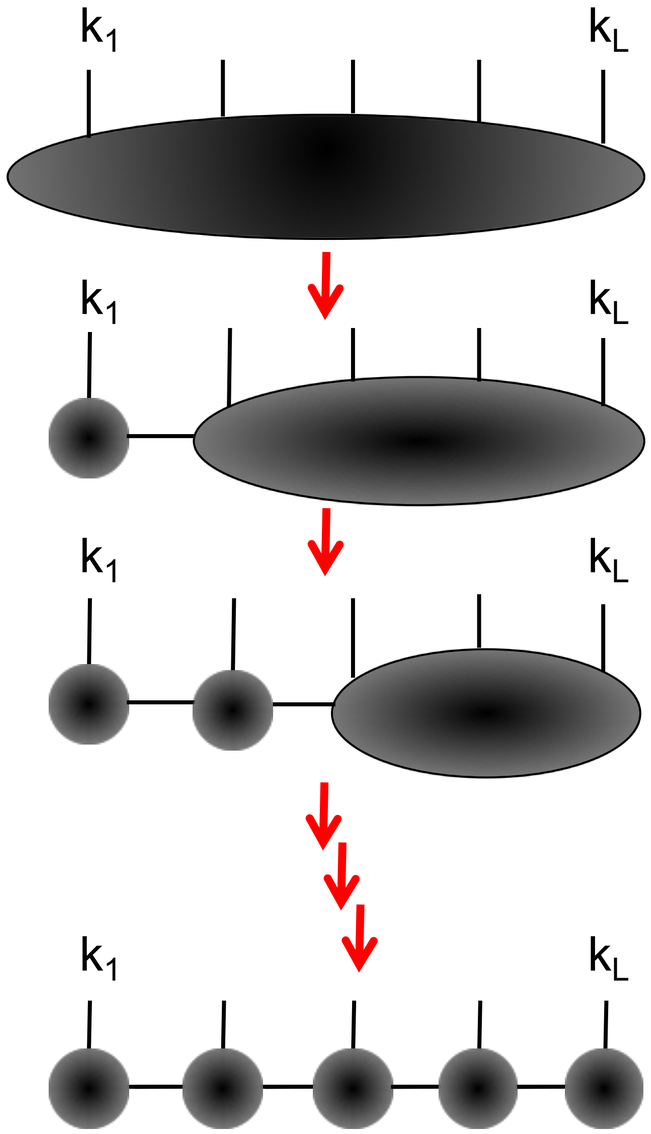
  with

  - interpretation of sums as matrix-matrix multiplications
  - first and last matrices are row- and column vectors!

- CI wave function rewritten as MPS wave function:

$$\left|\Psi\right\rangle = \sum_{\boldsymbol{k}} c_{\boldsymbol{k}} \left|\boldsymbol{k}\right\rangle = \sum_{k_1,k_2,\ldots,k_L} A^{k_1} A^{k_2} \cdots A^{k_{L-1}} A^{k_L} \left|\boldsymbol{k}\right\rangle$$

From a CI to an MPS parametrisation V

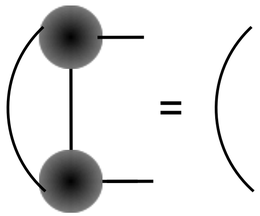


Properties of the MPS I

- Matrix dimensions grow exponentially up to $\dim(d^{L/2-1} \times d^{L/2})$ **if no truncation** occurs, i.e., all singular values are kept

- From $U^\dagger U = I$ follows that all matrices $\{A^{k_l}\}$ are **left-normalised**

$$\sum_{k_l} A^{k_l \dagger} A^{k_l} = I$$



- MPS built from left-normalised matrices is called **left-canonical**

- For any lattice bipartition at site l, the states on sites $1, \ldots, l$

$$|\, a_l \,\rangle_{\mathscr{L}} = \sum_{k_1, k_2, \ldots, k_l} \left(A^{k_1} \cdots A^{k_l} \right)_{1, a_l} |\, k_1, \ldots, k_l \,\rangle$$

span a left subsystem $\mathscr{L}$ and form an orthonormal basis

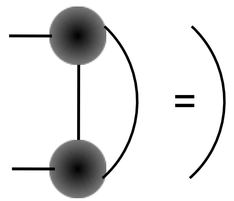
Properties of the MPS II

- Starting SVD on coefficient tensor from right-hand side

$$\Gamma_{(k_1,k_2,\ldots,k_{L-1}),k_L} = c_{k_1,k_2,\ldots,k_L}$$

yields **right-normalised** matrices $\{B^{k_l}\}$ (as $V^\dagger V = I$)

$$\sum_{k_l} B^{k_l} B^{k_l\dagger} = I$$



- MPS built from right-normalised matrices is called **right-canonical**

- For any lattice bipartition at site $l+1$, the states on sites $l+1\ldots, L$

$$|\, a_{l+1} \,\rangle_{\mathscr{R}} = \sum_{k_{l+1},k_{l+2},\ldots,k_L} \left(B^{k_{l+1}} \cdots B^{k_L}\right)_{a_l,1} |\, k_{l+1}, \ldots, k_L \,\rangle$$

span a right subsystem $\mathscr{R}$ and form an orthonormal basis

Gauge freedom and mixed-canonical form

- MPS representations are not unique $\leftrightarrow$ existence of a gauge degree of freedom
- Consider two adjacent matrices M^{k_l} and $M^{k_{l+1}}$ of shared column/row dimension D and a square invertible matrix X ($D \times D$)
- Invariance of MPS immediately follows from

$$M^{k_l} \to M^{k_l} X; \qquad M^{k_{l+1}} \to X^{-1} M^{k_{l+1}}$$

since

$$M^{k_l} \underbrace{X X^{-1}}_{=I} M^{k_{l+1}} = M^{k_l} \cdot M^{k_{l+1}}$$

Mixed-canonical MPS representation

- Gauge freedom allows to write an MPS in **mixed canonical** form at sites $\{l, l+1\}$

$$\left|\Psi\right\rangle = \sum_{\boldsymbol{k}} A^{k_1} \cdots A^{k_{l-1}} M^{k_l k_{l+1}} B^{k_{l+2}} \cdots B^{k_L} \left|\boldsymbol{k}\right\rangle$$

by starting from a general MPS wave function

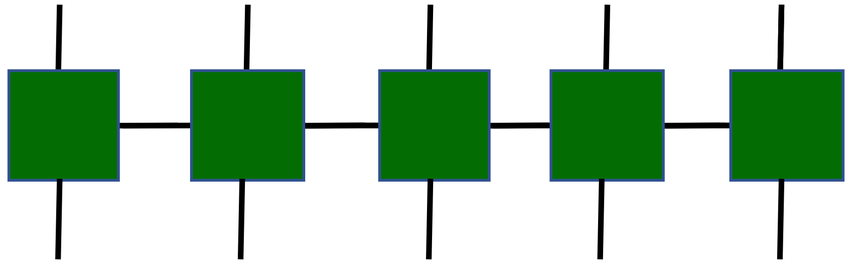
$$\left|\Psi\right\rangle = \sum_{\boldsymbol{k}} M^{k_1} M^{k_2} \cdots M^{k_L} \left|\boldsymbol{k}\right\rangle$$

and the **two-site MPS tensor** $M^{k_l k_{l+1}}$ reading as

$$M^{k_l k_{l+1}} \equiv M^{k_l k_{l+1}}_{a_{l-1}, a_{l+1}} = \sum_{a_l} M^{k_l}_{a_{l-1}, a_l} M^{k_{l+1}}_{a_l, a_{l+1}}$$

Matrix product operators I

- MPS concept applied to operators → matrix product operators (MPOs)



- N-electron operator $\hat{\mathscr{W}}$ in MPO form

$$\hat{\mathscr{W}} = \sum_{\boldsymbol{k}\boldsymbol{k}'} \sum_{b_1,\ldots,b_{L-1}} W^{k_1 k_1'}_{1,b_1} W^{k_2 k_2'}_{b_1,b_2} \cdots W^{k_L k_L'}_{b_{L-1},1} \left|\boldsymbol{k}\right\rangle \left\langle \boldsymbol{k}'\right|$$

$$= \sum_{\boldsymbol{k}\boldsymbol{k}'} W^{k_1 k_1'} W^{k_2 k_2'} \cdots W^{k_L k_L'} \left|\boldsymbol{k}\right\rangle \left\langle \boldsymbol{k}'\right|$$

$$\equiv \sum_{\boldsymbol{k}\boldsymbol{k}'} w_{\boldsymbol{k}\boldsymbol{k}'} \left|\boldsymbol{k}\right\rangle \left\langle \boldsymbol{k}'\right|$$

Matrix product operators II

- For efficiency, rearrange summations such that the contraction proceeds first over the local site indices $k_l k_l'$

$$\widehat{W^l_{b_{l-1},b_l}} = \sum_{k_l k_l'} W^{k_l k_l'}_{b_{l-1},b_l} \left| k_l \right\rangle \left\langle k_l' \right|$$

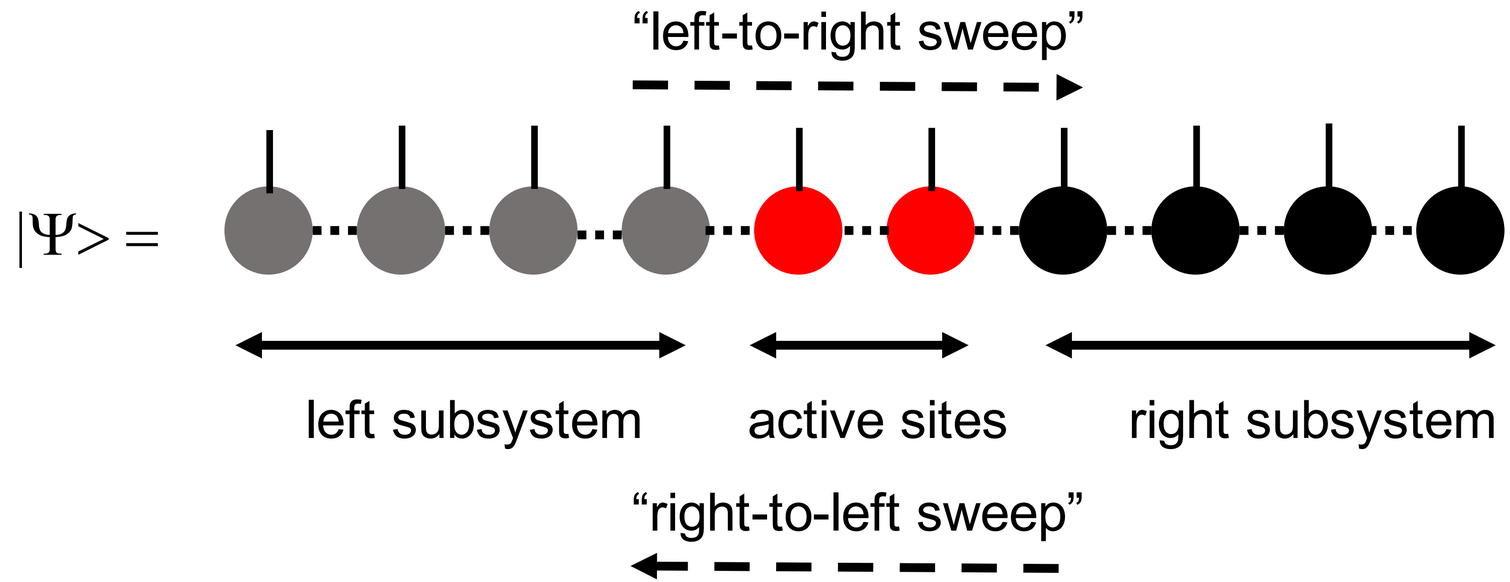
- This allows us to write the equation on previous slide as

$$\widehat{\mathscr{W}} = \sum_{b_1,\ldots,b_{L-1}} \widehat{W^1_{1,b_1}} \cdots \widehat{W^l_{b_{l-1},b_l}} \cdots \widehat{W^L_{b_{L-1},1}}$$

- **Note**: the entries of $\{\widehat{W^l_{b_{l-1},b_l}}\}$ matrices comprise the elementary, *local* operators acting on the l-th orbital, e.g.,

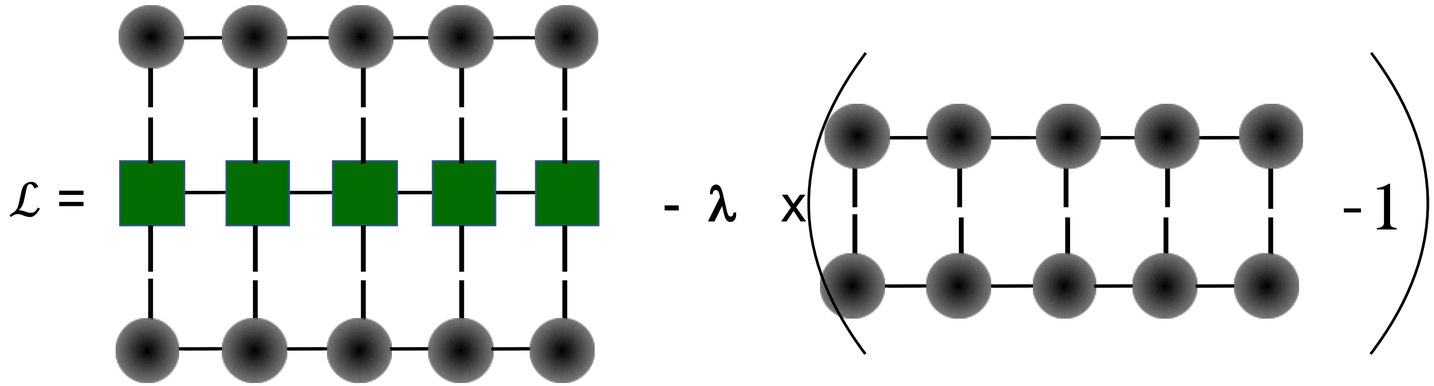
$$\tilde{a}^\dagger_{\uparrow_l} = \left| \uparrow\downarrow \right\rangle\left\langle \downarrow \right| + \left| \uparrow \right\rangle\left\langle 0 \right|$$

Variational MPS optimisation I



- **Goal**: find optimal approximation $|\tilde{\Psi}\rangle$ to $|\Psi\rangle$ (in a least-square sense)
- Prerequisite: initialise suitable (valid) trial MPS wave function $|\tilde{\Psi}\rangle$
  - choices: random guess, encode HF determinant, CI-DEAS, “old MPS” …
  - assume normalisation, i.e., $\langle\Psi|\Psi\rangle = 1$

Variational MPS optimisation II



- *Ansatz* for variational MPS optimization: extremize the Lagrangian

$$\mathscr{L} = \langle \Psi \left| \hat{H} \right| \Psi \rangle - \lambda \left(\langle \Psi \left| \Psi \right\rangle - 1 \right)$$

with the two-site $\{M^{k_l k_{l+1}}\}$ matrices as optimization parameters

- Optimize at each step of a ”sweep” entries of site matrices of **two orbitals** (“two-site DMRG”) while keeping all the others fixed

- Sweep through all sites multiple times until energy converges

Variational MPS optimisation III

- At sites $\{l, l+1\}$, take derivative of $\mathscr{L}$ with respect to complex conjugate of $M^{k_l,k_{l+1}}$

$$\frac{\partial}{\partial M^{k_l,k_{l+1}*}}\left(\langle\Psi|\,\hat{H}\,|\Psi\rangle - \lambda\left[\langle\Psi|\,\Psi\rangle - 1\right]\right) = 0$$

  which then yields

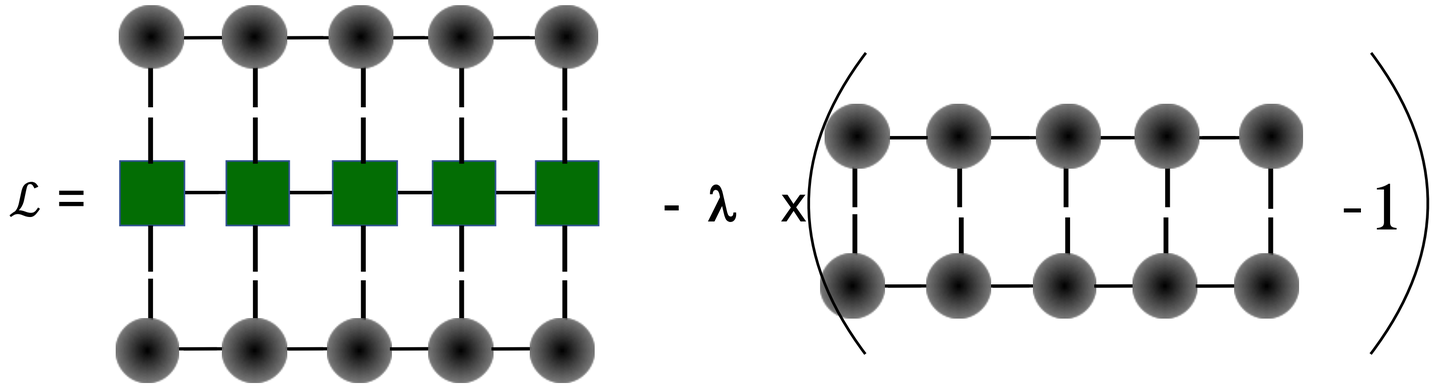
$$\sum_{\substack{a'_{l-1}a'_l \\ b_{l-1}b_{l+1}}}\sum_{k'_lk'_{l+1}} L^{b_{l-1}}_{a_{l-1},a'_{l-1}} W^{k_lk_{l+1},k'_lk'_{l+1}}_{b_{l-1},b_{l+1}} R^{b_{l+1}}_{a'_{l+1},a_{l+1}} M^{k'_lk'_{l+1}}_{a'_{l-1},a'_{l+1}} = \lambda \sum_{a'_{l-1}a'_l} \Psi^A_{a'_{l-1},a_{l-1}}$$

$$\times M^{k'_lk'_{l+1}}_{a'_{l-1},a'_{l+1}}$$

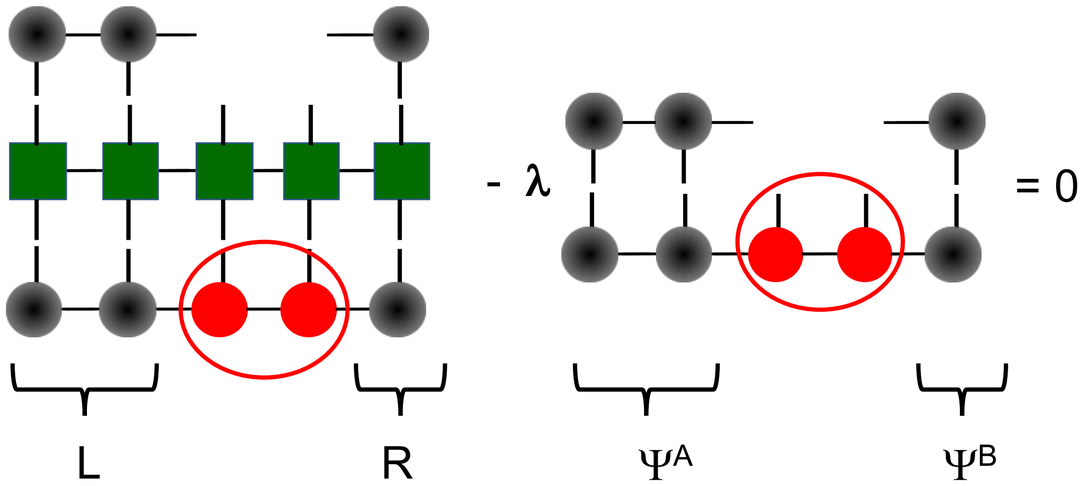
$$\times \Psi^B_{a'_{l+1},a_{l+1}}$$

- L and R: *left* and *right* boundaries obtained by contracting the MPO with the bra and ket MPS starting from left (right) up to sites $l-1 (l+1)$

Variational MPS optimisation IV



$$\frac{\partial}{\partial M^{k_l,k_{l+1}*}}$$

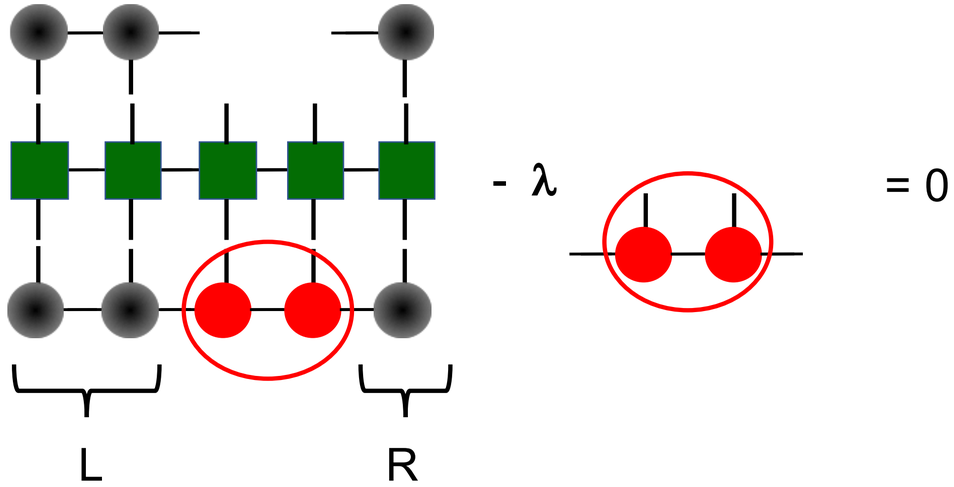


Variational MPS optimisation V

- **NB**: Simplify *generalized eigenvalue problem* to a *standard eigenvalue problem*

$$\sum_{\substack{a'_{l-1}a'_l \\ b_{l-1}b_{l+1}}} \sum_{k'_l k'_{l+1}} L^{b_{l-1}}_{a_{l-1},a'_{l-1}} W^{k_l k_{l+1},k'_l k'_{l+1}}_{b_{l-1},b_{l+1}} R^{b_{l+1}}_{a'_{l+1},a_{l+1}} M^{k'_l k'_{l+1}}_{a'_{l-1},a'_{l+1}} = \lambda M^{k'_l k'_{l+1}}_{a'_{l-1},a'_{l+1}}$$

if MPS is a canonical MPS!



- Requires the initial MPS to be right-normalized!

Variational MPS optimisation VI

- Recast last equation into a matrix eigenvalue equation

$$\mathscr{H} v - \lambda v = 0$$

  - by defining a local Hamiltonian matrix $\mathscr{H}$ at sites $\{l, l+1\}$

$$H_{(k_l k_{l+1} a_{l-1} a_{l+1}),(k'_l k'_{l+1} a'_{l-1} a'_{l+1})} = \sum_{b_{l-1}, b_{l+1}} L^{b_{l-1}}_{a_{l-1}, a'_{l-1}} W^{k_l k_{l+1}, k'_l k'_{l+1}}_{b_{l-1}, b_{l+1}} R^{b_{l+1}}_{a'_{l+1}, a_{l+1}}$$

  - and a vector v

$$v_{k'_l k'_{l+1} a'_{l-1} a'_{l+1}} = M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}}$$

- Solving EV problem —> eigenvalue λ^0 and corresponding eigenvector $v^0_{k'_l k'_{l+1} a'_{l-1} a'_{l+1}}$

Variational MPS optimisation VII

- Reshape $v^0_{k'_l k'_{l+1} a'_{l-1} a'_{l+1}}$ back to $M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}}$
- $M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}}$ is subsequently subject to a left- or right-normalisation (SVD!)

$$M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}} = M_{(k'_l, a'_{l-1})(k'_{l+1}, a'_{l+1})} = U_{(k'_l, a'_{l-1}) s_l} S_{s_l s_l} V_{s_l (a'_{l+1}, k'_{l+1})}$$

- By **discarding** the $3m$ smallest singular values in $S_{s_l s_l}$ to obtain $S_{a'_l a'_l}$ we achieve the **desired reduction in bond dimensionality**!
- The maximum (fixed) number m of retained singular values is usually called **number of renormalized block states**

Variational MPS optimisation VIII

- Discarding $3m$ smallest singular values corresponds to discarding the last $3m$ columns (rows) of U (V) such that

$$A^{k'_l}_{a'_{l-1},a'_l} \equiv U_{(k'_l,a'_{l-1})a'_l}$$

$$M^{k'_{l+1}}_{a'_l,a'_{l+1}} = \frac{1}{1 - \sum_{s_l=m+1}^{4m} S_{s_l s_l}} S_{a'_l a'_l} V_{a'_l(a'_{l+1},k'_{l+1})}$$

- Energy calculated as a function of the truncation error ϵ

$$\epsilon = \sum_{s_l=m+1}^{4m} S_{s_l s_l} = ||\Psi_{16m^2} - \Psi_{4m^2}||$$

can be employed to obtain an error estimate through extrapolation

Variational MPS optimisation IX

- Moving from sites $\{l, l+1\}$ to sites $\{l+1, l+2\}$ then completes the local optimization step

Scaling of variational MPS optimisation

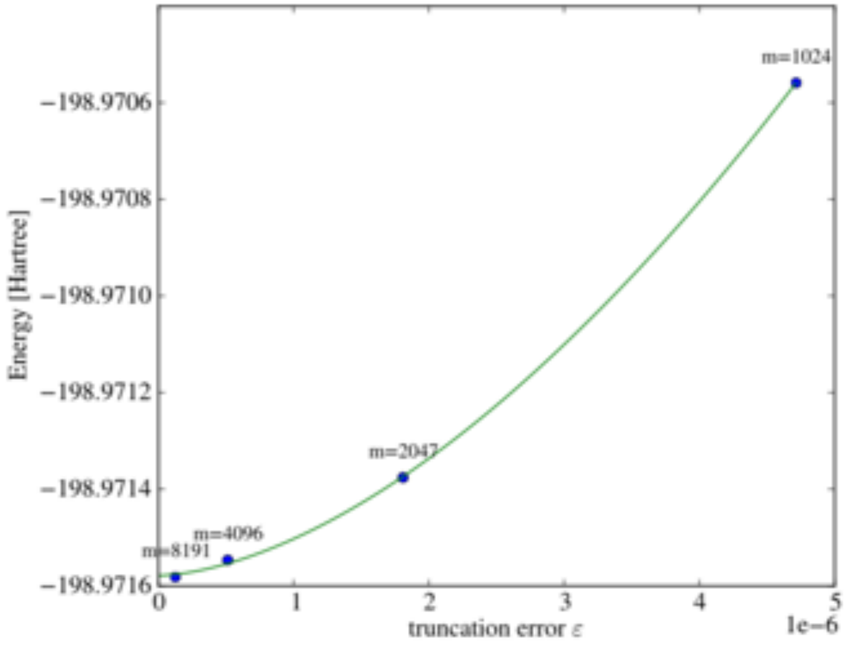
- **Scaling is dominated** by cost of contracting the operator with the MPS on one site and is proportional to the number of non-zero elements in the MPO matrices $\{ \widehat{W} \}$
  - in a naïve MPO ansatz this step scales as $\mathcal{O}(L^5)$
  - in an optimized code scaling reduces to $\mathcal{O}(L^4)$
- Further reduction through symmetry: $U(1)$ and $SU(2)$
- SVD scales as $\mathcal{O}(m^3)$ (but there are L of them in a sweep)
- Taking into account all operations a sweep scales $\approx \mathcal{O}(L^4 m^3)$

Extrapolation

- Extrapolate E based on truncation error ϵ for different values of m

$$\ln\left(\frac{E_{\mathrm{DMRG}} - E_{\mathrm{FCI}}}{E_{\mathrm{FCI}}}\right) = a \ln \epsilon + b$$

- Example: ground-state calculation of F_2



Determining factors of DMRG convergence

- Size L of the CAS
- Type of molecular orbitals (HF, NO's, localized orbitals, …)
- MPS guess for the right subsystem (initial sweep)
- Ordering of orbitals (exploit quantum information / graph theory)
- Number of renormalized block states m

One should never calculate results for just a single m, but increase it in various runs until results converge!

Properties of DMRG

- Variational
- Size-consistent
- (approximate) FCI for a CAS
- Polynomial scaling ($\approx L^4 m^3$)
- MPS wave function
- For large m invariant wrt orbital rotations

- Variational
- Size-consistent
- FCI for a CAS
- Factorial scaling
- Linearly parametrised wave function
- Invariant wrt orbital rotations

(Incomplete) List of DMRG codes for QC

- Budapest-DMRG code (Matlab, no source code available)
- MOLMPS (C++, ?)
- (Stack)Block and Block2 (C++, source code available)
- CheMPS2 (C++, Fortran, source code available)
- QCMaquis (C++, Fortran, source code available)
- …

Other classical methods for large CAS

- FCI-**Q**uantum **M**onte **C**arlo aka FCIQMC
- Heat-Bath CI (aka SHCI)
- selective CI / CIPSI-like approaches
- v(ariational) 2RDM
- …

—> Extensions to treat dynamical electron correlation available!

The road ahead …

Thinking outside the box II

Standard CI approach

- CI-type diagonalization for a **preselected** set of many-particle basis states

$$\left|\Psi\right\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} \left|k_1\right\rangle \otimes \left|k_2\right\rangle \otimes \ldots \otimes \left|k_L\right\rangle$$

DMRG

- **Determine** CI coefficients from correlations among orbitals

$$\left|\Psi\right\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} \left|k_1\right\rangle \otimes \left|k_2\right\rangle \otimes \ldots \otimes \left|k_L\right\rangle$$

Quantum Computing

- "**Learn**" the energy

$$\left\langle\Psi\right| \hat{H}_e \left|\Psi\right\rangle = \sum_k c_k \left\langle\Psi\right| P_k \left|\Psi\right\rangle$$

using an entangled set of qubits

$$\left|\Psi\right\rangle = \mathbf{U}(\vec{\theta}) \left|k_1\right\rangle \otimes \left|k_2\right\rangle \otimes \ldots \otimes \left|k_L\right\rangle$$

Quantum Chemistry on a Quantum Computer: Concepts and Challenges

Some important references

- Quantum Chemistry in the Age of Quantum Computing
  Aspuru-Guzik *et al.,* Chem. Rev. **119***,* 10856 (2019)
- Quantum computational chemistry
  McArdle, Endo, Aspuru-Guzik, Benjamin, Yuan, Rev. Mod. Phys. **92**, 015003 (2020)
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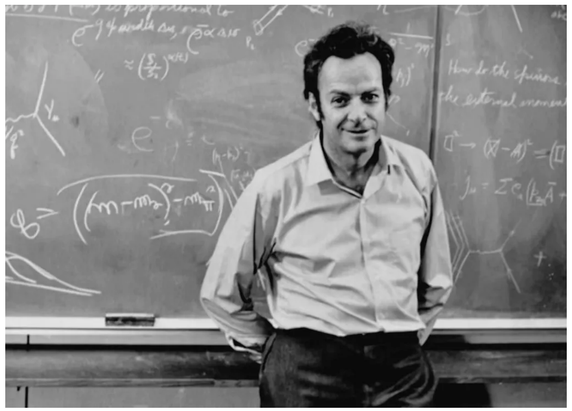
  Grimsley, Economou, Barnes, Mayhall, Nat. Comm.**10**, 3007 (2019)
- Simulated Quantum Computation of Molecular Energies,
  Aspuru-Guzik, Dutoi, Love, Head-Gordon, Science **309**, 1704 (2005)
- Quantum chemistry, classical heuristics, and quantum advantage,
  Garnet Kin-Lic Chan, Faraday Discuss., 2024, doi: 10.1039/D4FD00141A

The origins of quantum computing

Simulating quantum physics

Yuri Manin
1980



Richard Feynman
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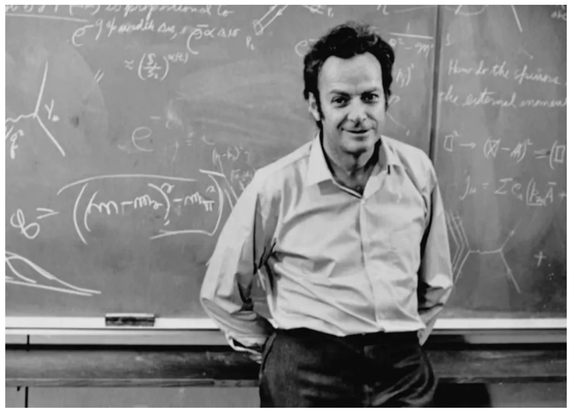


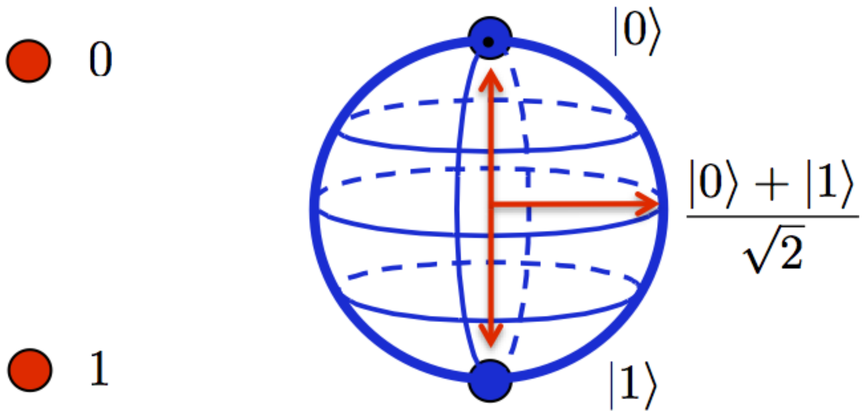
Richard Feynman
1982

Simulating some quantum mechanical effects on a classical computer is unfeasible

→ Use a quantum one!

The origins of quantum computing

Simulating quantum physics



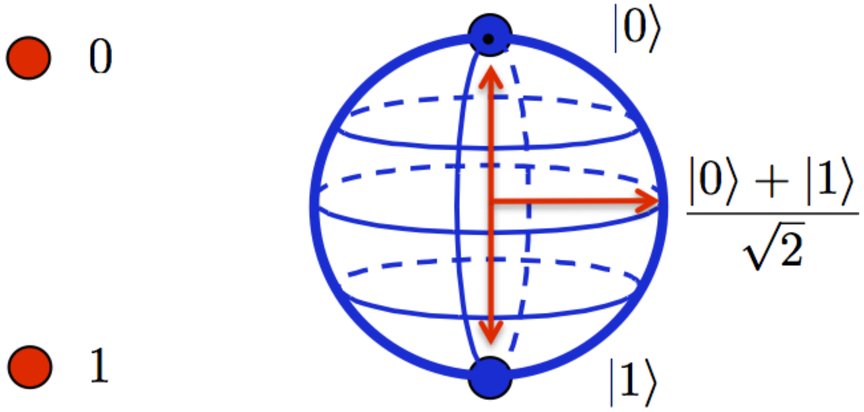
From **bits** to … → **qubits**

- Classical bit can be **either** in state $|0\rangle$ **or** state $|1\rangle$
- Qubit can be in a **superposition** of both states

$$|\psi\rangle = \alpha |0\rangle + \beta |1\rangle \equiv \alpha \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \beta \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

The origins of quantum computing

Simulating quantum physics



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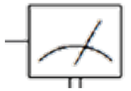
From **bits** to … → **qubits**

$$|\psi\rangle = |0\rangle \xrightarrow{\text{superposition}} |\psi\rangle = \alpha|0\rangle + \beta|1\rangle \xrightarrow{QC} |\psi\rangle = \gamma|0\rangle + \delta|1\rangle$$

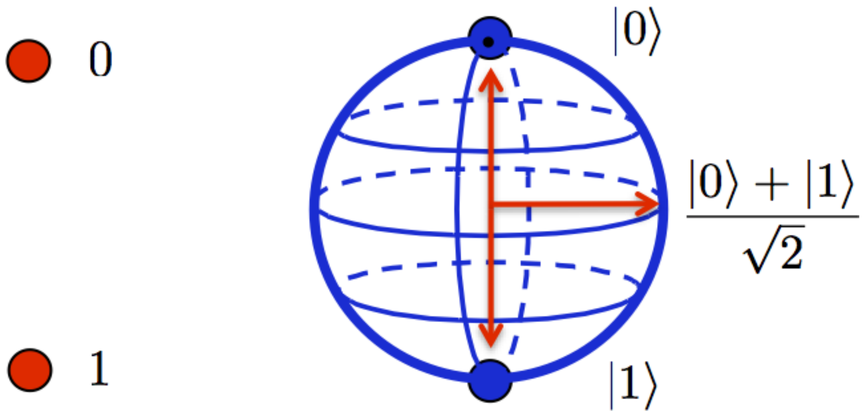


$$|\psi\rangle = |0\rangle$$

$$|\psi\rangle = |1\rangle$$

The origins of quantum computing

Simulating quantum physics



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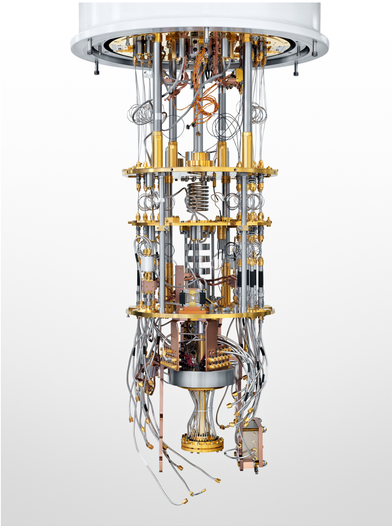
$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle \equiv \alpha\begin{bmatrix}1\\0\end{bmatrix} + \beta\begin{bmatrix}0\\1\end{bmatrix}$$

- Measuring the state of the qubit with probability P

$$P\left(|\psi\rangle = |0\rangle\right) = \gamma^2 \text{ and } P\left(|\psi\rangle = |1\rangle\right) = \delta^2$$

$|\psi\rangle = |0\rangle$ —**superposition**→ $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$ —**QC**→ $|\psi\rangle = \gamma|0\rangle + \delta|1\rangle$ → $|\psi\rangle = |0\rangle$ or $|\psi\rangle = |1\rangle$

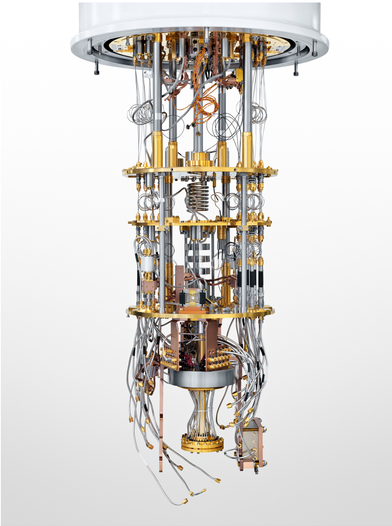
Using a quantum computer
as a quantum physics simulator



Arbitrary state of its qubits

$$|\Psi\rangle = \sum_{\vec{f}} \alpha_{\vec{f}} |f_1 f_2 \dots f_M\rangle$$

Using a quantum computer
as a quantum physics simulator



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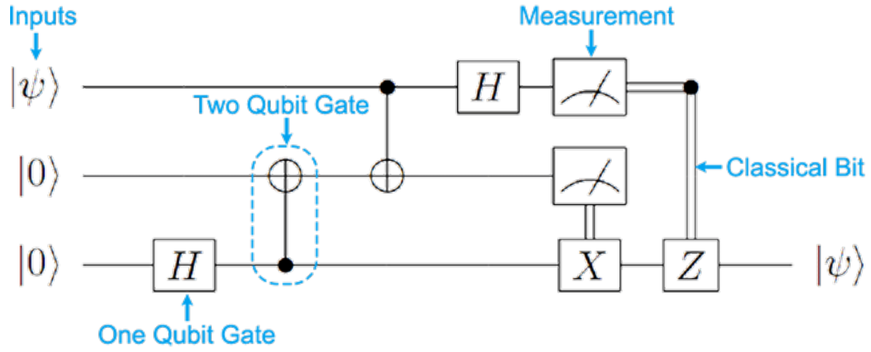
A universal quantum computer can solve problems beyond quantum simulation (e.g. factorisation)



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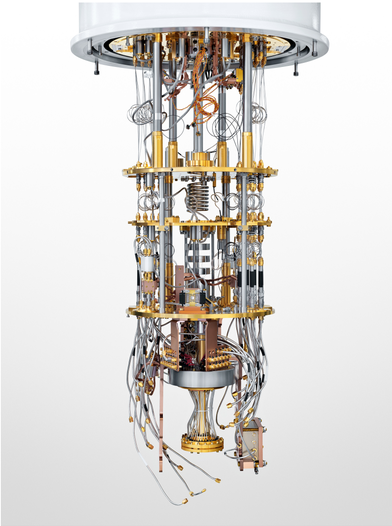

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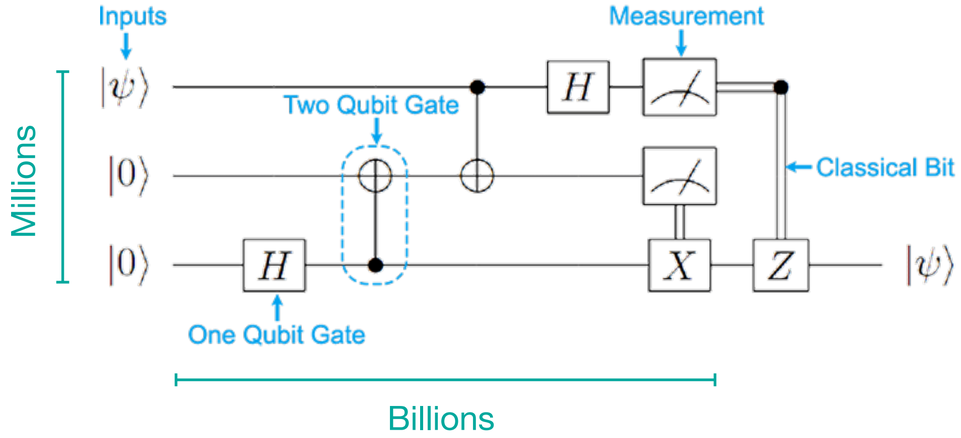

Quantum 5, 433 (2021)

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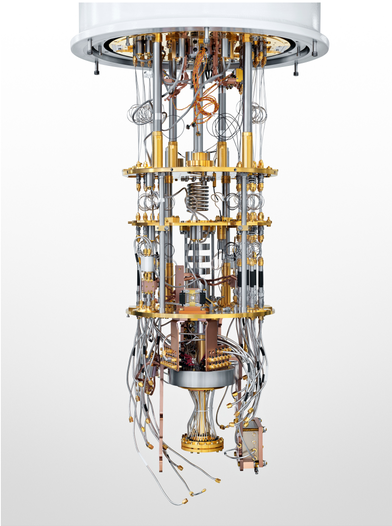

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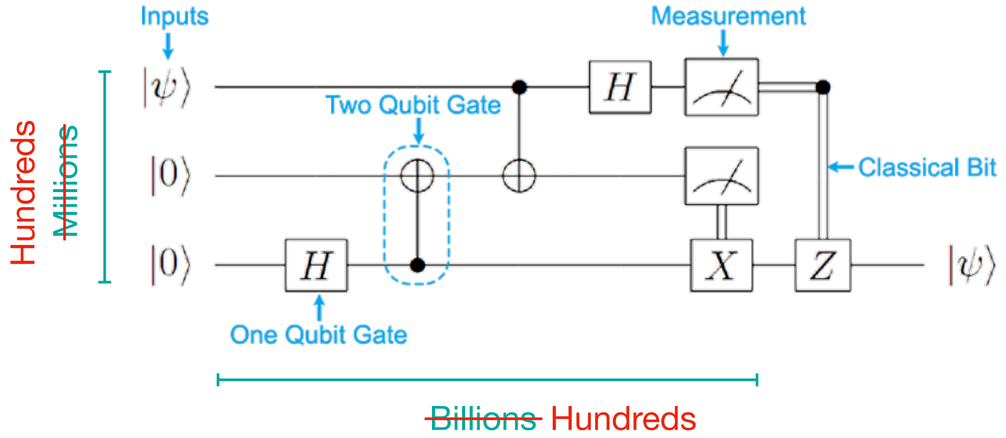

Quantum 5, 433 (2021)

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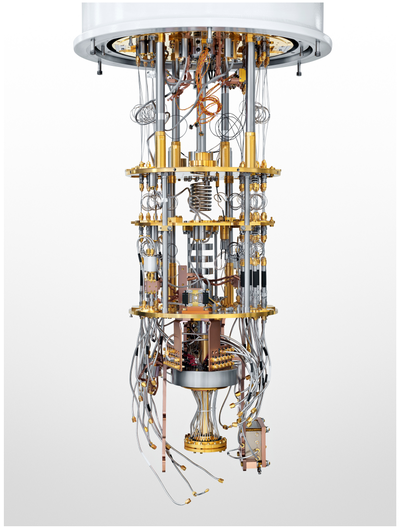

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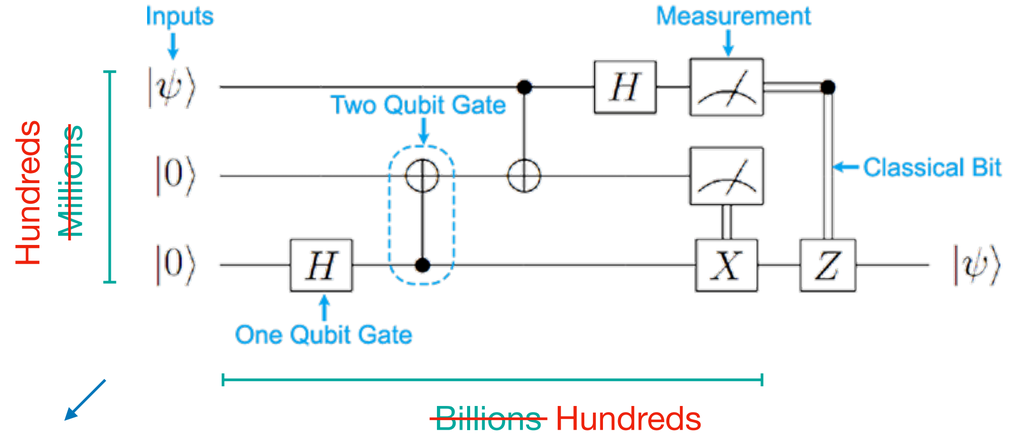


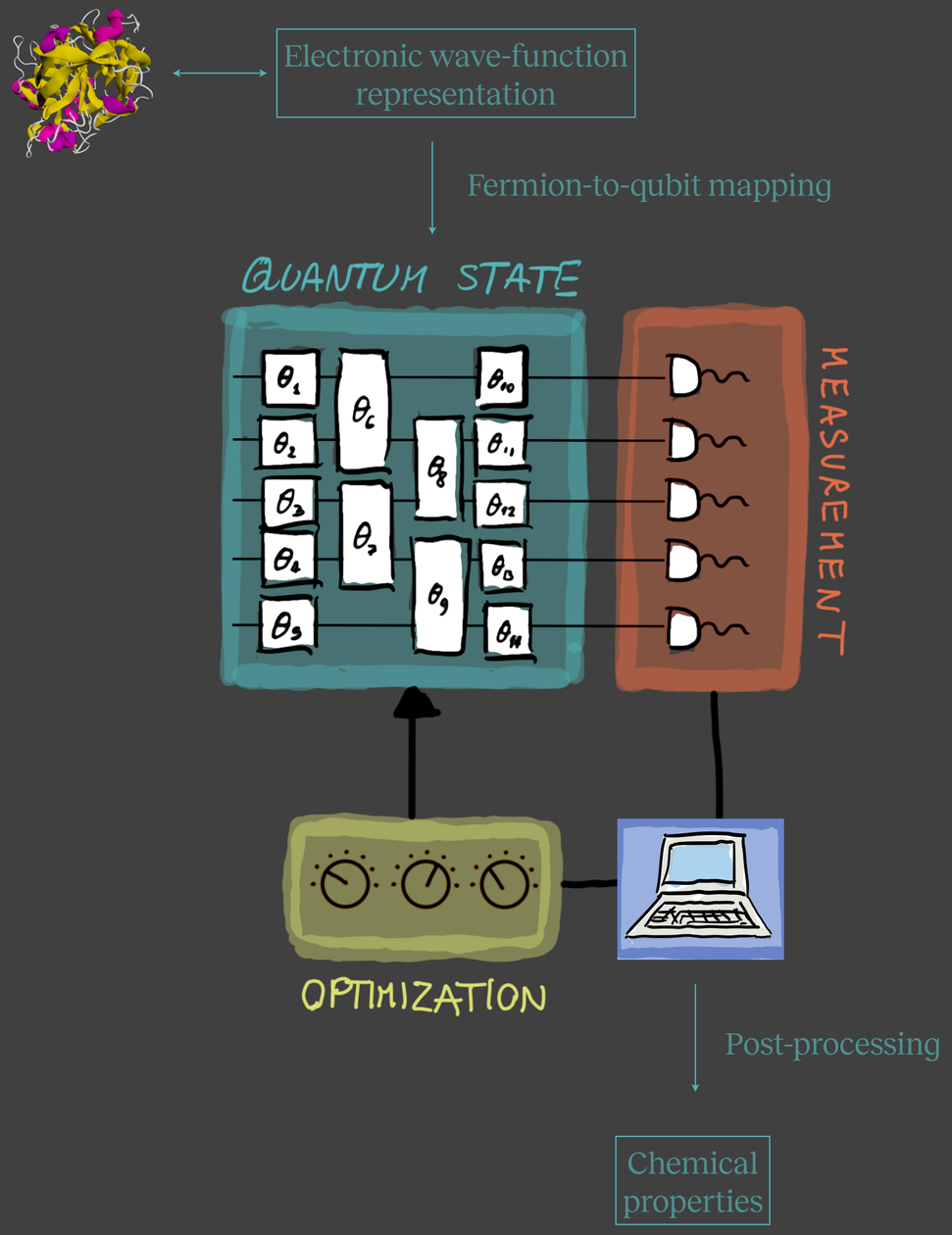
We are in the era of the Noisy Intermediate-Scale Quantum computers: soon useful for simulation!

Quantum 5, 433 (2021)

Quantum computer technologies

Qubit Type	Pros/Cons	Select Players
Superconducting	***Pros***: High gate speeds and fidelities. Can leverage standard lithographic processes. Among first qubit modalities so has a head start. ***Cons***: Requires cryogenic cooling; short coherence times; microwave interconnect frequencies still not well understood.	rigetti, Google, IBM Q, QuTech, OQC, IQM, qci Quantum Circuits, Inc, 本源量子 Origin Quantum
Trapped Ions	***Pros***: Extremely high gate fidelities and long coherence times. Extreme cryogenic cooling not required. Ions are perfect and consistent. ***Cons***: Slow gate times/ operations and low connectivity between qubits. Lasers hard to align and scale. Ultra-high vacuum required. Ion charges may restrict scalability.	IONQ, AQT, QUANTINUUM, oxford ionics, Universal Quantum
Photonics	***Pros***: Extremely fast gate speeds and promising fidelities. No cryogenics or vacuums required. Small overall footprint. Can leverage existing CMOS fabs. ***Cons***: Noise from photon loss; each program requires its own chip. Photons don't naturally interact so 2Q gate challenges.	PsiQuantum, XANADU, QUIX QUANTUM, ORCA Computing
Neutral Atoms	***Pros***: Long coherence times. Atoms are perfect and consistent. Strong connectivity, including more than 2Q. External cryogenics not required. ***Cons***: Requires ultra-high vacuums. Laser scaling challenging.	ColdQuanta, QuEra Computing Inc., atom computing, PASQAL
Silicon Spin/Quantum Dots	***Pros***: Leverages existing semiconductor technology. Strong gate fidelities and speeds. ***Cons***: Requires cryogenics. Only a few entangled gates to-date with low coherence times. Interference/cross-talk challenges.	intel, Silicon Quantum Computing, diraq, QUANTUM MOTION, QUANTUM BRILLIANCE

Source: Quantum Computing Modalities - A Qubit Primer Revisited - The Quantum Leap (quantum tech.blog)

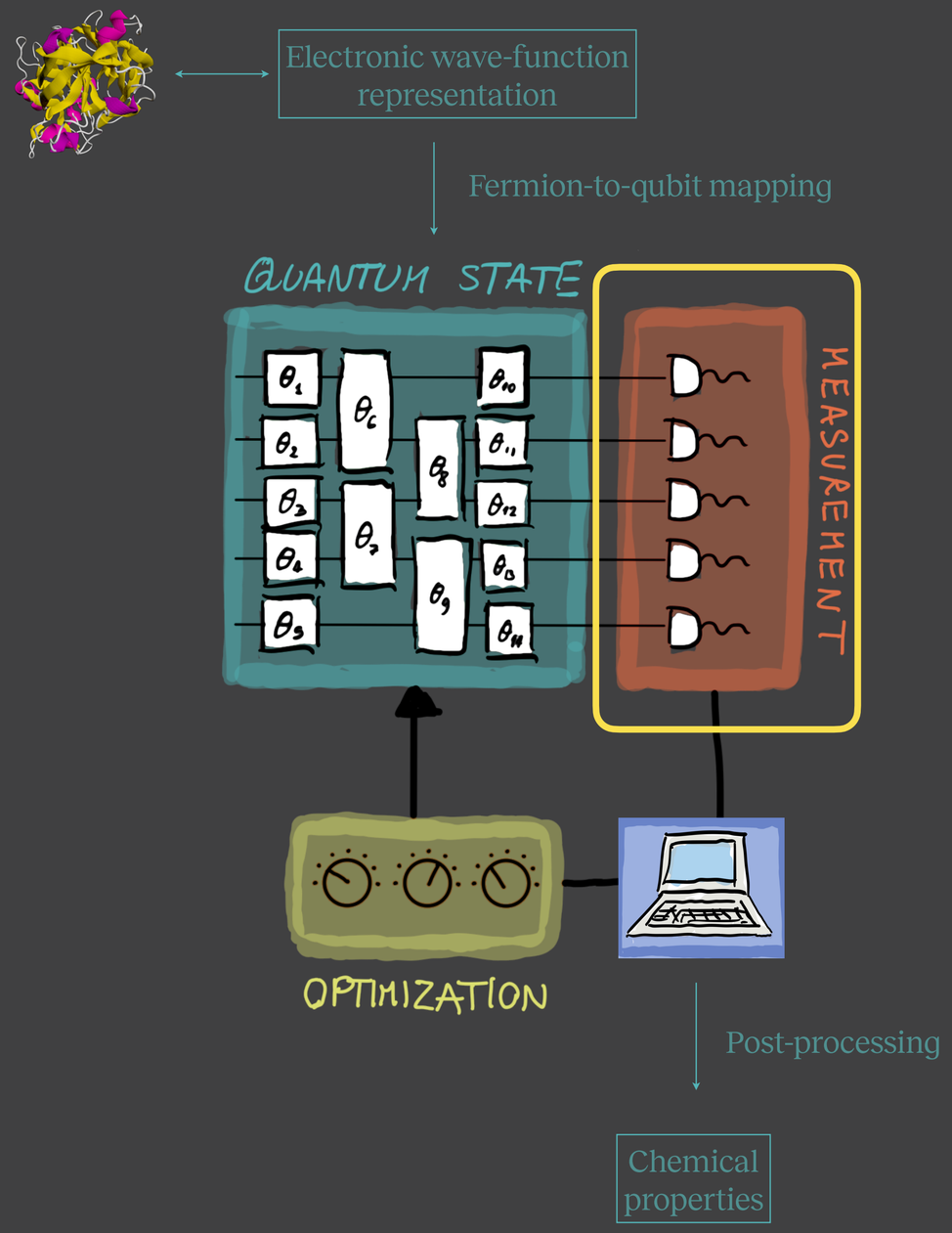


Quantum Computing for Quantum Chemistry in a Nutshell

The state of the quantum processor mathematically represents the state of the molecule

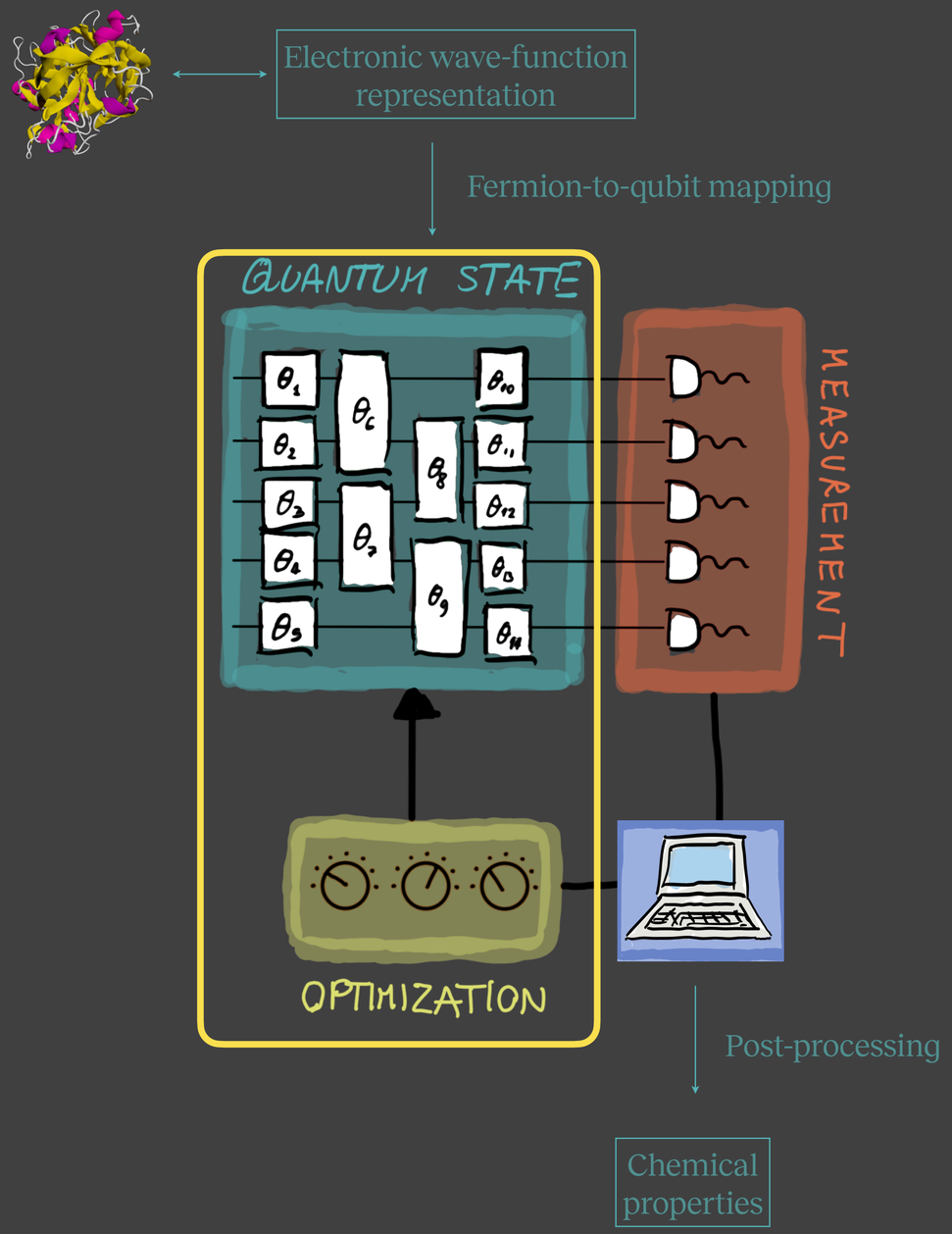
The goal is to find the state of the molecule for which the energy is minimal

The energy of the molecule needs to be measured



Challenges in near-term QC

1. Measurement stage is time-consuming
2. Hilbert space is a big space
3. Qubits are a scarce resource
4. Noise biases the results
5. Resource efficient/aware representation



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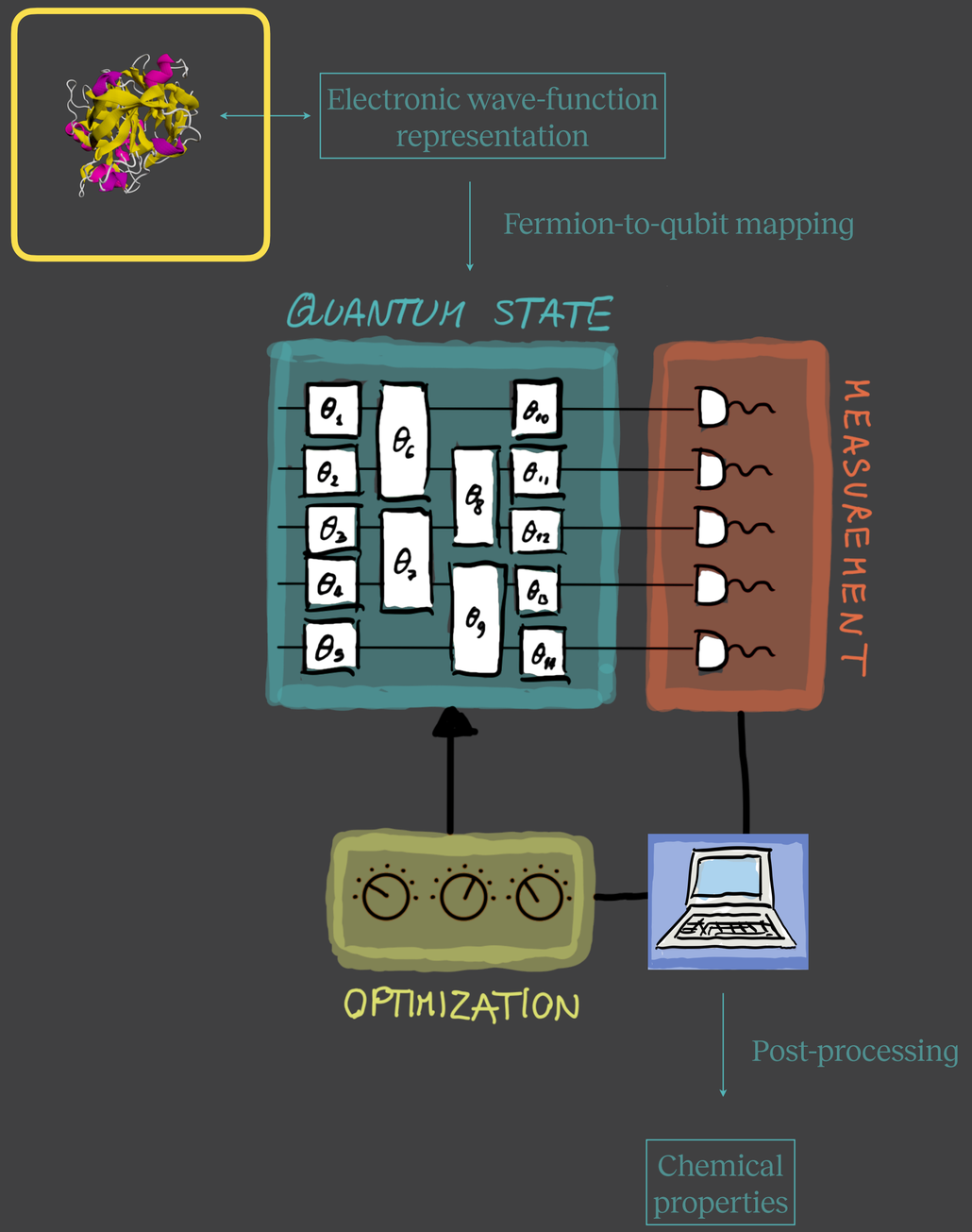

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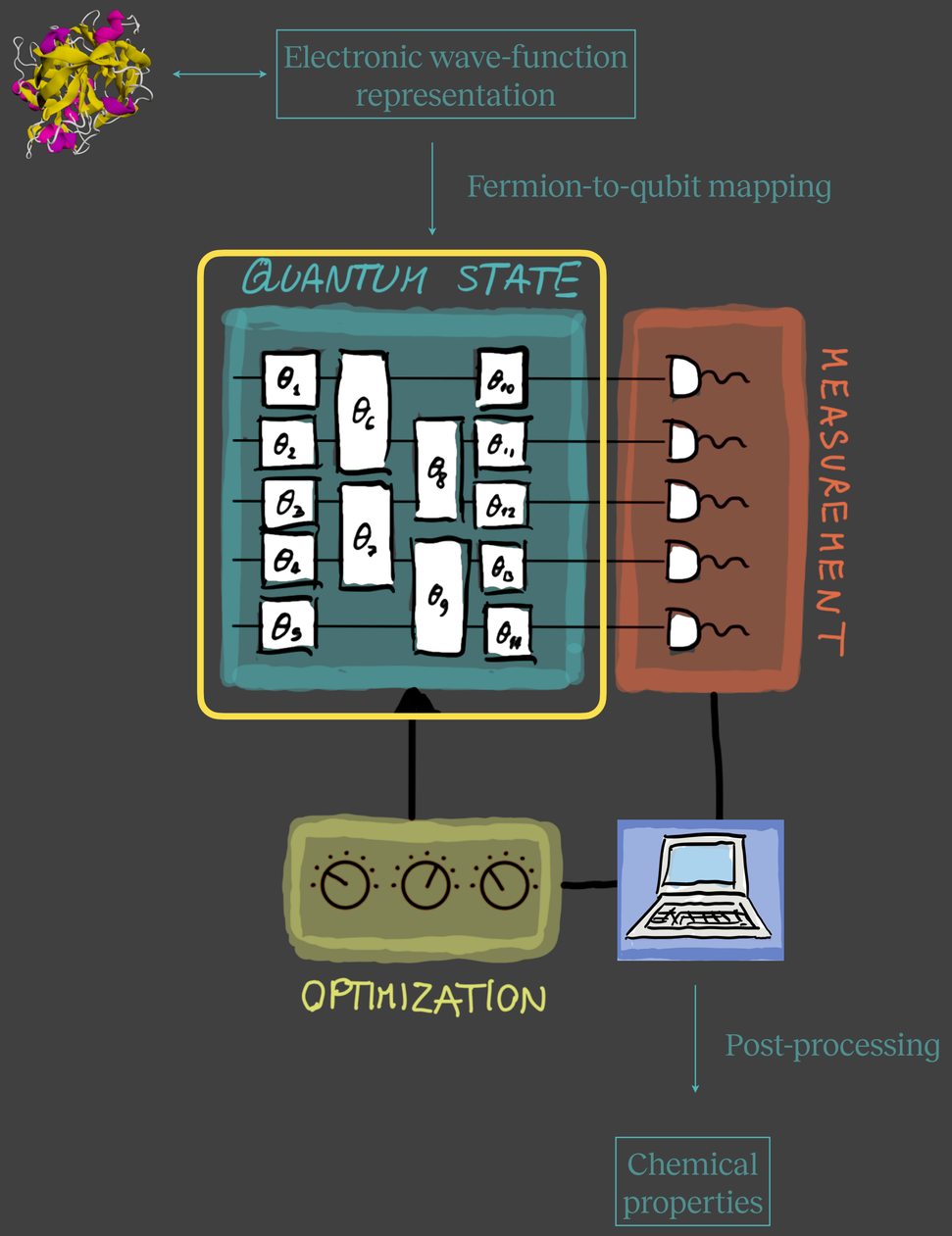

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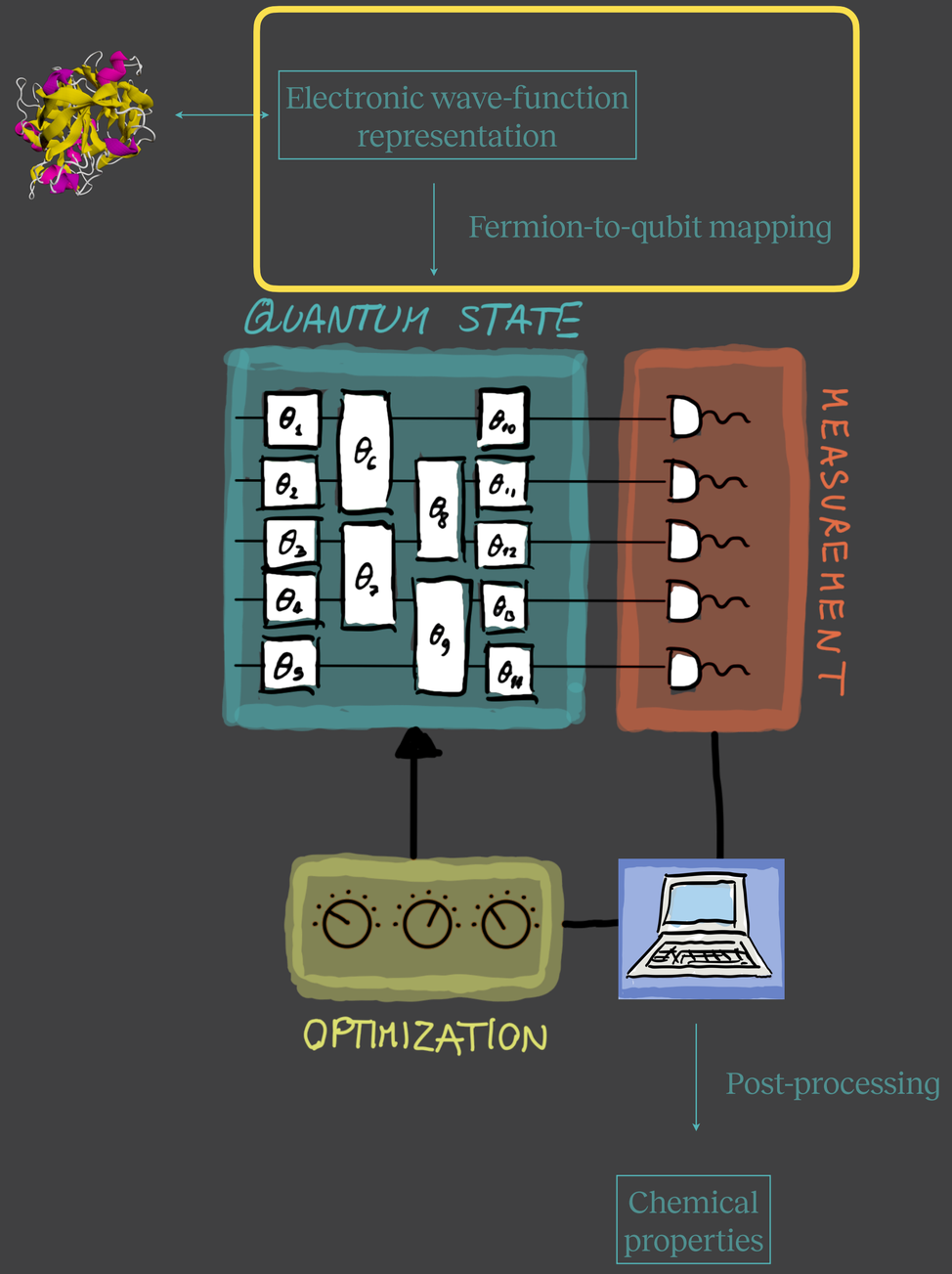

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Mapping “the problem” from fermion to qubit space

Mapping the problem from fermion to qubit space

General considerations

- *N*-electron wave function

$$|\Psi\rangle = \sum_{\zeta} c_{\zeta} \left|\Phi_{\zeta}\right\rangle \longrightarrow |\Psi\rangle$$

- Second-quantized Hamiltonian

$$\hat{H}_e = \sum_{p,q} h_{pq}\, \hat{E}_{pq} + \frac{1}{2} \sum_{p,q,r,s} (pq\,|\,rs)\, \left(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\right) \longrightarrow ?$$

- Fermions are indistinguishable particles, qubits are distinguishable
  —> we need to account for anti-commutation of fermionic operators in the map!

$$\{\hat{a}_p, \hat{a}_q\} = 0 \qquad \{\hat{a}_p^{\dagger}, \hat{a}_q^{\dagger}\} = 0 \qquad \{\hat{a}_p, \hat{a}_q^{\dagger}\} = \delta_{pq}$$

Mapping the problem from fermion to qubit space

N-electron wave function

$$\left|\Psi\right\rangle = \sum_{\mathbf{f}} c_{\mathbf{f}} \left|f_{M-1}\cdots f_1 f_0\right\rangle$$

Exact for infinite *M*!

Mapping the problem from fermion to qubit space

N-electron wave function

$$\left|\Psi\right\rangle = \sum_{\mathbf{f}} c_{\mathbf{f}} \left|f_{M-1}\cdots f_1 f_0\right\rangle$$

Exact for infinite *M*!

- Trivial interaction of fermionic creation/annihilation operators on ON

$$\hat{a}_p^\dagger \left|f_{M-1}\cdots f_{p+1}\ 0\ f_{p-1}\cdots f_0\right\rangle = (-1)^{\sum_{s=0}^{p-1} f_s} \left|f_{M-1}\cdots f_{p+1}\ 1\ f_{p-1}\cdots f_0\right\rangle$$

$$\hat{a}_p^\dagger \left|f_{M-1}\cdots f_{p+1}\ 1\ f_{p-1}\cdots f_0\right\rangle = 0$$

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$$\hat{a}_p \left|f_{M-1}\cdots f_{p+1}\ 0\ f_{p-1}\cdots f_0\right\rangle = 0$$

Mapping the problem from fermion to qubit space

N-electron wave function

- Trivial translation of fermionic ON vector basis to qubit ON vector basis

$$\left|f_{M-1}\cdots f_1 f_0\right\rangle \longrightarrow \left|q_{M-1}\right\rangle\cdots\otimes\left|q_1\right\rangle\otimes\left|q_0\right\rangle \equiv \left|q_{M-1}\cdots q_1 q_0\right\rangle$$

- What about creation/annihilation operators for qubits?

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Use a simple recipe for one-qubit creation and annihilation operators?

$$\hat{Q}^{+}\left|1\right\rangle = 0 \qquad \hat{Q}^{+}\left|0\right\rangle = \left|1\right\rangle \qquad \hat{Q}^{-}\left|1\right\rangle = \left|0\right\rangle \qquad \hat{Q}^{-}\left|0\right\rangle = 0$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

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Do not obey the fermionic anti-commutation relations!

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Use a simple recipe for one-qubit creation and annihilation operators?

$$\hat{Q}^{+}\left|1\right\rangle = 0 \qquad \hat{Q}^{+}\left|0\right\rangle = \left|1\right\rangle \qquad\qquad \hat{Q}^{-}\left|1\right\rangle = \left|0\right\rangle \qquad \hat{Q}^{-}\left|0\right\rangle = 0$$

Do not obey the fermionic anti-commutation relations!

- Better ansatz? Form operators based on Pauli matrices!

$$\hat{Q}^{+} = \left|1\right\rangle\left\langle 0\right| \equiv \frac{1}{2}\left(\sigma_x - i\sigma_y\right) = \frac{1}{2}\left(X - iY\right)$$

$$\hat{Q}^{-} = \left|0\right\rangle\left\langle 1\right| \equiv \frac{1}{2}\left(\sigma_x + i\sigma_y\right) = \frac{1}{2}\left(X + iY\right)$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Why are Pauli matrices a suitable choice?

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Why are Pauli matrices a suitable choice?

Single-qubit quantum gates are 2×2 unitary matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Why are Pauli matrices a suitable choice?

Single-qubit quantum gates are 2×2 unitary matrices

—> Pauli matrices are 2×2 Hermitian (unitary) matrices

—> Pauli matrices are involutory: $\sigma_p^2 = \mathbf{1} \; \forall p \in [x, y, z]$

—> Pauli matrices anti-commute: $\left\{ \sigma_p, \sigma_q \right\} = 2I\delta_{pq} \qquad \forall p, q \in [x, y, z]$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Because of anti-commutation among Paulis, $\hat{Q}^{\pm}$ and σ_z anti-commute
- Represent action of fermionic operators $\hat{a}_p^{(\dagger)}$ for index p by acting with $\hat{Q}^{\pm}$ on qubit p and with σ_z on all qubits with index $q < p$ and with the identity $\mathbf{1}$ on the remaining qubits

Mapping the problem from fermion to qubit space

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Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

Major drawback of Jordan-Wigner mapping: **k-locality!**

k-locality: each term in the Hamiltonian acts non-trivially on at most k qubits

—> non-locality of "parity term $\left[\sigma_z^{\otimes p}\right]$" that appears in $\hat{a}_p^{(\dagger)}$ introduces a number of extra qubit operations which scale as $\mathcal{O}(M)$!

Example: how does it work for mapping one-electron terms

$$\hat{h} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q \, ?$$

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fermi_ham = qc_ham_qiskit.second_q_ops()[0]
fermi_ham.set_truncation(0)
print("Fermionic Hamiltonian",fermi_ham)
qubit_converter = QubitConverter(mapper=JordanWignerMapper())
Hq = qubit_converter.convert(fermi_ham)
print("J-W Qubit Hamiltonian",Hq)
```

✓ 0.4s

```
Fermionic Hamiltonian Fermionic Operator
register length=4, number terms=5
  1.0 * ( +_0 -_0 )
+ 3.0 * ( +_1 -_1 )
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Mapping the problem from fermion to qubit space

Parity mapping

- Alternative idea to occupation number basis —> parity basis:

  Use qubit p to store the parity $\mathscr{P}$ of all occupied orbitals up to p

$$\mathscr{P}_p = \mod\left(\sum_{s=0}^{p} f_s\ ,\ 2\right)$$

- Parity of set of orbitals with $q < p$ determines whether $\hat{a}_p^{(\dagger)}$ introduces a phase of -1

  —> it suffices to only have σ_z acting on qubit $p-1$

Mapping the problem from fermion to qubit space

Parity mapping

- BUT: we cannot represent the creation or annihilation of a particle in qubit q_p with $\hat{Q}_p^{(\pm)}$ since q_p stores the parity of all orbitals with index $q \leq p$
- Representing for example $\hat{a}_p^\dagger$ in terms of $\hat{Q}_p^{\pm}$ depends on qubit $(p-1)$:
  - qubit $(p-1)$ is in state $\left|0\right\rangle$: act on qubit p with $\hat{Q}_p^{+}$
  - qubit $(p-1)$ is in state $\left|1\right\rangle$: act on qubit p with $\hat{Q}_p^{-}$

Mapping the problem from fermion to qubit space

Parity mapping

- Operator equivalent to $\hat{Q}^{\pm}$ in parity basis is $\hat{P}^{\pm}$ and a **<u>two-qubit</u>** operator!

$$\hat{P}_p^{\pm} \equiv \hat{Q}_p^{\pm} \otimes \left|0\right\rangle\left\langle 0\right|_{p-1} - \hat{Q}_p^{\mp} \otimes \left|1\right\rangle\left\langle 1\right|_{p-1}$$

$$= \frac{1}{2}\left(X_p \otimes Z_{p-1} \mp iY_p\right)$$

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Parity mapping

- Major drawback of parity mapping: k**-locality!**

  —> non-locality of “update term $\left[\sigma_x^{\otimes M-p}\right]$” that appears in $\hat{a}_p^{(\dagger)}$ introduces a number of extra qubit operations which scale as $\mathcal{O}(M)$!

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- Trailing string of σ_z (J-W) replaced by leading string of σ_x …

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Notes on other mappings

- Major drawback of parity and J-W mapping: **k-locality which is also referred to as Pauli weight**

- Other more elaborate mappings exist which scale as $\mathcal{O}(\log_2 M)$ [Bravyi-Kitaev —> “combines ideas” of J-W and parity mappings] or even up to $\mathcal{O}(\log_3 M)$

Mapping the problem from fermion to qubit space

Bravyi-Kitaev

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Hq = qubit_converter.convert(fermi_ham)
print("Parity Qubit Hamiltonian",Hq)

qubit_converter = QubitConverter(mapper=BravyiKitaevMapper())
Hq = qubit_converter.convert(fermi_ham)
print("Bravyi-Kitaev Qubit Hamiltonian",Hq)
```

✓ 0.7s

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- Customised (tree-based) mappings tailored to QC hardware layout are also possible!

Mapping the problem from fermion to qubit space

Notes on other mappings

- Common outcome of mappings: $\hat{H}_e$ is expressed as a sum of Pauli strings P_k

$$\hat{H}_e = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q \quad \longrightarrow \quad \hat{H}_e = \sum_k c_k P_k$$

Calculating the energy
on a quantum computer

- The Hamiltonian is given as a linear combination of Pauli strings

$\hat{H}_e = \sum_k c_k P_k$ ← Each term is a product of local operators $P_k = \bigotimes_{s=0}^{M-1} \sigma_{k_s,(s)}$

- We can calculate expectation values on the quantum computer

$$\left|\Psi\right\rangle = \sum_{\mathbf{f}} c_{\mathbf{f}} \left|f_{M-1}\ldots f_1 f_0\right\rangle \longrightarrow \left\langle\Psi\right| \hat{H}_e \left|\Psi\right\rangle = \sum_k c_k \left\langle\Psi\right| P_k \left|\Psi\right\rangle$$

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“Easy” on a quantum computer: only requires measuring Pauli strings

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$$\left|\Psi\right\rangle = \sum_{\mathbf{f}} c_{\mathbf{f}} \left|f_{M-1}\cdots f_1 f_0\right\rangle$$ — $\left|\Psi\right\rangle$? — $\sum_k c_k \left\langle\Psi\right| P_k \left|\Psi\right\rangle$

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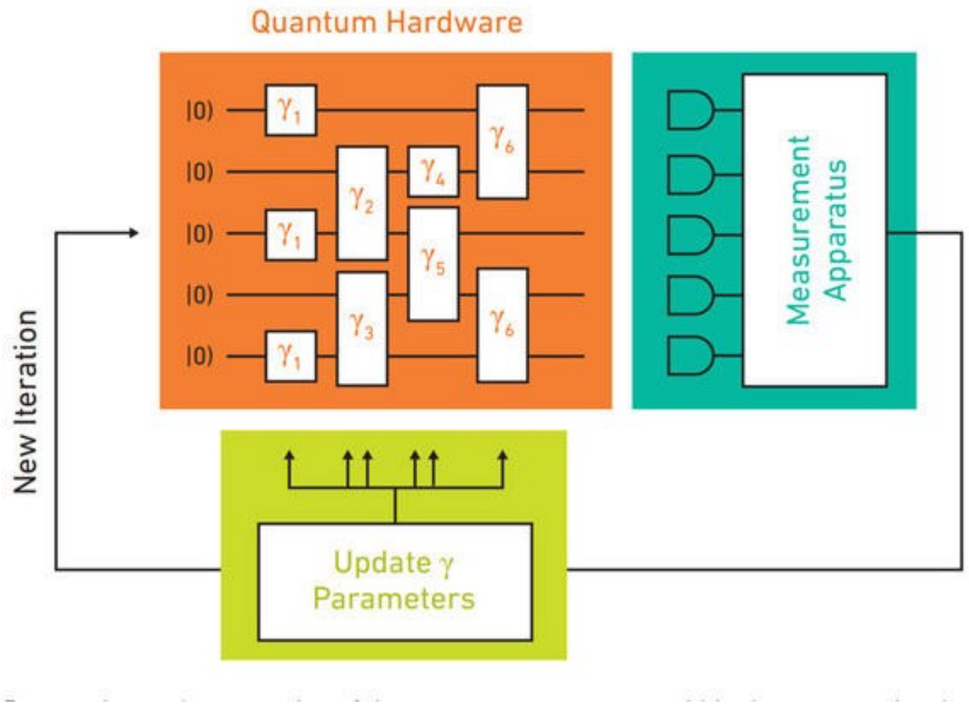
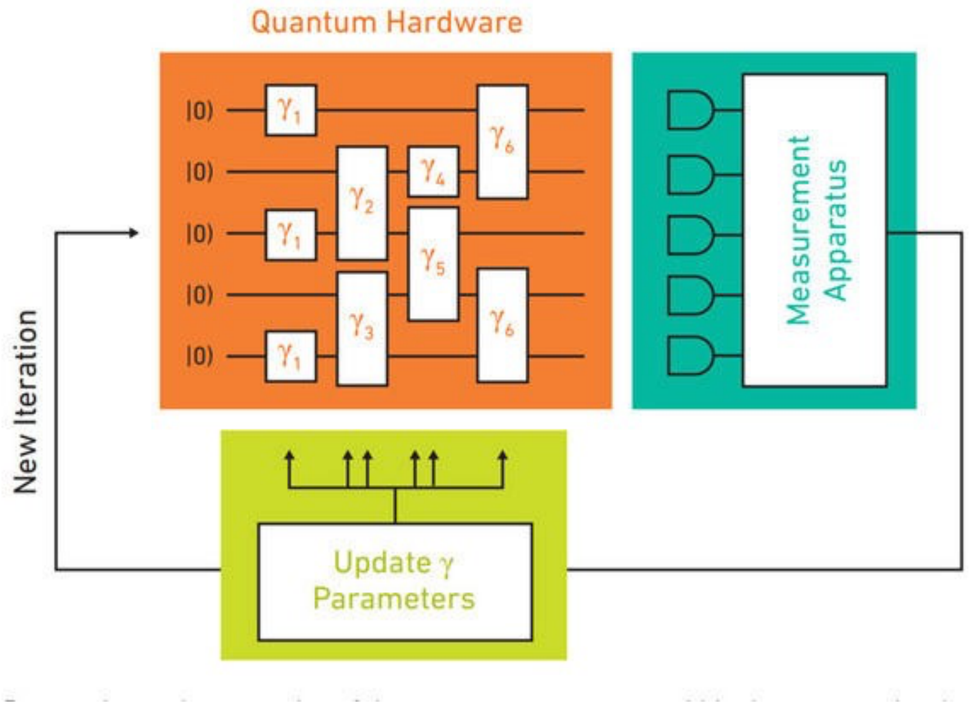
Variational optimisation with the Variational Quantum Eigensolver



Variational optimisation with the Variational Quantum Eigensolver

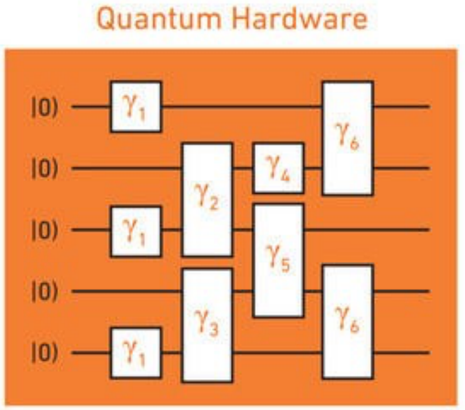


... which is just one example, many algorithms exist, not to mention fault-tolerant ones...

Solving the problem

The Variational Quantum Eigensolver

- Prepare *some* quantum state using a so-called variational form (ansatz)



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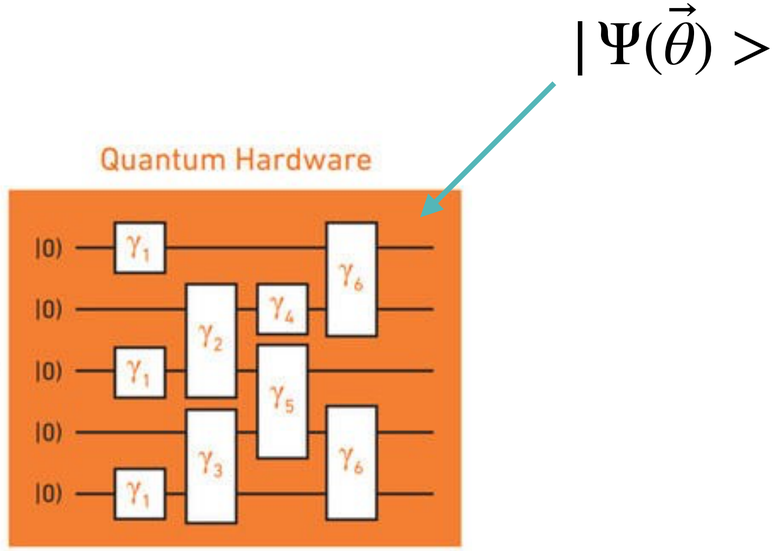

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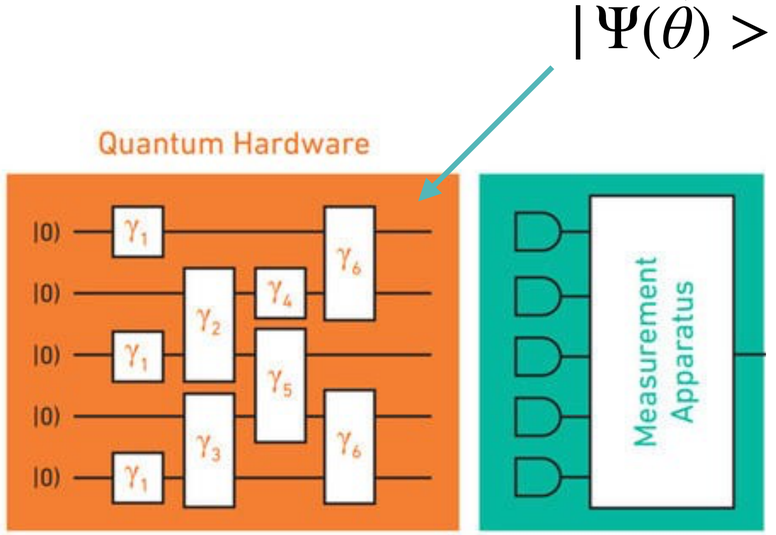
$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \right| \hat{H}_e \left| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$



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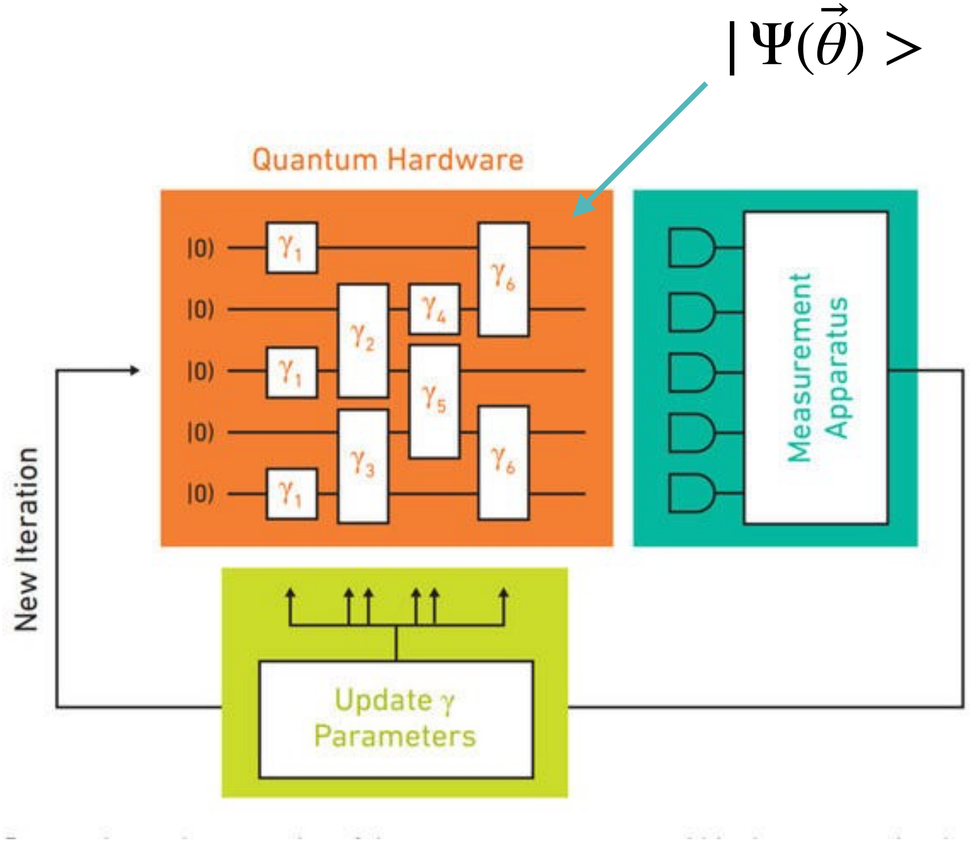
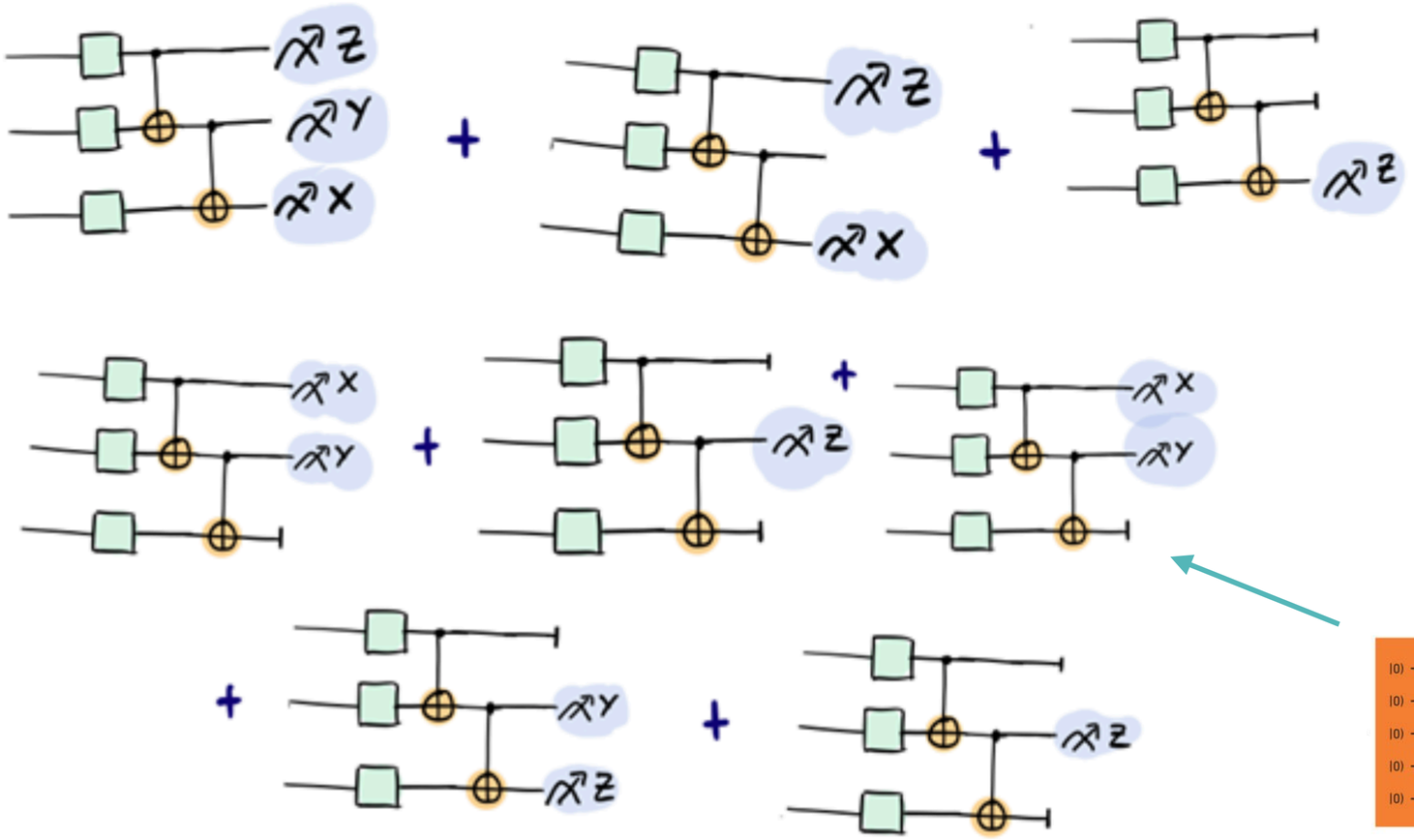
- Find the ground state variationally: minimising over the parameters $\{\vec{\theta}\}$

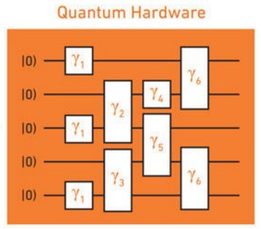


Measuring the energy
in a VQE simulation



$$\langle \Psi | \hat{H}_e | \Psi \rangle = \sum_k c_k \langle \Psi | P_k | \Psi \rangle$$

Every Pauli string evaluated independently through repeated measurements



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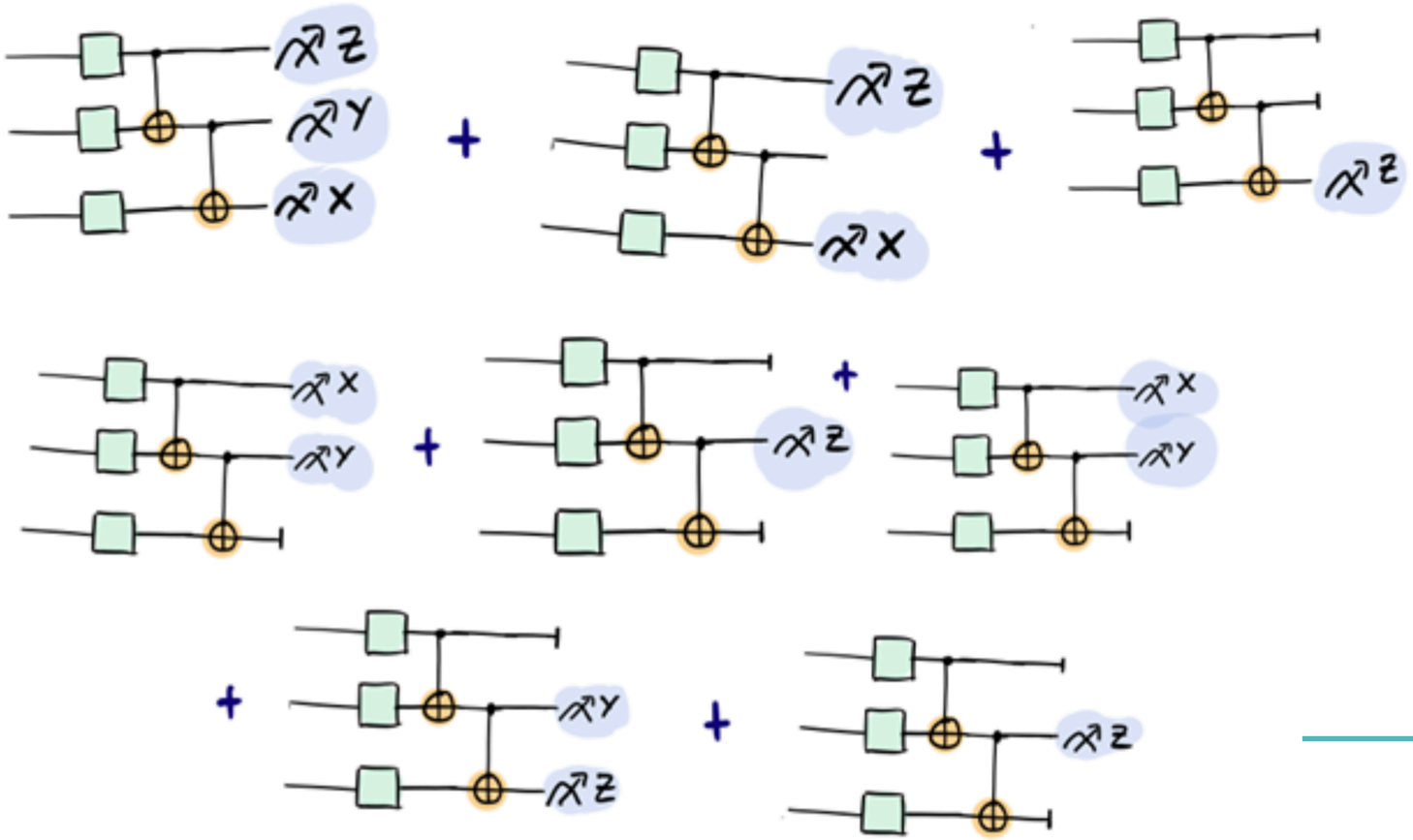


$$\langle \Psi | \hat{H}_e | \Psi \rangle = \sum_k c_k \langle \Psi | P_k | \Psi \rangle$$

Every Pauli string evaluated independently through repeated measurements

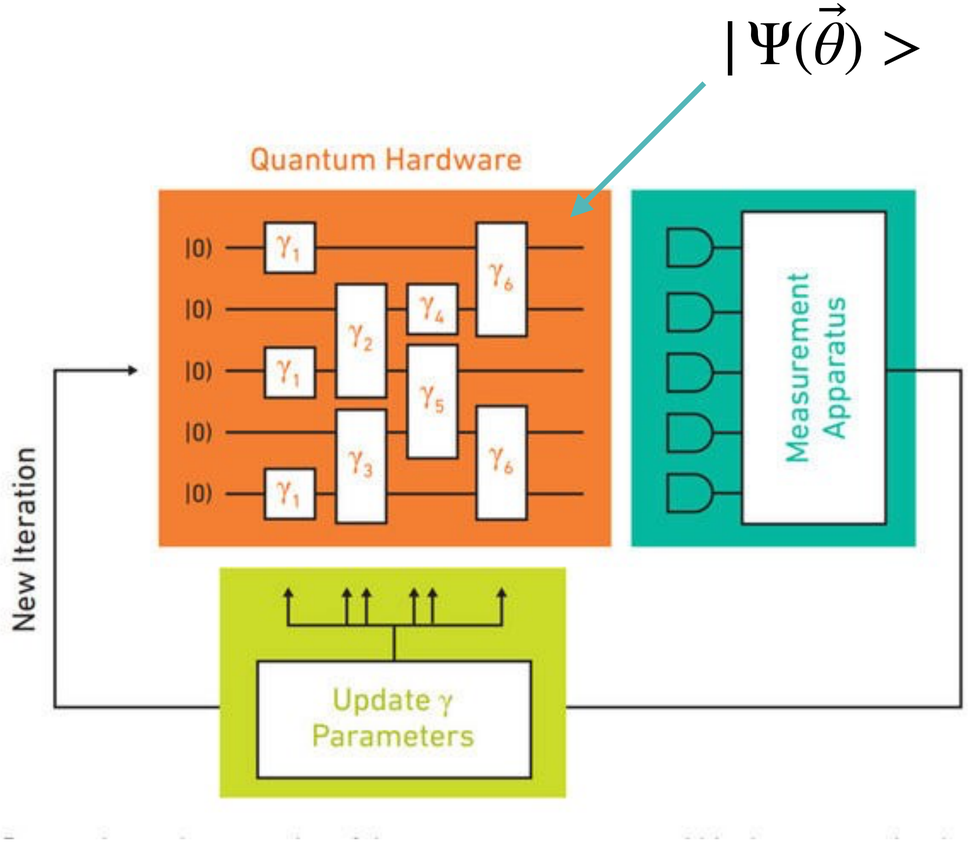
Repeat each many times to estimate the mean $\langle \Psi | P_k | \Psi \rangle$

Solving the problem?

The Variational Quantum Eigensolver

Sounds good, BUT

- How do we know the ansatz contains the ground state?
- How do we find the corresponding parameters?
- How efficient is the whole approach?
- What about the noise?



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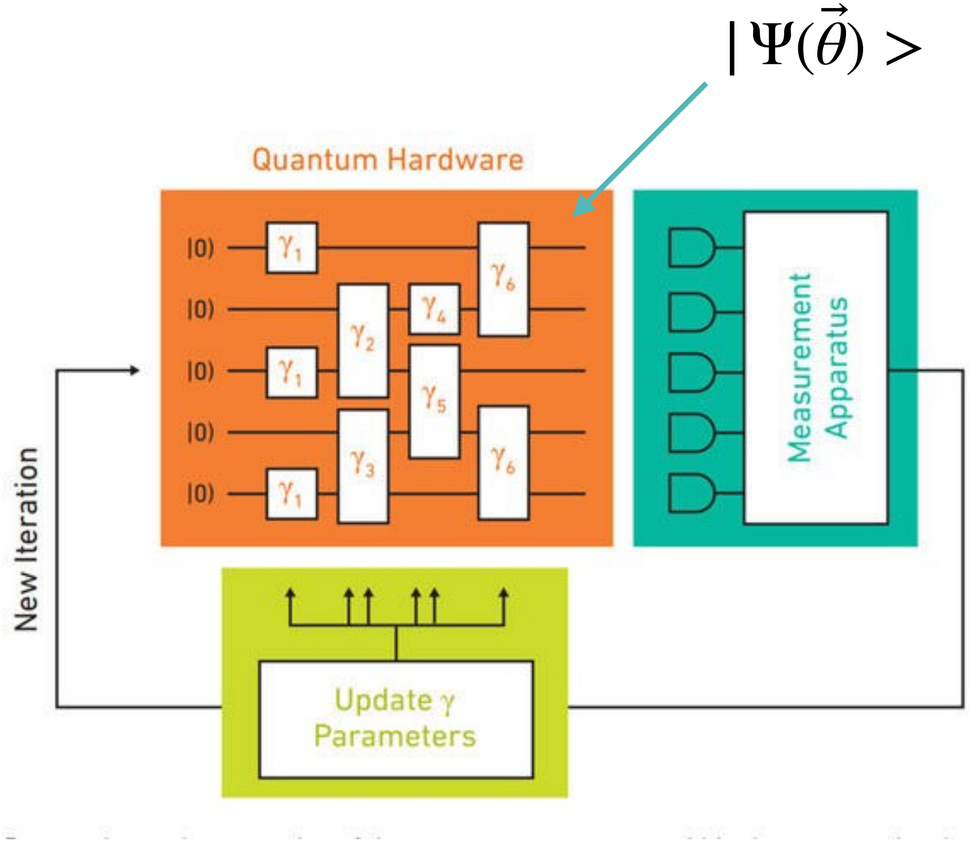
The Variational Quantum Eigensolver

- There are mainly two broad strategies in circuit ansatz design
  - physically motivated ansätze
  - hardware heuristic ansätze
    —> parametrized circuits comprising single-qubit rotations and entangling blocks chosen to take advantage of specific quantum hardware capabilities



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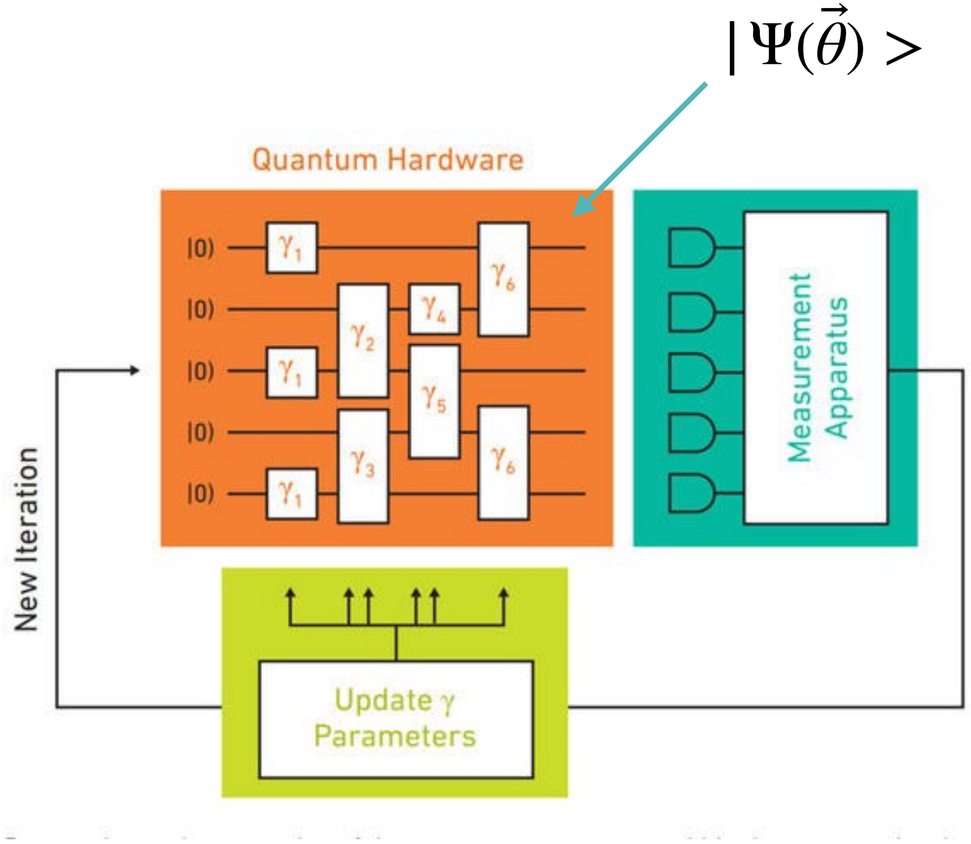

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The Variational Quantum Eigensolver
UCCSD ansatz

- UCCSD ansatz has the form

$$\left|\Psi_{\text{UCCSD}}\right\rangle = e^{\hat{T}_1+\hat{T}_2}\left|\Psi_{\text{ref}}\right\rangle \quad \text{with}$$

$$\hat{T}_1 = \sum_{i,a} \hat{\tau}_i^a = \sum_{i,a} \tau_i^a (a_a^\dagger a_i - a_i^\dagger a_a)$$

$$\hat{T}_2 = \sum_{i,j,a,b} \hat{\tau}_{ij}^{ab} = \sum_{i,j,a,b} \tau_{ij}^{ab} (a_a^\dagger a_b^\dagger a_i a_j - a_j^\dagger a_i^\dagger a_b a_a)$$

- Commonly approximation: Trotterize unitary to first order

$$\left|\Psi_{\text{tUCCSD}}\right\rangle = \prod_{c\in\{ia\}} e^{\hat{\tau}_c} \prod_{d\in\{ijab\}} e^{\hat{\tau}_d}\left|\Psi_{\text{ref}}\right\rangle$$

—> Low-order trotterized form may fail to reach chemical accuracy

—> Large number of exponential factors prohibits preparation on quantum processors

The Variational Quantum Eigensolver

ADAPT-VQE ansatz

- The ADAPT-VQE algorithm grows ansätze by appending one unitary at a time to a trial state

- Requires to

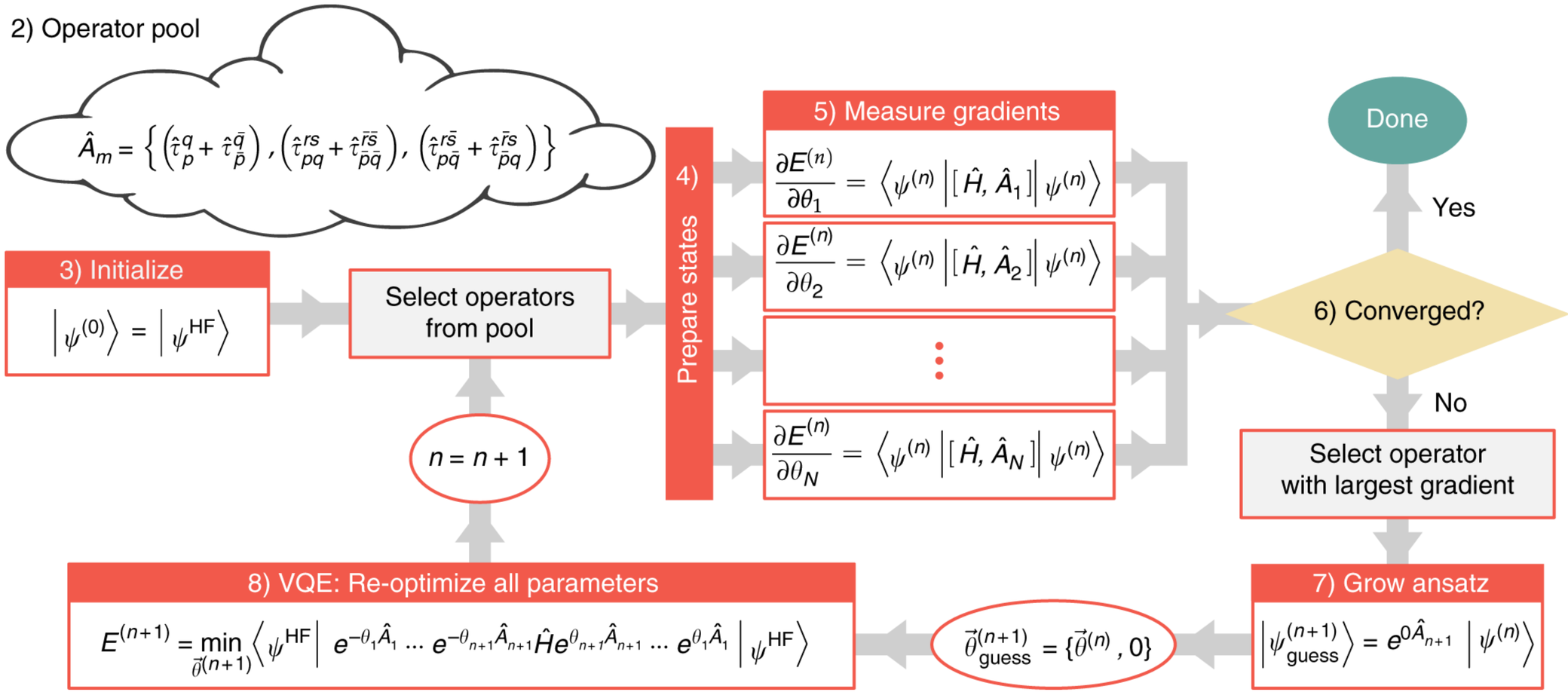
  - a priori define an operator pool $\mathscr{P} = \{P_i\}$, a collection of antihermitian generators —> $\hat{\tau}_i^a$ and $\hat{\tau}_{ij}^{ab}$ in UCCSD

  - choose a reference state calculate (HF or anything reasonable)

$$\left.\frac{\partial E}{\partial \theta_i}\right|_{\theta_i=0} = \left[\frac{\partial}{\partial \theta_i}\left\langle \Psi^{(k)}\right| e^{-\theta_i P_i} H e^{\theta_i P_i}\left|\Psi^{(k)}\right\rangle\right]\Bigg|_{\theta_i=0} = \left\langle \Psi^{(k)}\right|[H, P_i]\left|\Psi^{(k)}\right\rangle$$

- The operator with the largest gradient norm is appended to the ansatz

Choosing an ansatz - ADAPT-VQE

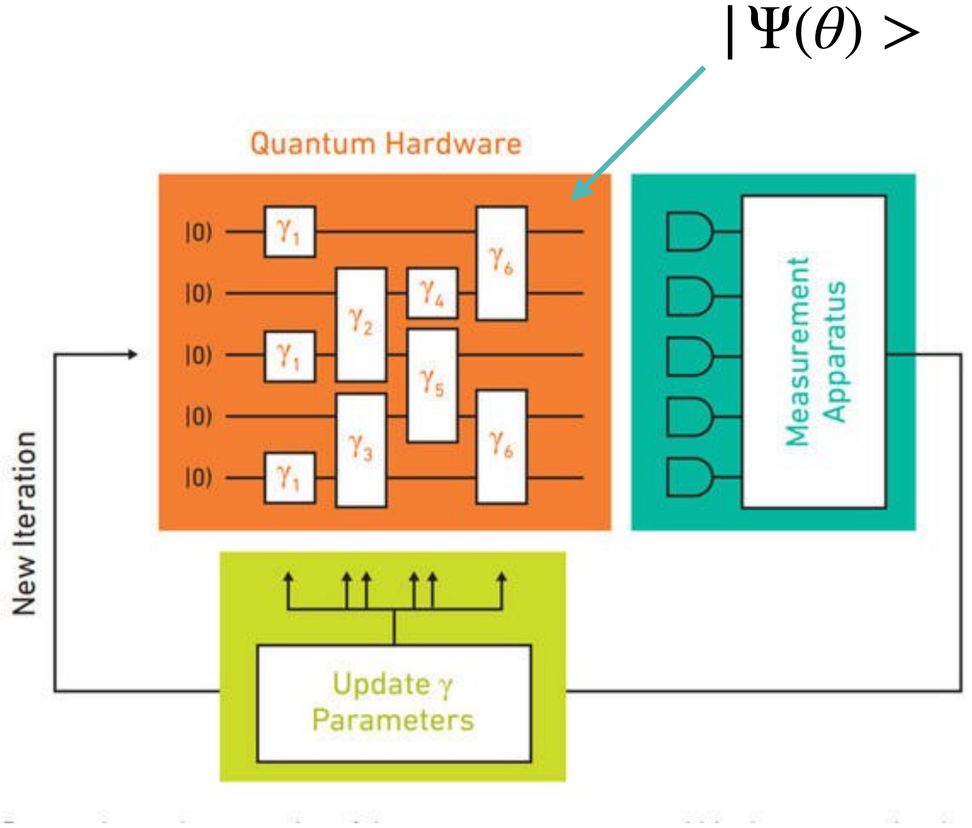


Nat. Comm., 10, 3007 (2019)

Solving the problem?
The Variational Quantum Eigensolver

Sounds good, BUT

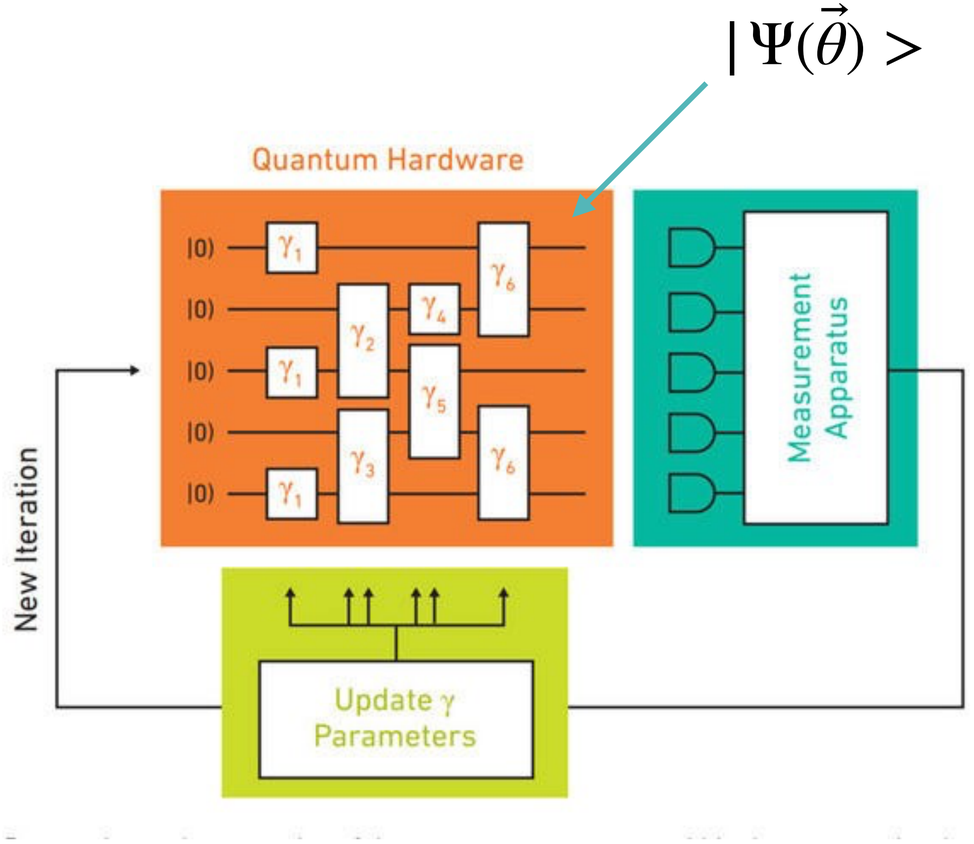
- How do we know the ansatz contains the ground state?
- How do we find the corresponding parameters?
- How efficient is the whole approach?
- What about the noise?



$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \right| \hat{H}_e \left| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$

Solving the problem?

The Variational Quantum Eigensolver



Identifying challenges towards practical quantum advantage through resource estimation: the measurement roadblock in the variational quantum eigensolver

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Molecule	H_2O	CO_2	CH_4	CH_4O	C_2H_6	C_2H_4	C_2H_2	C_2H_6O	C_3H_8	C_3H_6	C_3H_4
N_{el}	8	16	8	14	14	12	10	20	20	18	16
N_q	104	208	104	182	182	156	130	260	260	234	208
$K \cdot 10^{-3}$	1.9	16	1.6	8.4	8.5	6.6	3.1	24	16	23	18
$M \cdot 10^{-9}$	3.9	32	3.2	17	17	13	6.2	48	31	46	36
t (days)	2.3	39	1.9	18	18	12	4.6	71	47	62	44

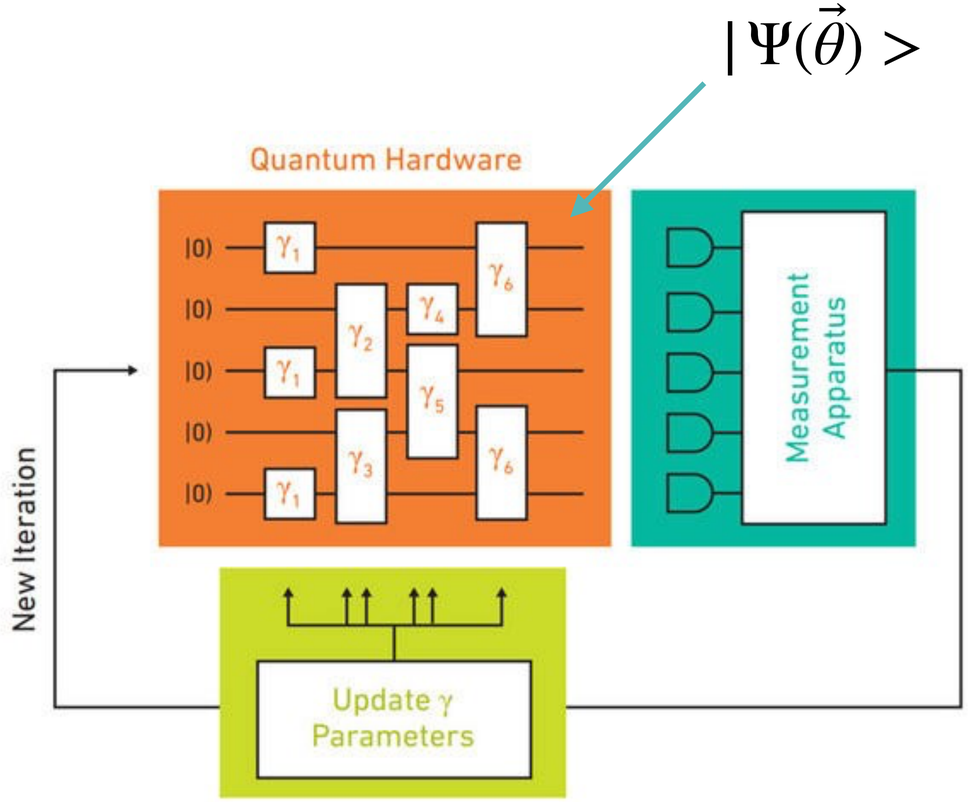
TABLE IV. Estimated runtimes t in days for a single energy evaluation using the number of measurements M from extrapolated

arXiv: 2012.04001

$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \middle| \hat{H}_e \middle| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$

Solving the problem?

The Variational Quantum Eigensolver



- How do we know the ansatz contains the ground state?
- How do we find the corresponding parameters?
- How efficient is the whole approach?
- What about the noise?

$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \middle| \hat{H}_e \middle| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$

Efficient measurement strategies are required!

Noise mitigation is crucial!

Molecular properties / Dynamical correlation

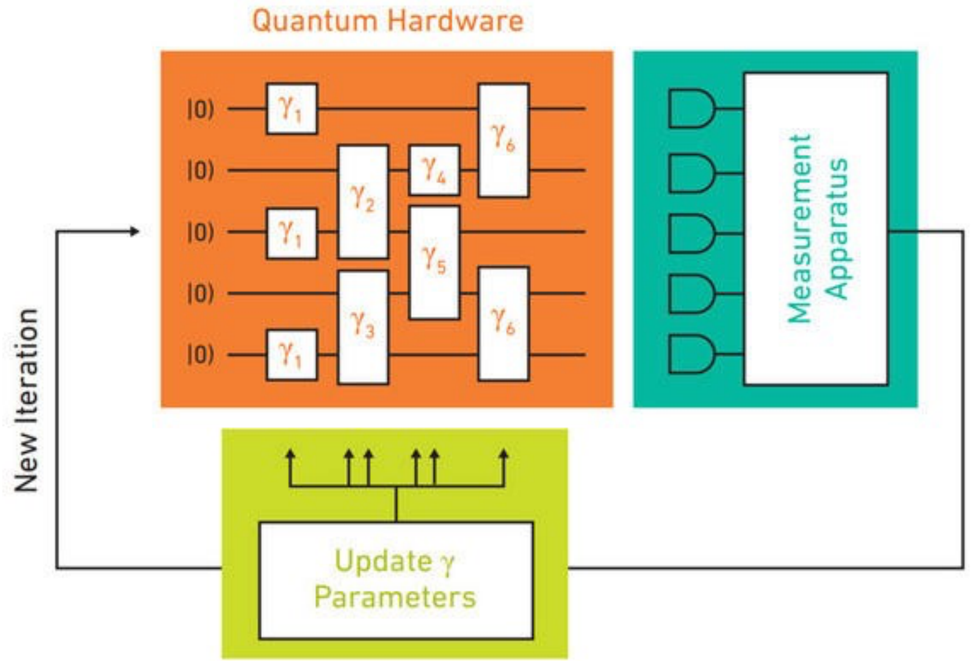
The Variational Quantum Eigensolver

- Expectation values of one-electron $\hat{O}_1$ and two-electron $\hat{O}_2$ operators can be straightforward obtained from optimal VQE

$$\left\langle \hat{O}_1 \right\rangle = \sum_{pq} o_{pq} \left\langle \hat{a}_p^\dagger \hat{a}_q \right\rangle$$

$$\left\langle \hat{O}_2 \right\rangle = \sum_{pqrs} o_{pqrs} \left\langle \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \right\rangle$$

- Higher-order RDMs …
  —> CASPT2/NEVPT2, response theory, …
- *quantum* equation-of-motion …
- …



$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \middle| \hat{H}_e \middle| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$

CONCLUSION

Quantum computers without algorithms are useless machines

With proper algorithms we can make quantum computers work

We need to know how to measure

We need to mitigate errors and correct for them