

Multiconfigurational methods: past, present and the road ahead

Stefan Knecht

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

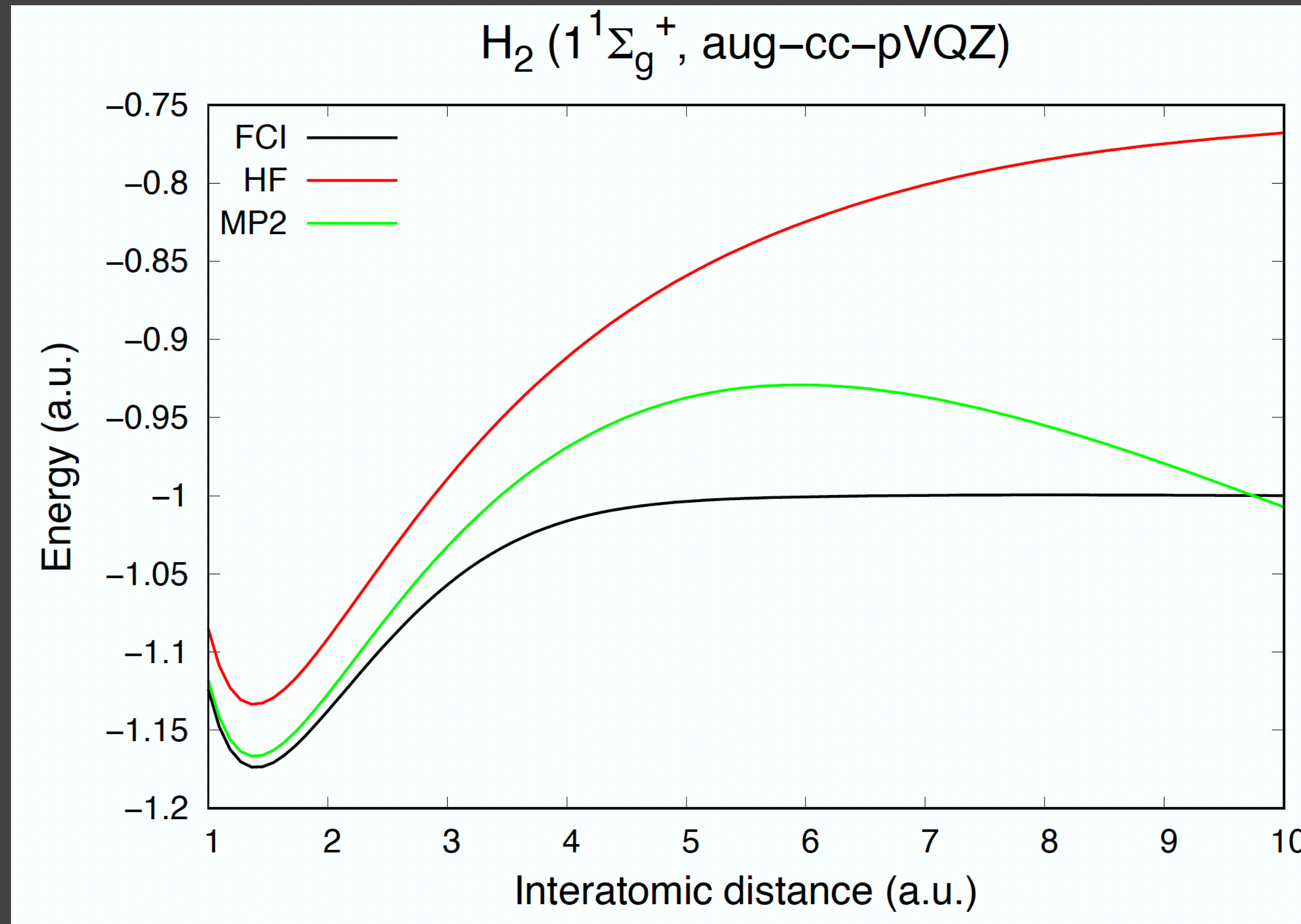
Road ahead: Beyond “classical quantum chemistry”

- Quantum Chemistry on Quantum Computers

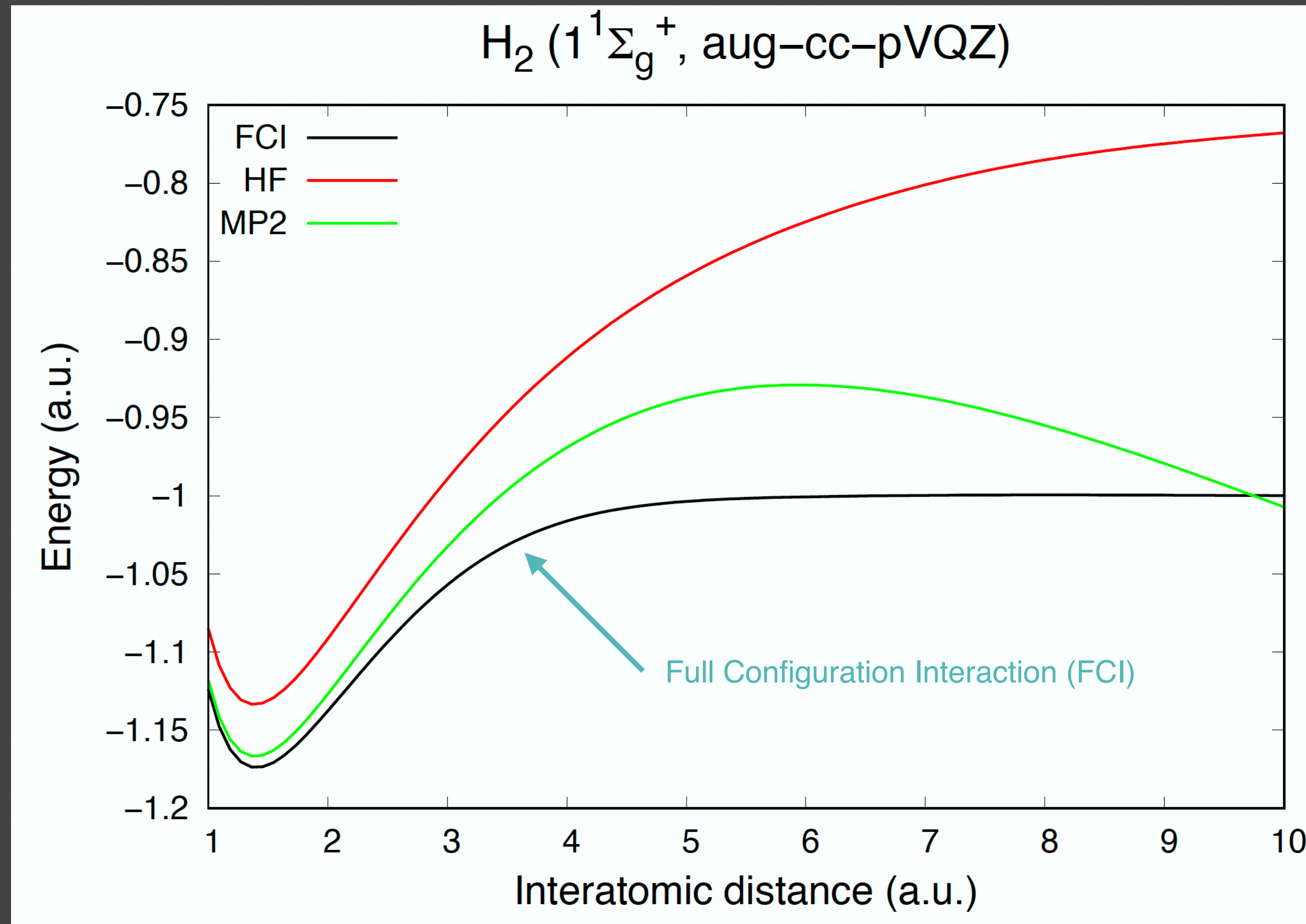
Concepts

First example: Things to learn
from H_2 ...

Potential energy curve of H₂



Potential energy curve of H₂



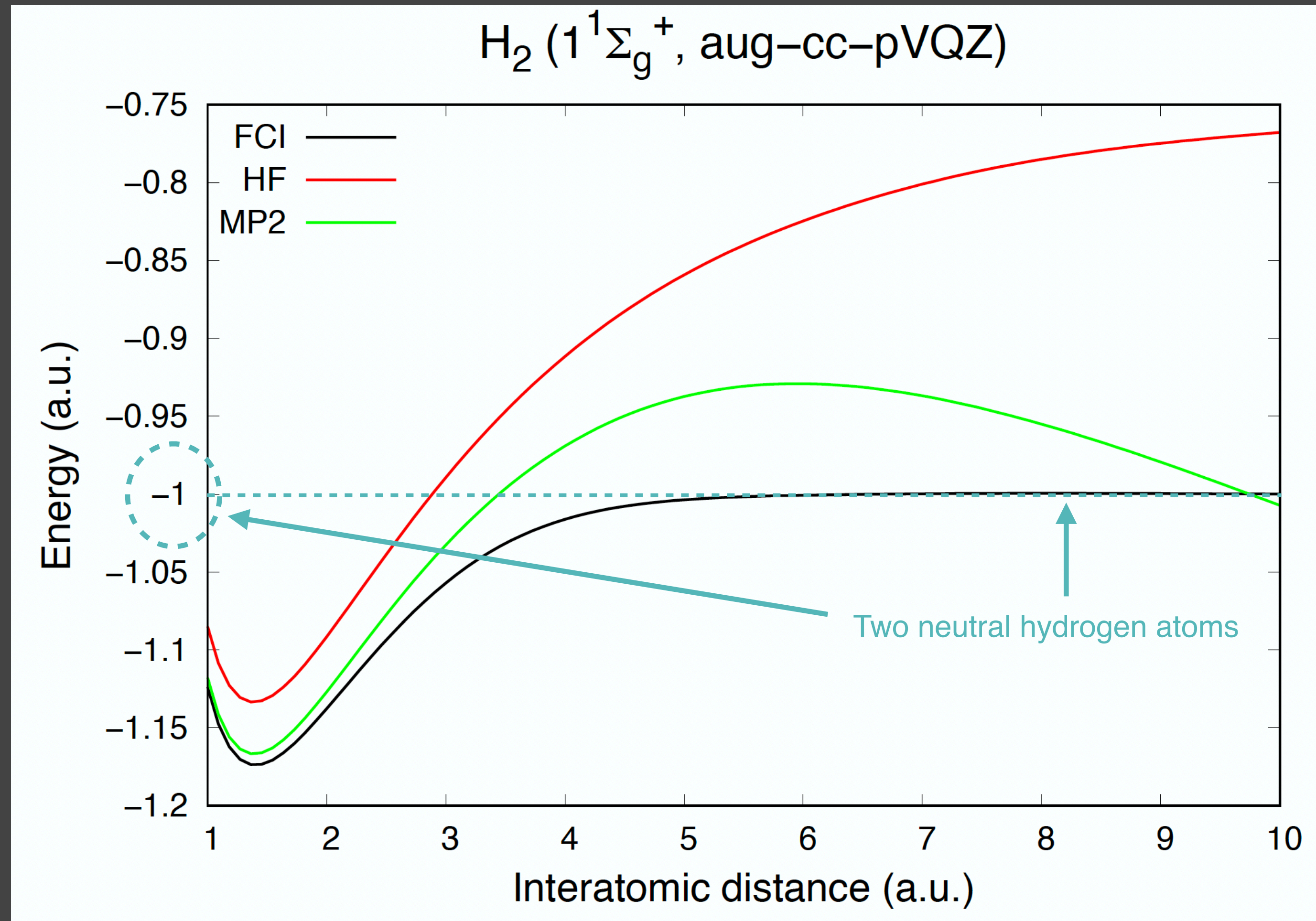
A quick reminder on CI

- Expand wave function as a linear combination of Slater determinants

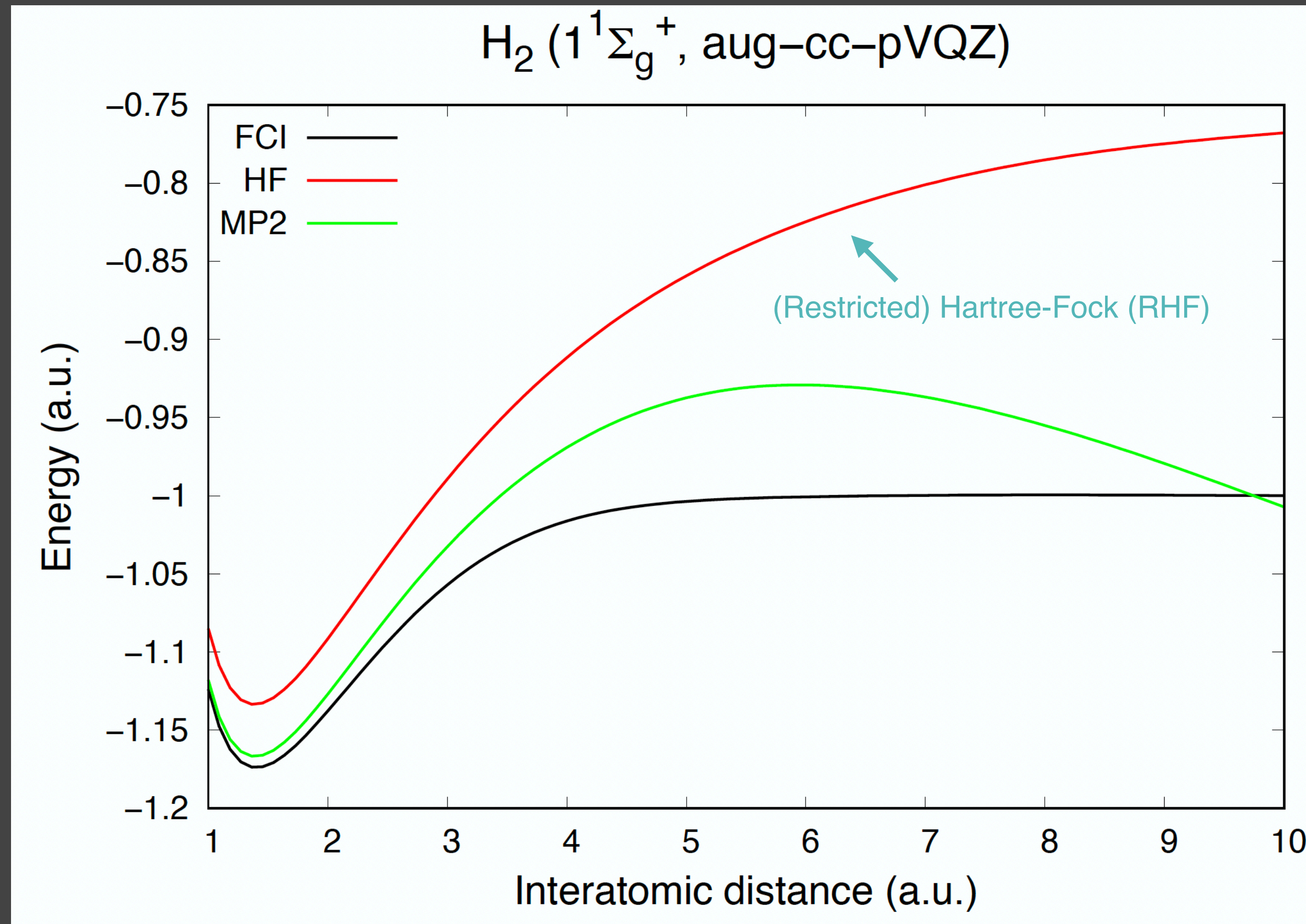
$$|\Psi\rangle = \sum_{\zeta} c_{\zeta} |\Phi_{\zeta}\rangle$$

- Orbital coefficients are fixed
- The parameters c_{ζ} are chosen to minimise the energy
- Leads to eigenvalue problem $Hc = Ec$ with $H_{\zeta\eta} = \langle \Phi_{\zeta} | \hat{H} | \Phi_{\eta} \rangle$
- If all determinants $\{\Phi\}$ of a given basis are included, we solve the Schrödinger equation projected onto the basis \rightarrow full CI (FCI)

Potential energy curve of H₂



Potential energy curve of H₂



A quick reminder on (R)HF

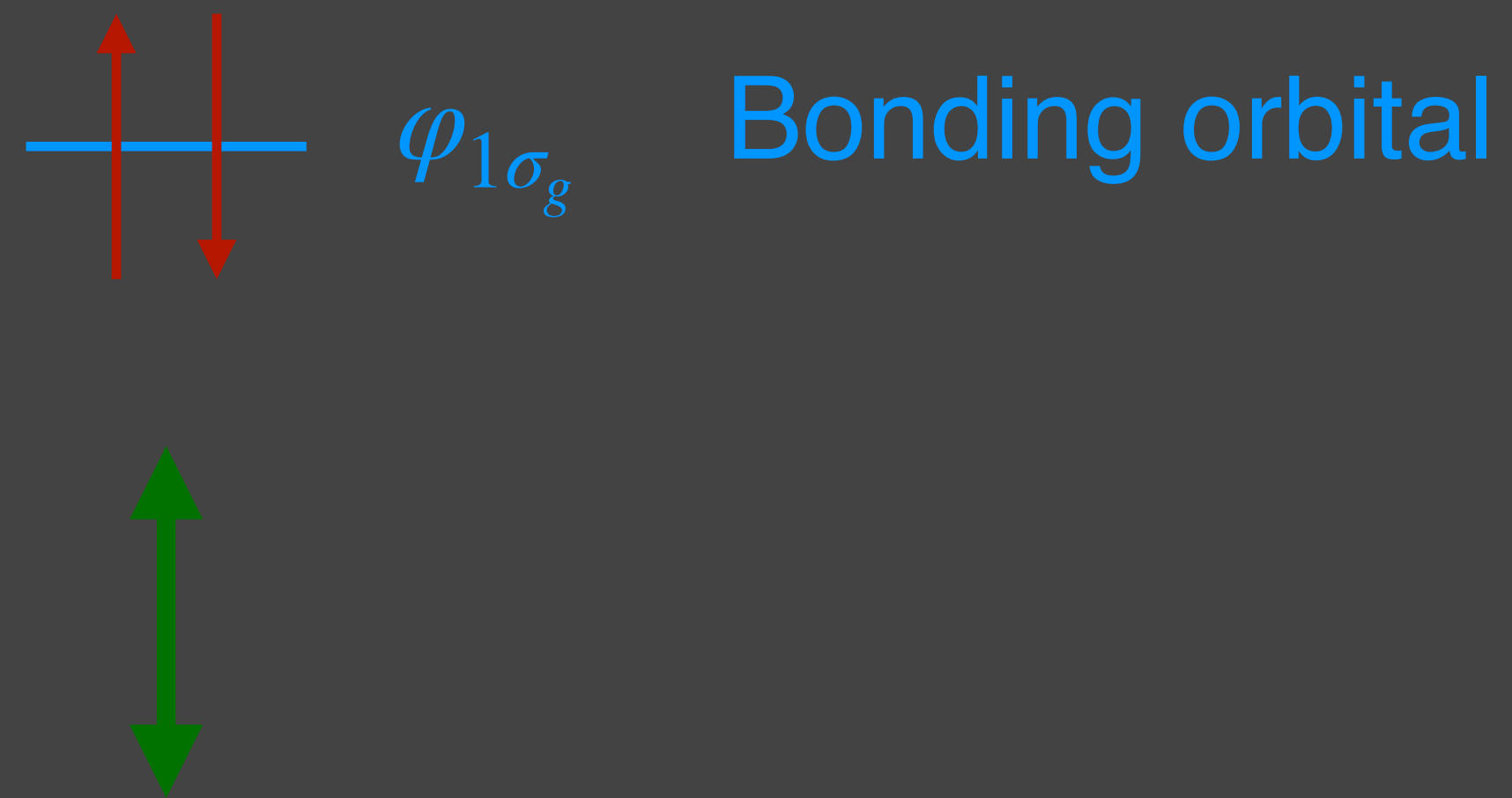
- Minimize the energy of one Slater determinant or a symmetry/spin-defined combination of Slater determinants
- Individual unoccupied orbitals have a limited meaning (HOMO/LUMO \rightarrow Koopman's theorem)

(R)HF wave function of H₂



$$\begin{aligned}\Phi^{RHF}(x_1, x_2) &= \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_g, \alpha}(x_1) \varphi_{1\sigma_g, \beta}(x_2) - \varphi_{1\sigma_g, \alpha}(x_2) \varphi_{1\sigma_g, \beta}(x_1) \right) \\ &= \varphi_{1\sigma_g}(\mathbf{r}_1) \varphi_{1\sigma_g}(\mathbf{r}_2) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_1 \alpha} \delta_{\sigma_2 \beta} - \delta_{\sigma_2 \alpha} \delta_{\sigma_1 \beta} \right)\end{aligned}$$

(R)HF wave function of H₂



$$\begin{aligned}\Phi^{RHF}(x_1, x_2) &= \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_g, \alpha}(x_1) \varphi_{1\sigma_g, \beta}(x_2) - \varphi_{1\sigma_g, \alpha}(x_2) \varphi_{1\sigma_g, \beta}(x_1) \right) \\ &= \boxed{\varphi_{1\sigma_g}(r_1) \varphi_{1\sigma_g}(r_2)} \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_1 \alpha} \delta_{\sigma_2 \beta} - \delta_{\sigma_2 \alpha} \delta_{\sigma_1 \beta} \right)\end{aligned}$$

(R)HF wave function of stretched H₂ in a minimal basis



Bonding orbital

$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}} (s_A(\mathbf{r}) + s_B(\mathbf{r}))$$

$$= \varphi_{1\sigma_g}(\mathbf{r}_1) \varphi_{1\sigma_g}(\mathbf{r}_2) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_1\alpha} \delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha} \delta_{\sigma_1\beta} \right)$$

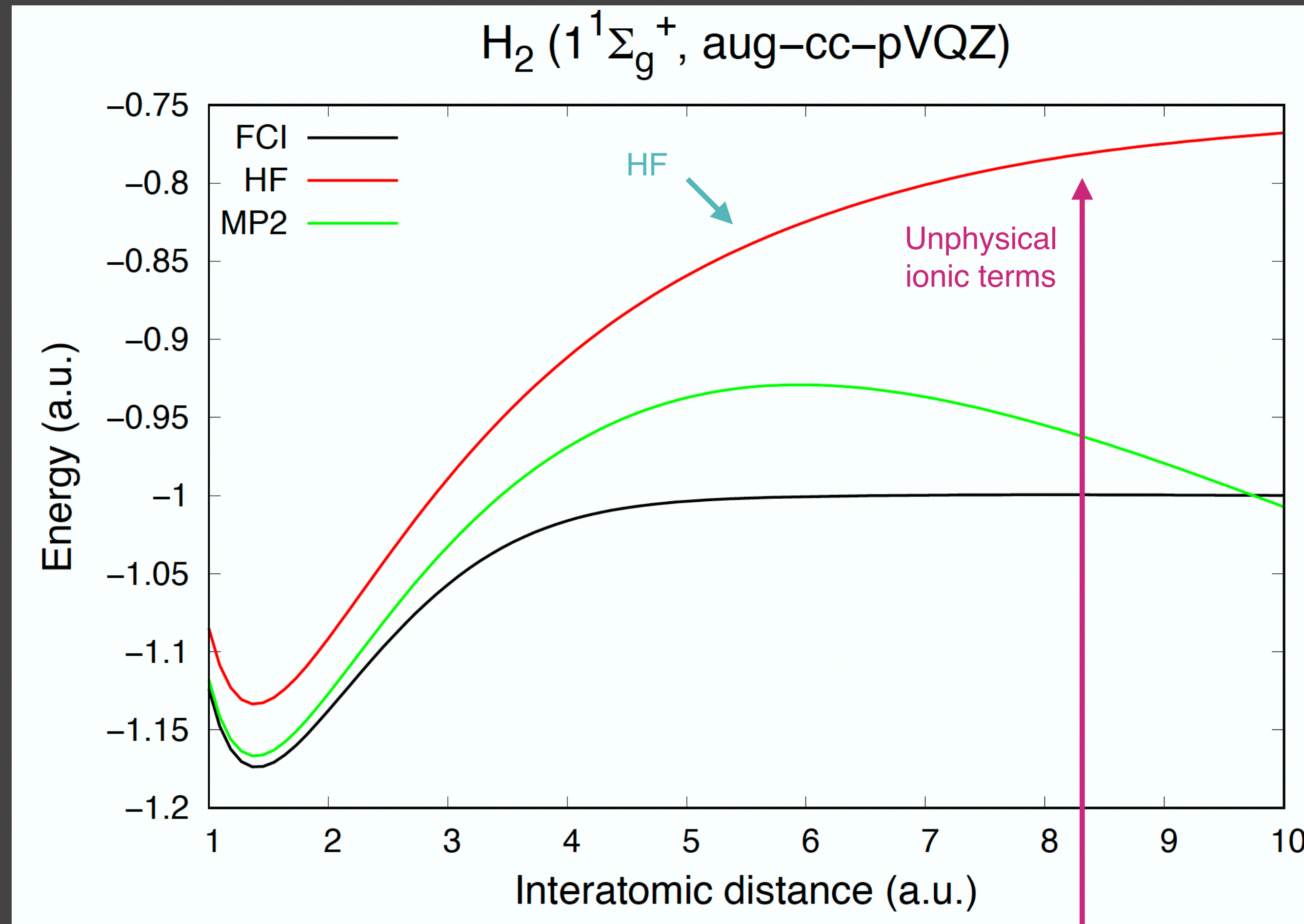
(R)HF wave function of stretched H₂ in a minimal basis



$$\frac{1}{2} (s_A(\mathbf{r}_1)s_B(\mathbf{r}_2) + s_A(\mathbf{r}_2)s_B(\mathbf{r}_1) + s_A(\mathbf{r}_1)s_A(\mathbf{r}_2) + s_B(\mathbf{r}_1)s_B(\mathbf{r}_2))$$

$$= \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) \times \frac{1}{\sqrt{2}} (\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta})$$

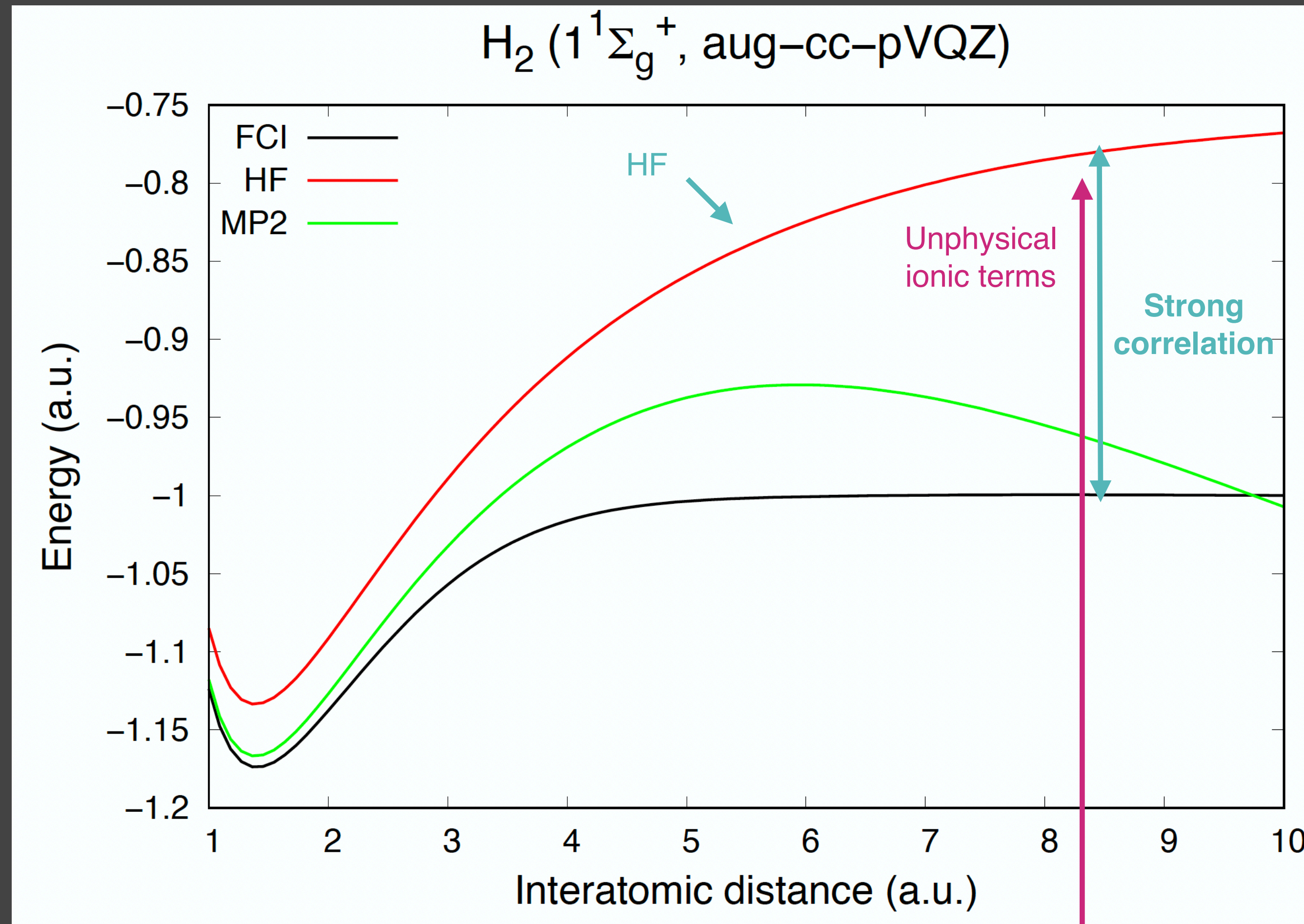
Potential energy curve of H₂



$$\frac{1}{2} \left(s_A(\mathbf{r}_1)s_B(\mathbf{r}_2) + s_A(\mathbf{r}_2)s_B(\mathbf{r}_1) + s_A(\mathbf{r}_1)s_A(\mathbf{r}_2) + s_B(\mathbf{r}_1)s_B(\mathbf{r}_2) \right)$$

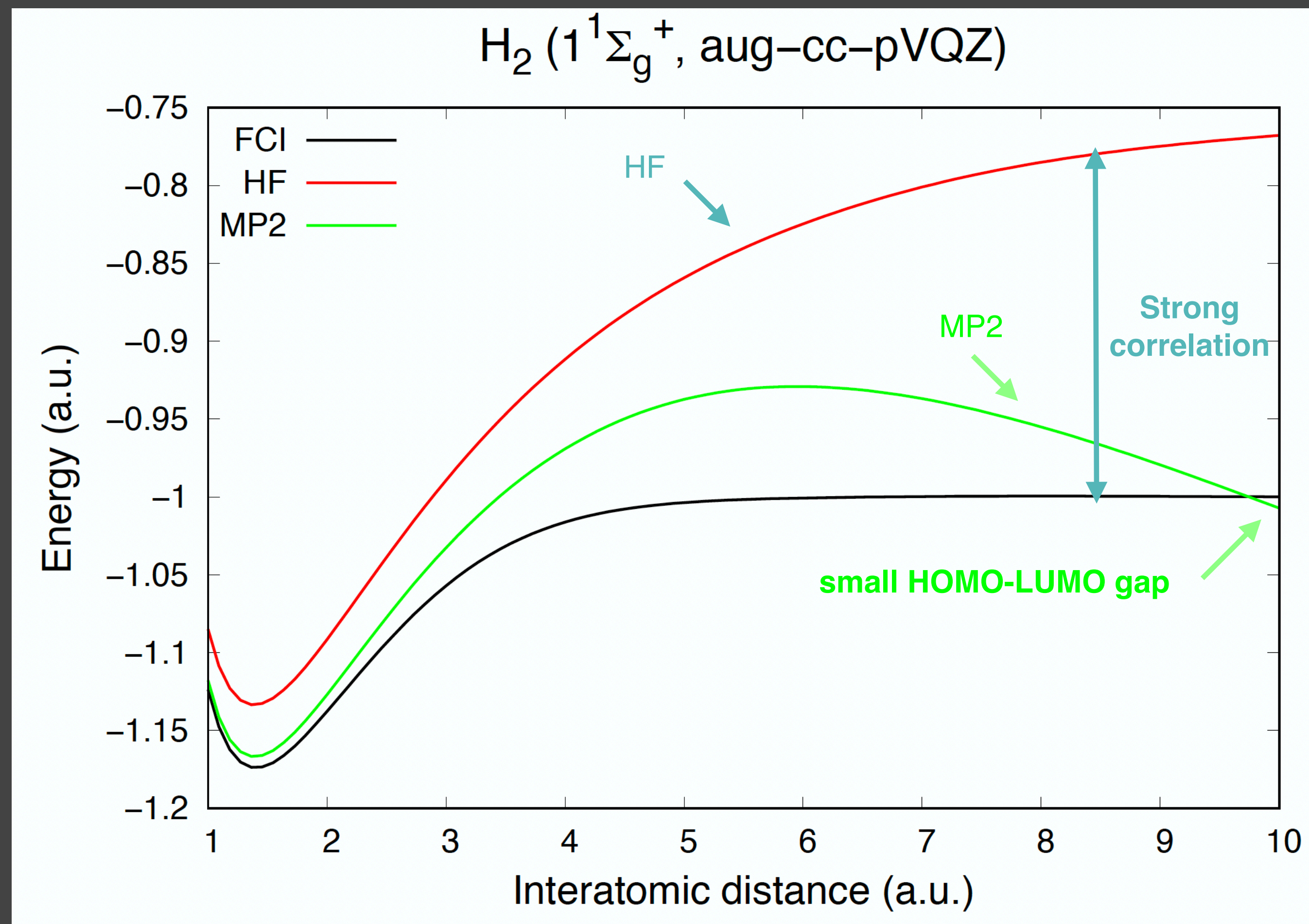
H⁻ ····· H⁺ H⁺ ····· H⁻

Potential energy curve of H₂

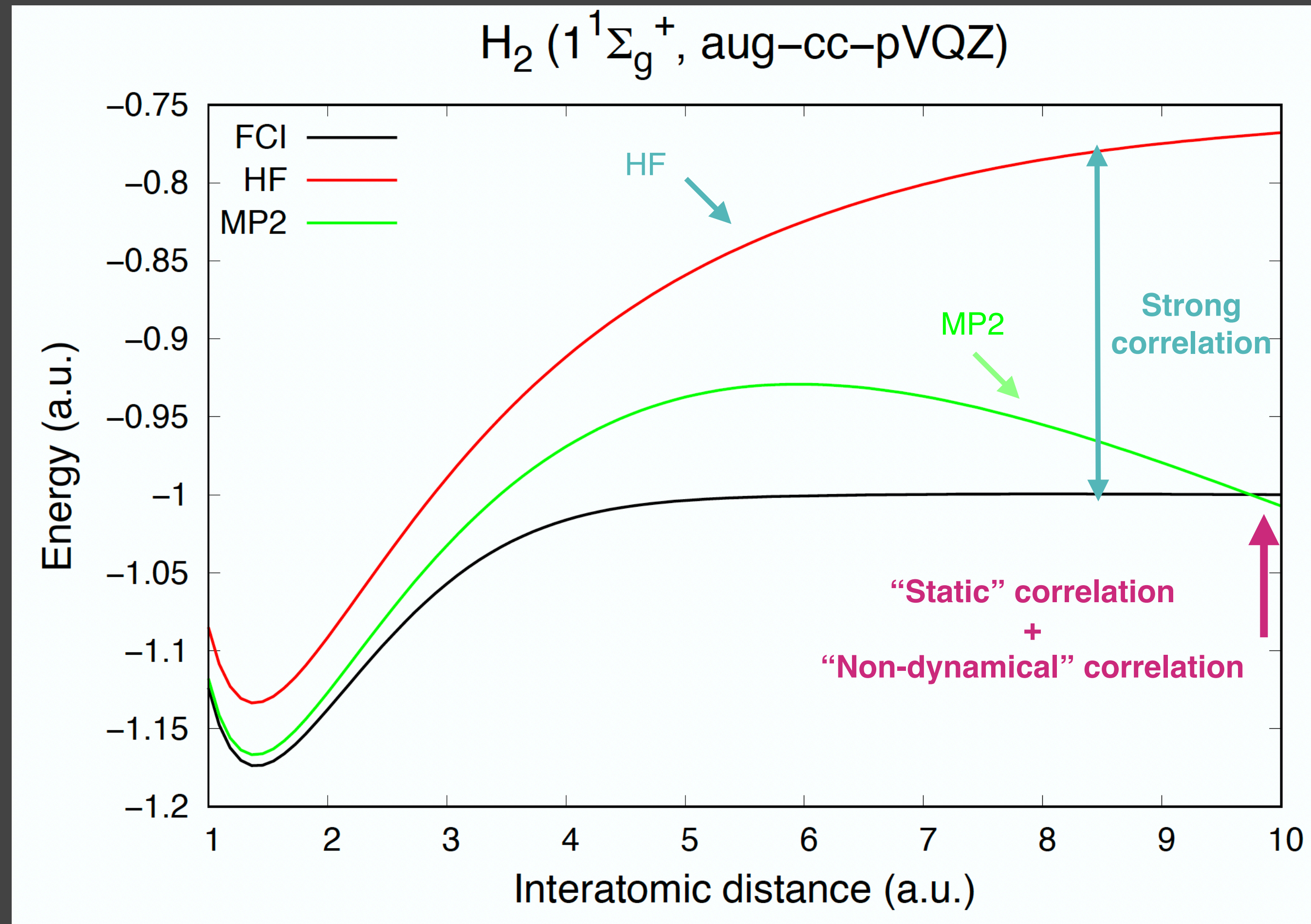


$$\frac{1}{2} \left(s_A(\mathbf{r}_1)s_B(\mathbf{r}_2) + s_A(\mathbf{r}_2)s_B(\mathbf{r}_1) + s_A(\mathbf{r}_1)s_A(\mathbf{r}_2) + s_B(\mathbf{r}_1)s_B(\mathbf{r}_2) \right)$$

Potential energy curve of H₂



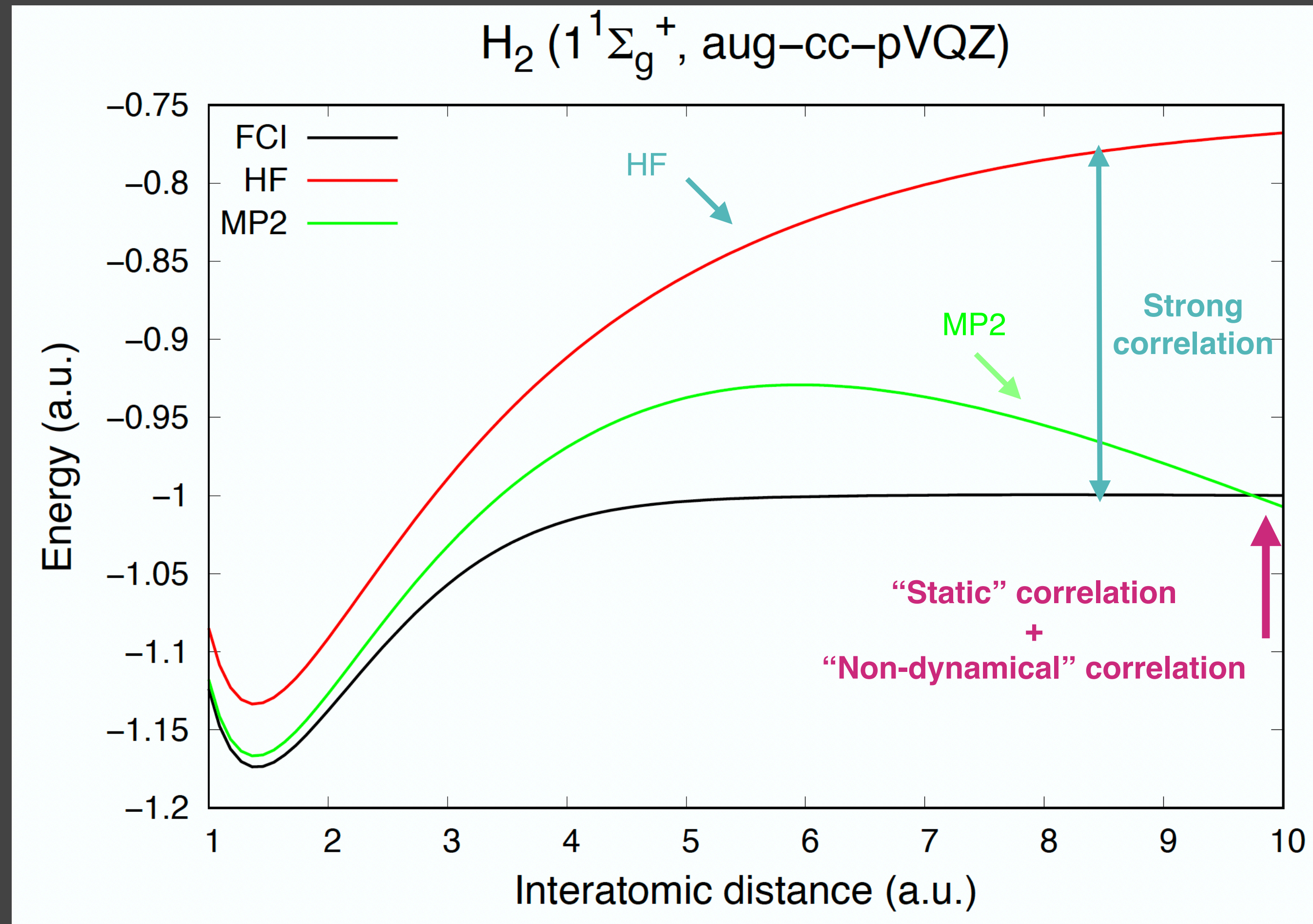
Potential energy curve of H₂



"Static" correlation
+
"Non-dynamical" correlation
=
Strong correlation

Near-degeneracies give rise to static correlation!

Potential energy curve of H₂



"Static" correlation
+
"Non-dynamical" correlation
=
Strong correlation

Near-degeneracies give rise to static correlation!

Better *ansatz*?

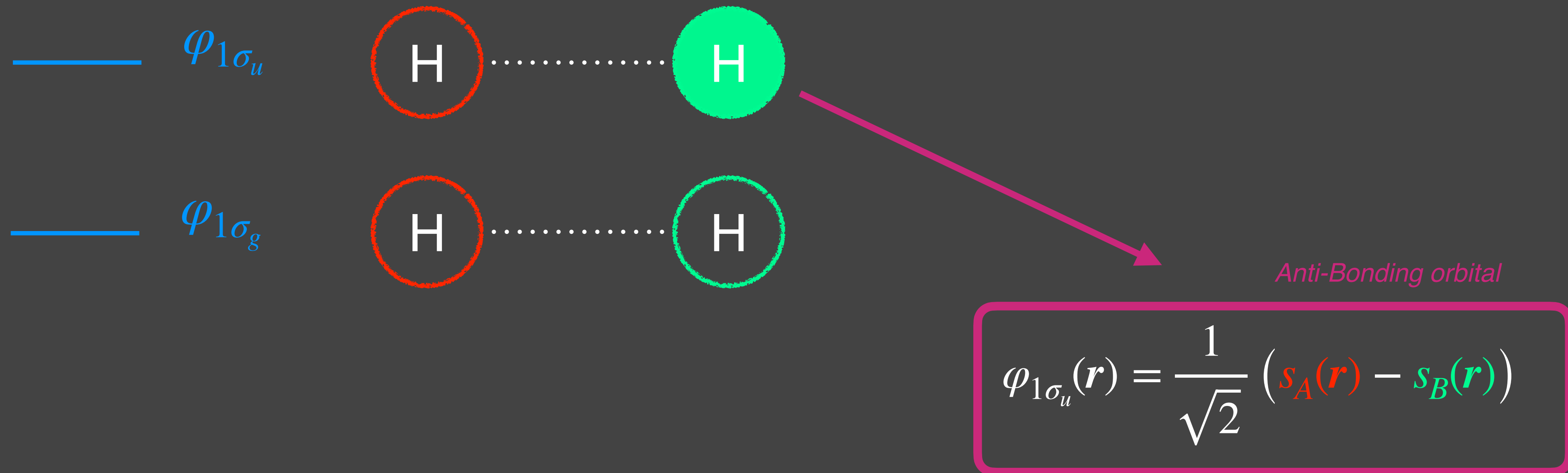
Multi-configurational wave function



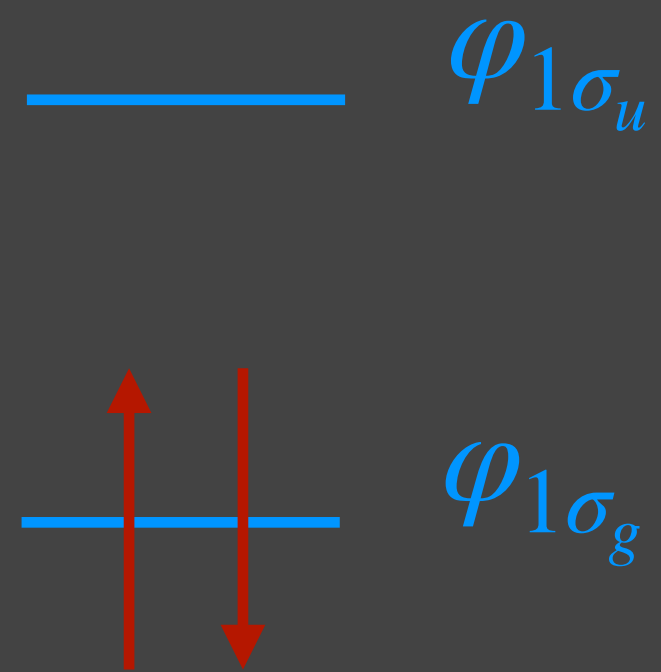
Bonding orbital

$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}} (s_A(\mathbf{r}) + s_B(\mathbf{r}))$$

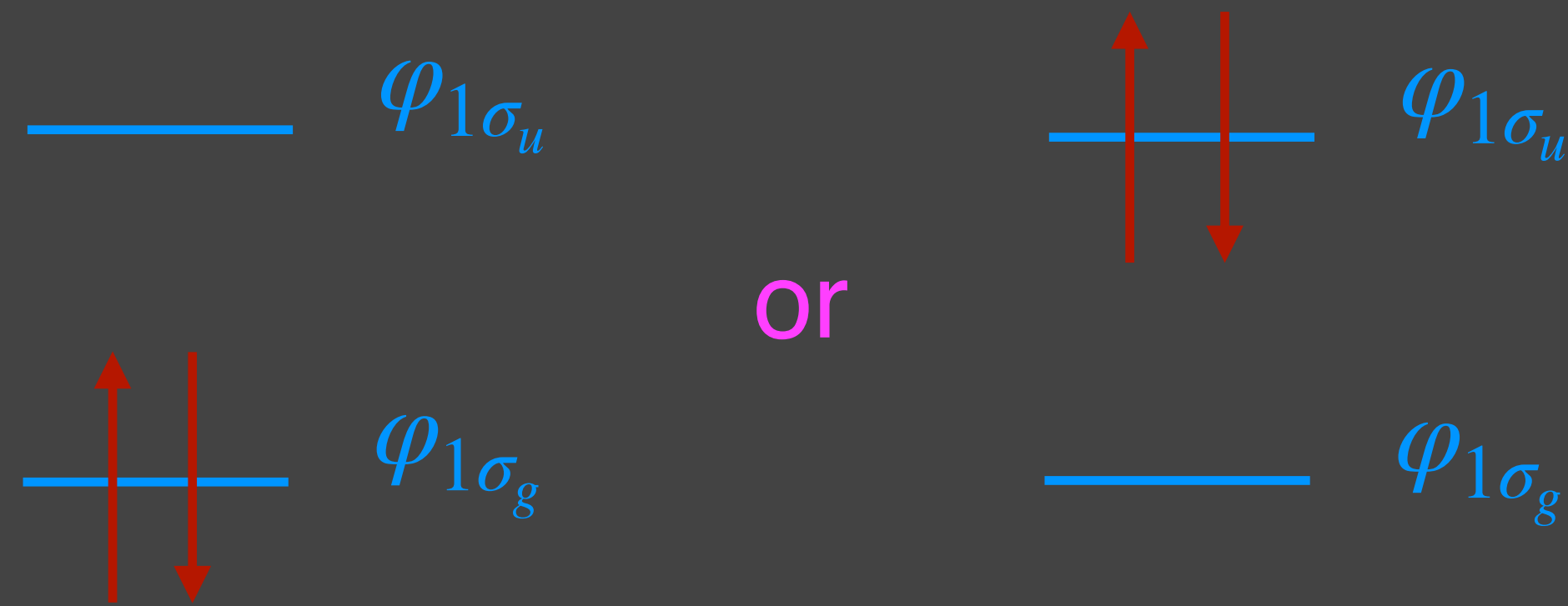
Multi-configurational wave function



Multi-configurational wave function



$$|\Psi\rangle = \left| (1\sigma_g)^2 \right\rangle$$



$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left[\left| (1\sigma_g)^2 \right\rangle - \left| (1\sigma_u)^2 \right\rangle \right]$$

$$\equiv \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2) \right)$$

Multi-configurational wave function

$$\varphi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}} (s_A(\mathbf{r}) - s_B(\mathbf{r}))$$

$$|\Psi\rangle \equiv \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2) \right)$$

$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}} (s_A(\mathbf{r}) + s_B(\mathbf{r}))$$

Multi-configurational wave function

$$\begin{aligned} |\Psi\rangle &\equiv \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2) \right) \\ &= \frac{1}{\sqrt{2}} \left(\underset{\text{H}\cdots\cdots\text{H}}{s_A(\mathbf{r}_1)s_B(\mathbf{r}_2)} + \underset{\text{H}\cdots\cdots\text{H}}{s_A(\mathbf{r}_2)s_B(\mathbf{r}_1)} \right) \end{aligned}$$

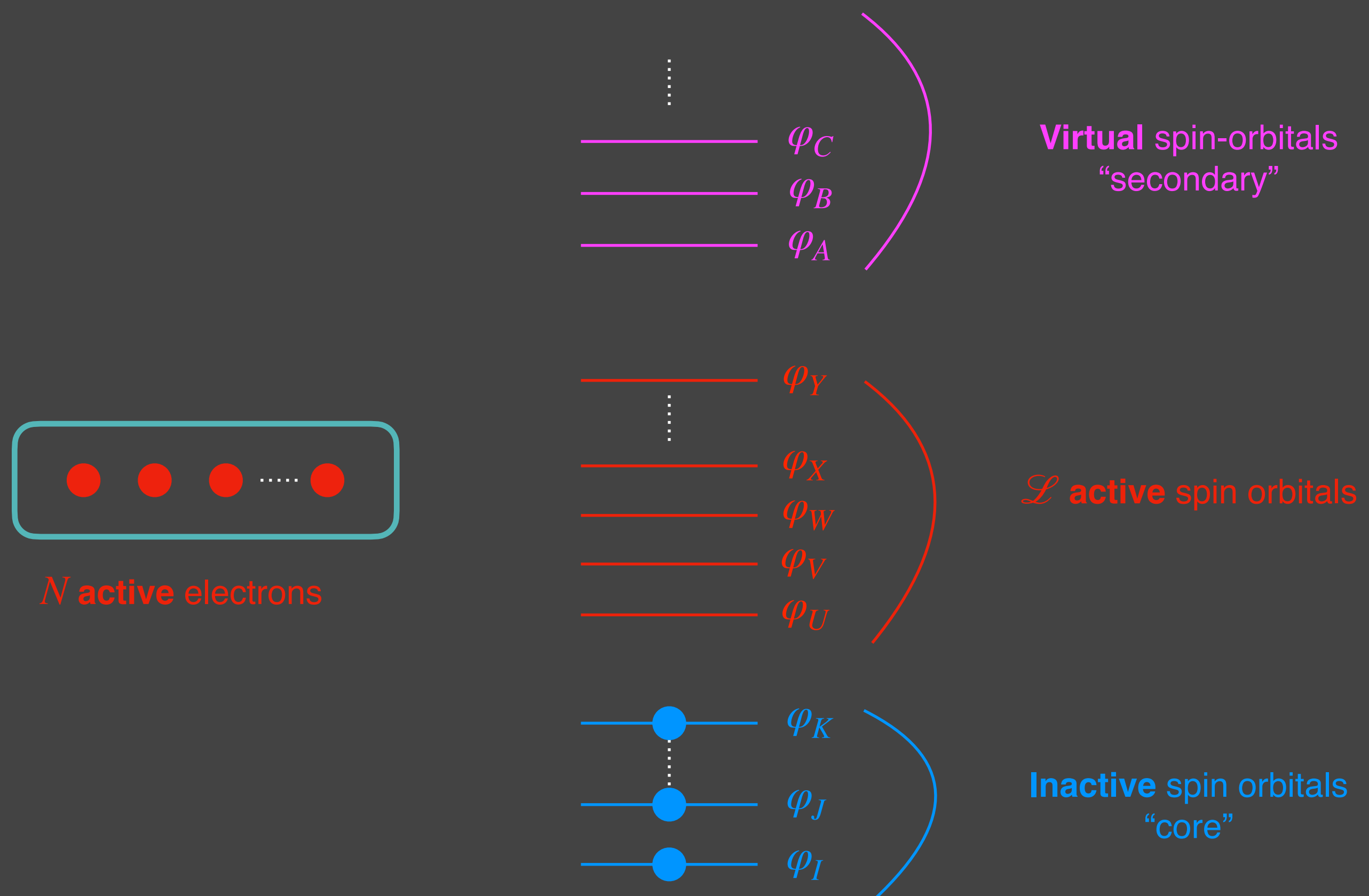
Multi-configurational wave function

$$|\Psi\rangle \equiv \frac{1}{\sqrt{2}} \left(\overbrace{\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)}^{\Phi_{(1\sigma_g)}^2} - \overbrace{\varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)}^{\Phi_{(1\sigma_u)}^2} \right)$$

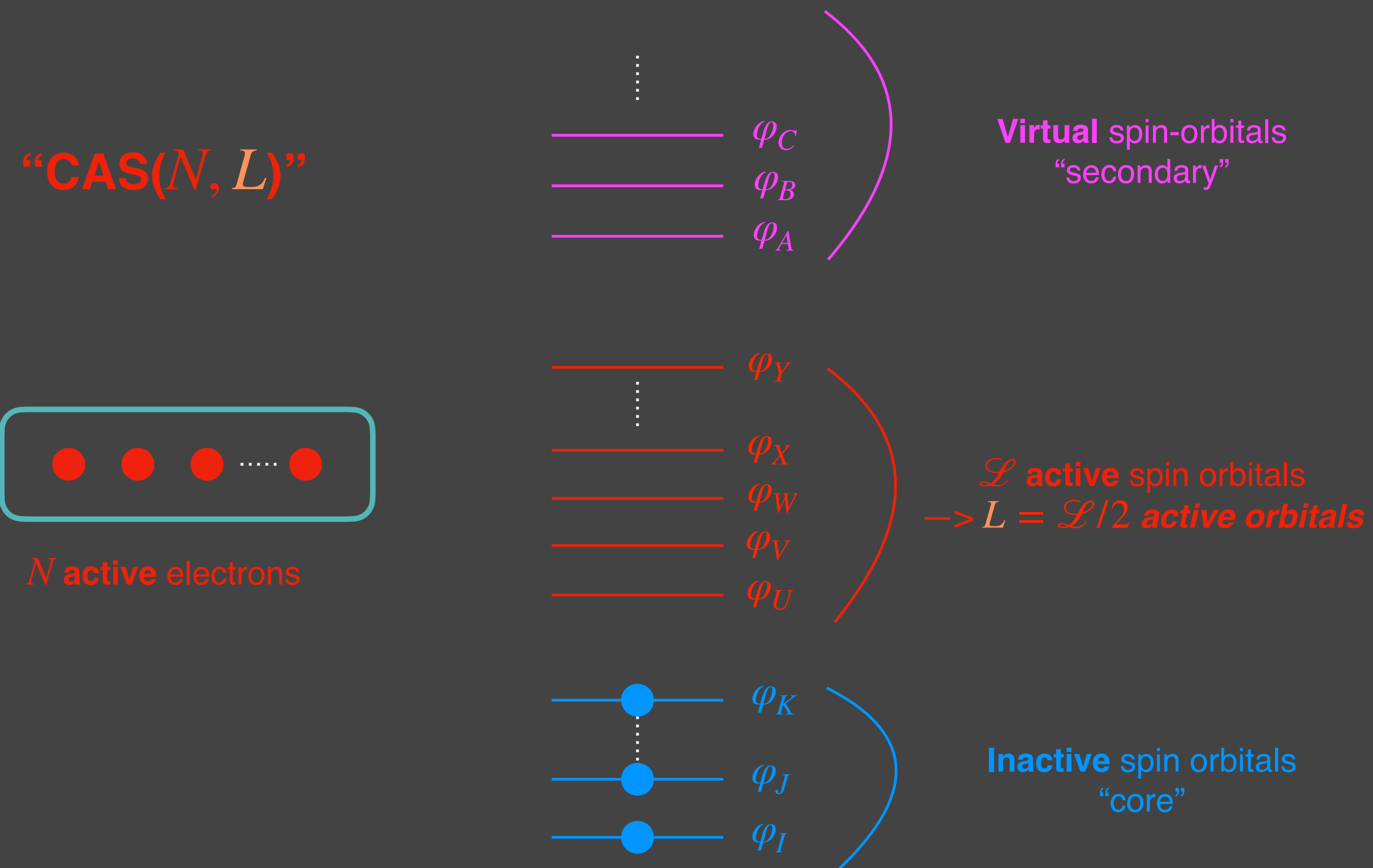
The Past ...



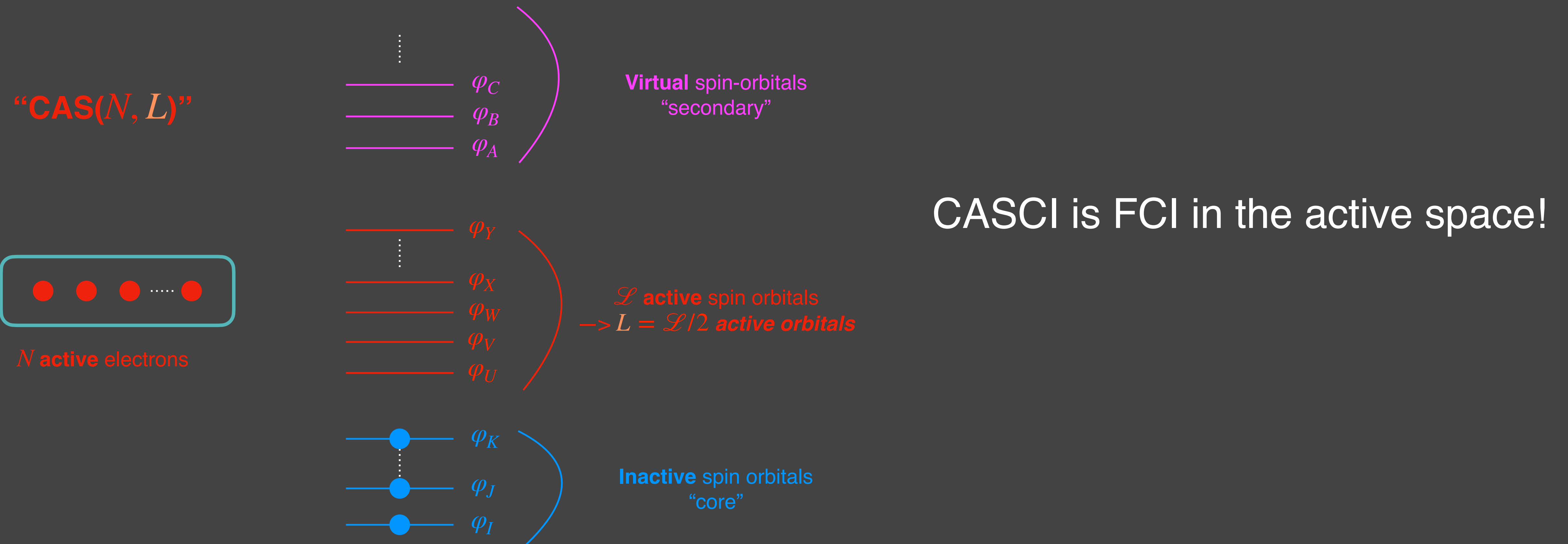
Complete Active Space CI (CASCI)



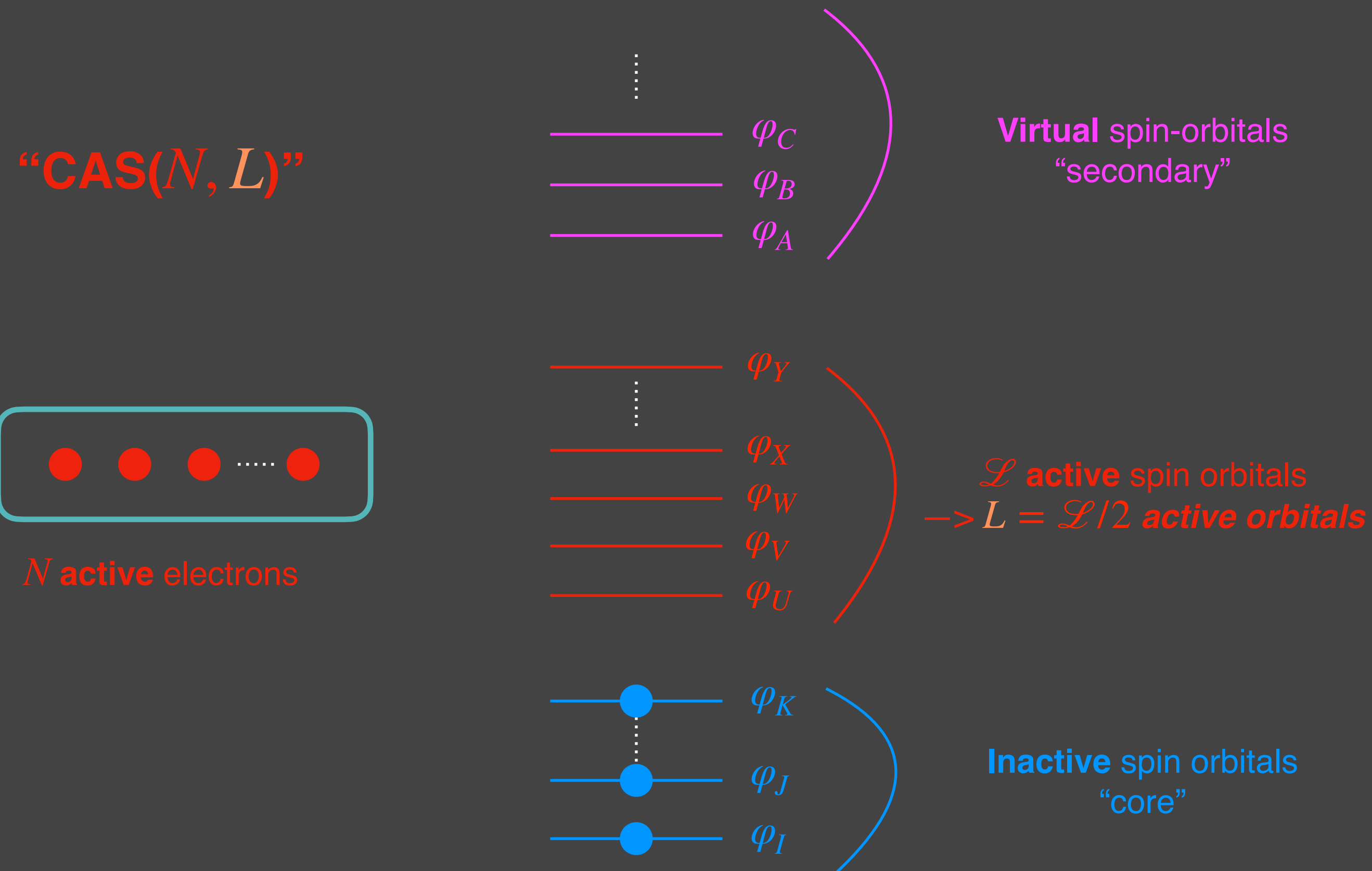
Complete Active Space CI (CASCI)



Complete Active Space CI (CASCI)



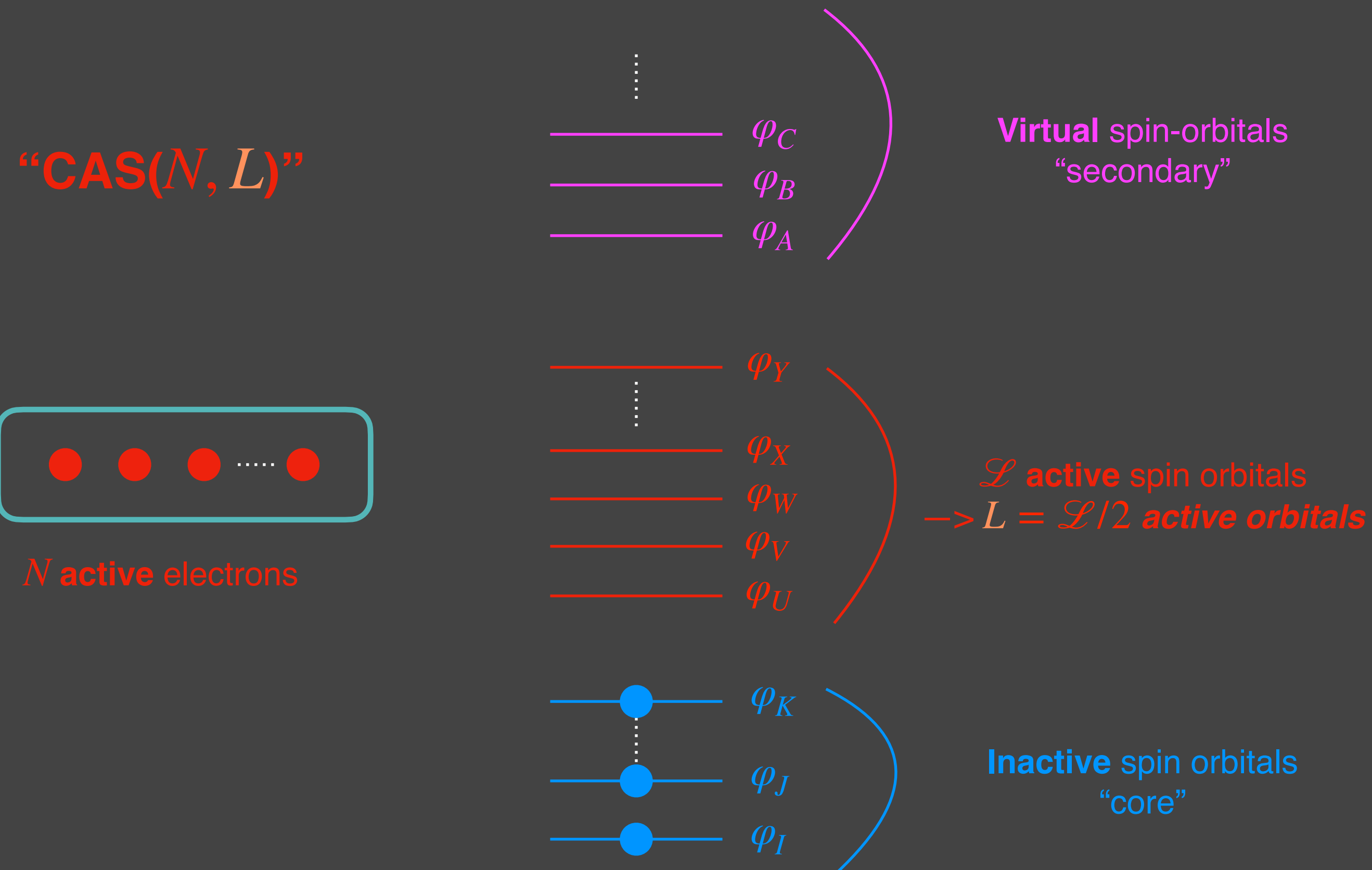
Complete Active Space CI (CASCI)



CASCI is FCI in the active space!

$$|\Psi^{\text{CASCI}}\rangle = \sum_{\zeta \in \text{CAS}} c_{\zeta} |\Phi_{\zeta}\rangle$$

Complete Active Space CI (CASCI)

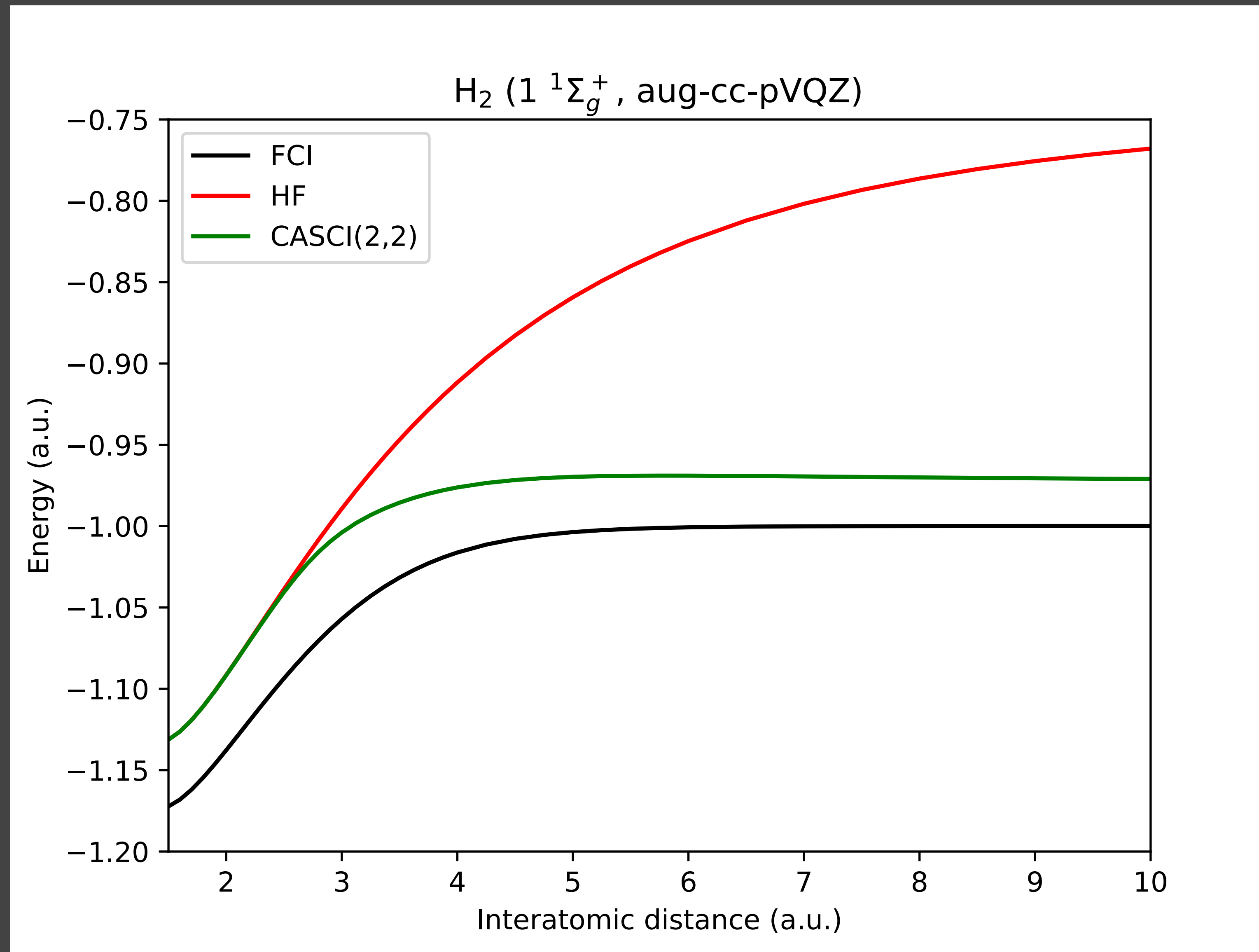


CASCI is FCI in the active space!

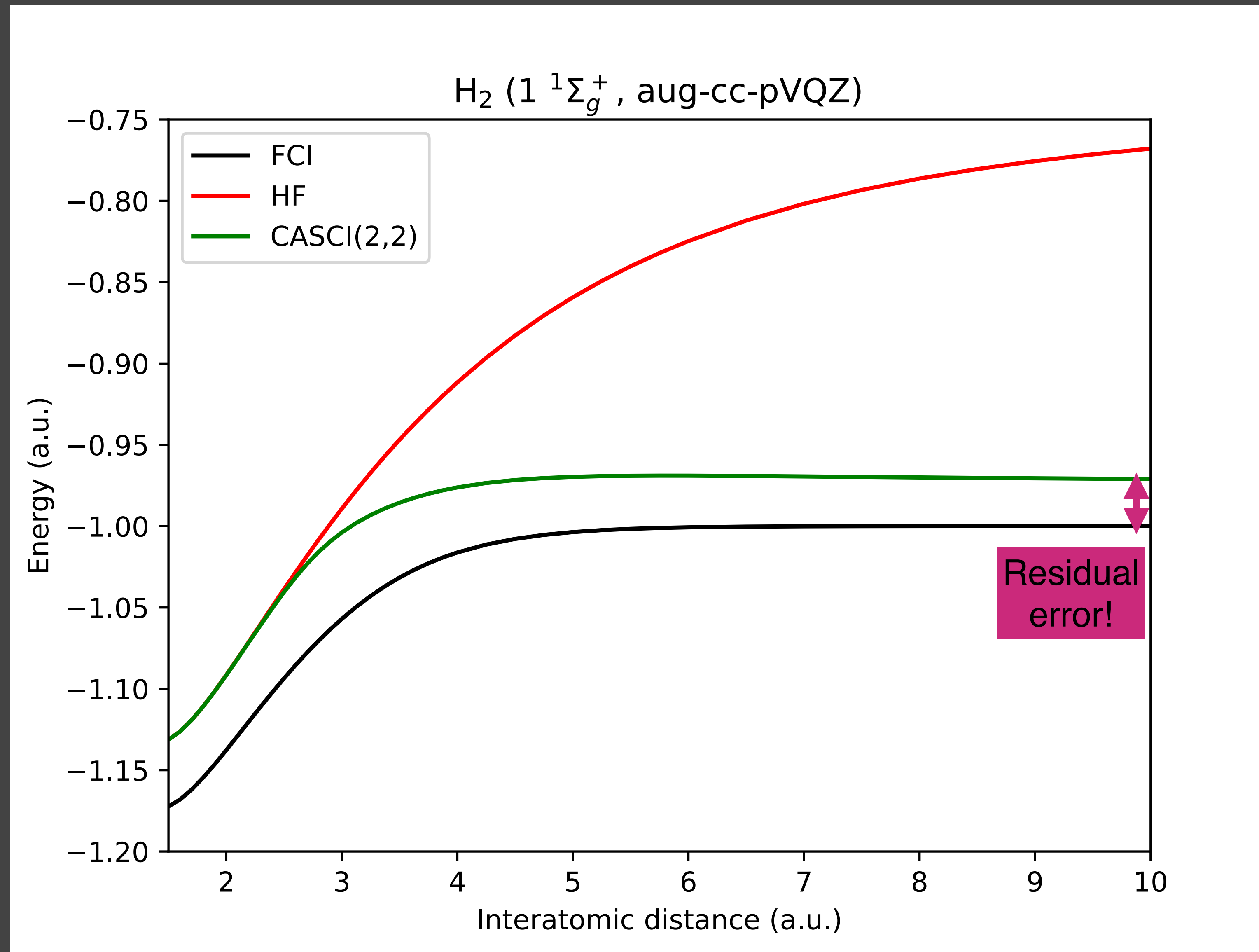
$$|\Psi^{\text{CASCI}}\rangle = \sum_{\zeta \in \text{CAS}} c_{\zeta} |\Phi_{\zeta}\rangle$$

How does it work for our H_2 example?

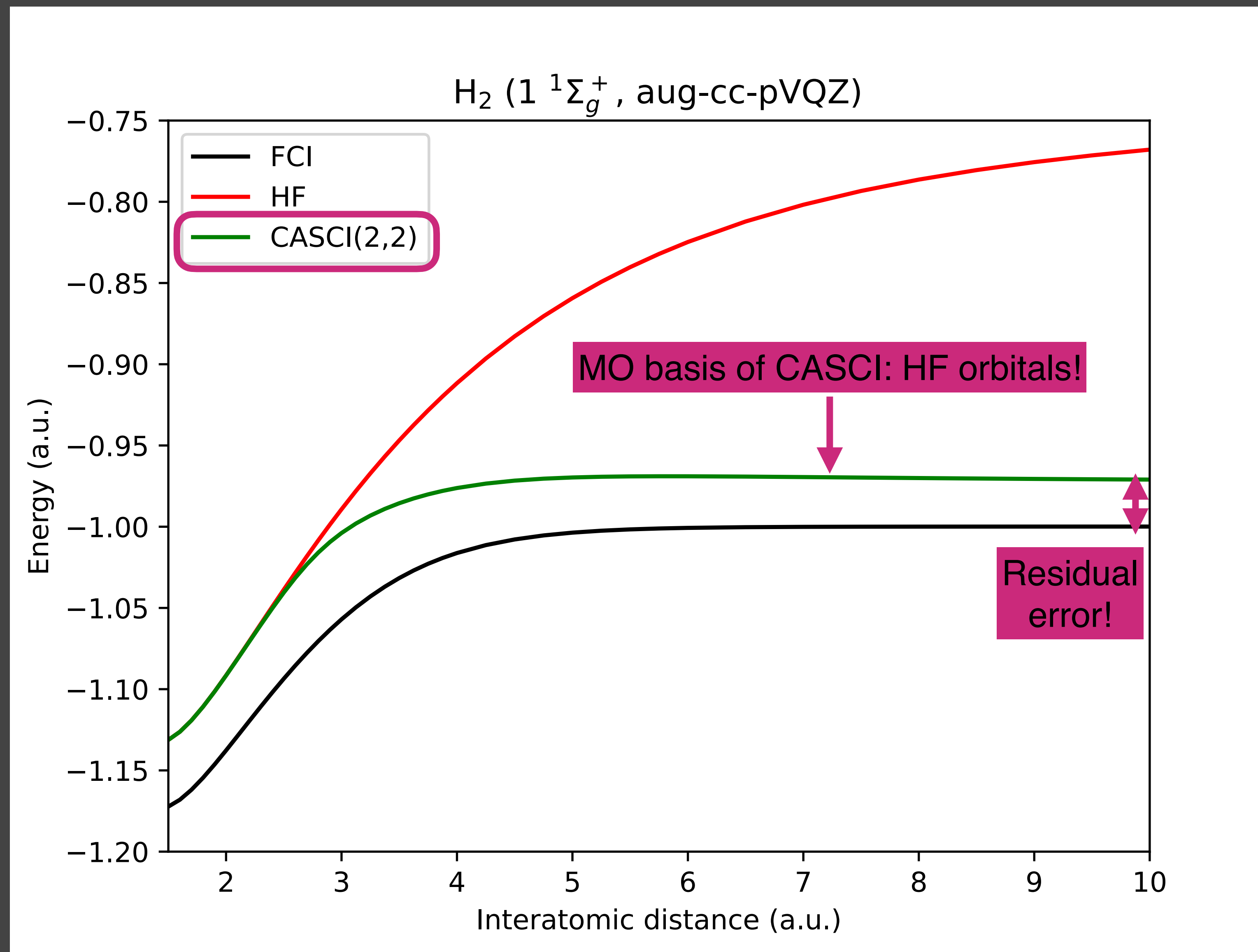
CASCI for H₂



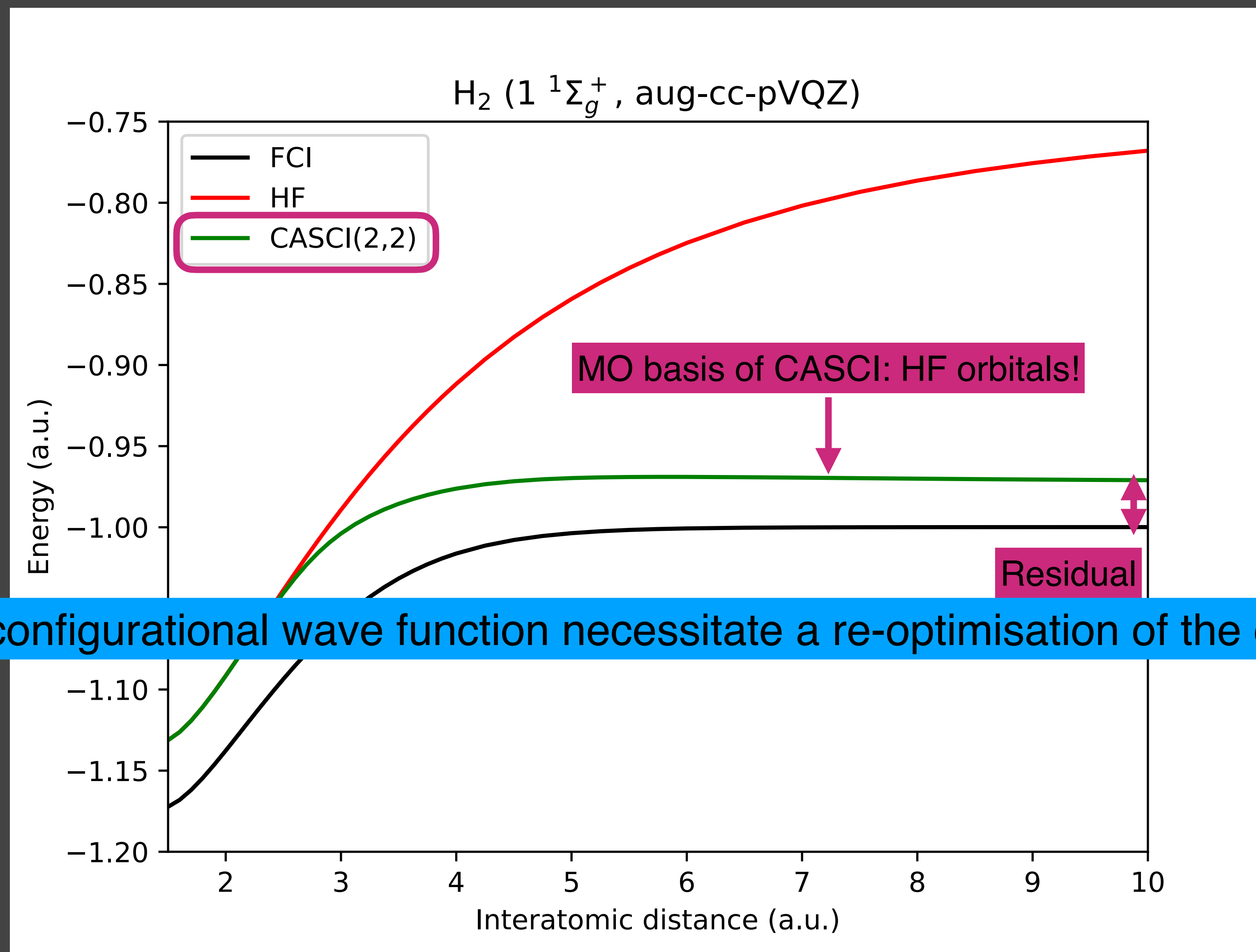
CASCI for H₂



CASCI for H₂

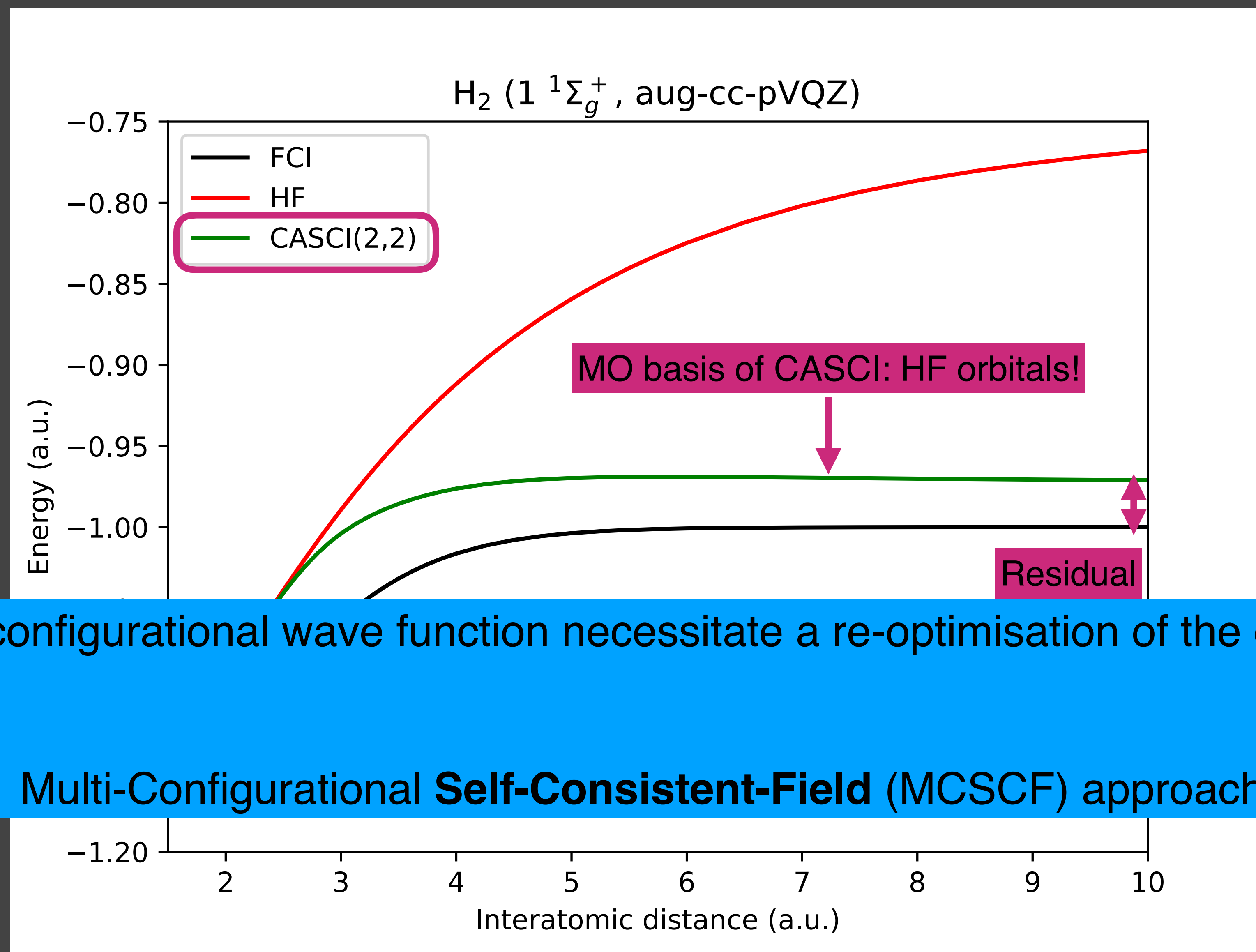


CASCI for H₂



Multi-configurational wave function necessitate a re-optimisation of the orbitals!

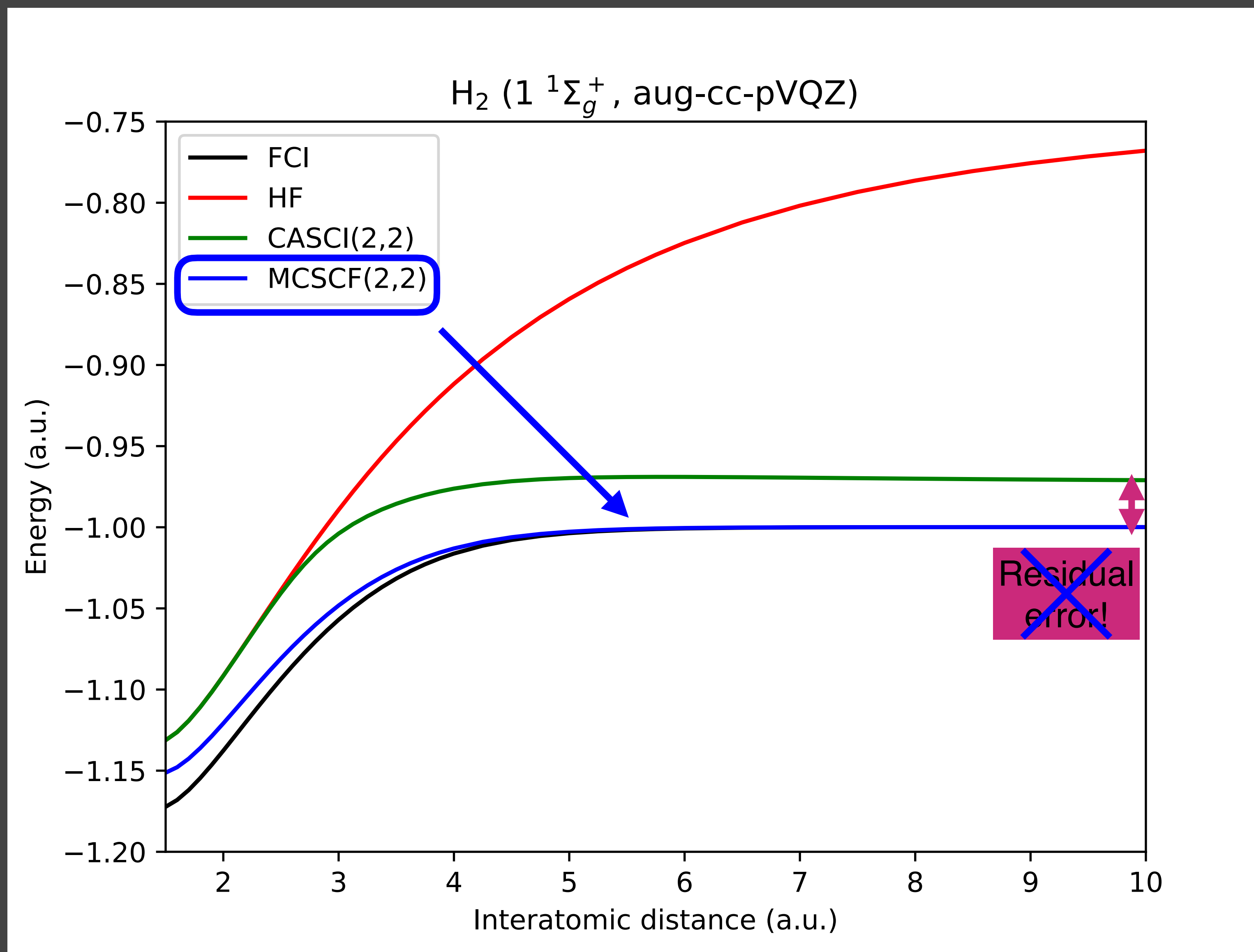
CASCI for H₂



Multi-configurational wave function necessitate a re-optimisation of the orbitals!

Multi-Configurational **Self-Consistent-Field** (MCSCF) approach

CASCI / MCSCF for H₂



MCSCF: concepts and purpose

MCSCF - concepts I

- Introduce as small number of (active) orbitals: $\approx 10 - 20$ with occupation numbers η allowed to vary

- Active orbitals with occupations: $0 \ll \eta \ll 2$

- Select configurations (**many-particle basis states**) to include

- Form of the wave function ($|\tilde{\Phi}_\zeta\rangle \rightarrow$ SD, ONVs or CSFs):

$$|\tilde{\Psi}\rangle = \sum_{\zeta} c_{\zeta} |\tilde{\Phi}_{\zeta}\rangle$$

- **OPTIMISE** the orbitals and the CI coefficients c_{ζ}

MCSCF - concepts II

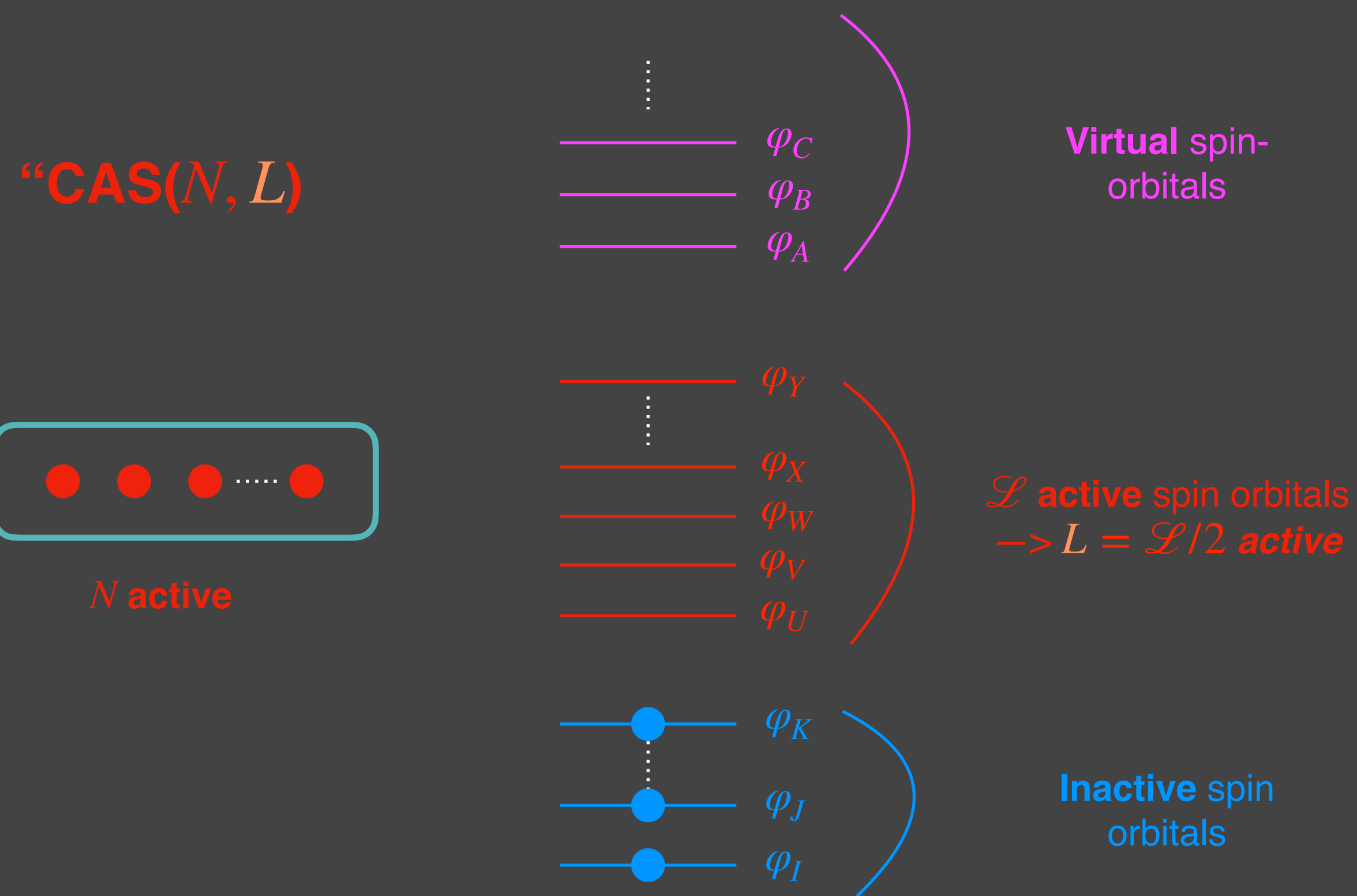
- Simplify general MCSCF ansatz by including **all** configurations generated by allocating all **active electrons** to these **active orbitals**:
FCI in the active space ($\leftarrow\rightarrow$ **CASCI!**)
- Picking a proper set of active orbitals is still required (can be automated too) but configuration generation is automated
- MCSCF optimisation based on this simplification is coined as *complete active space self-consistent field* — or simply **CASSCF**

MCSCF - purpose

- MCSCF **does not describe** the short-range correlation contributions that arise as $r_{12} \rightarrow 0$, that is ***dynamical correlation***
- MCSCF aims at including ***non-dynamical correlation*** that arises from
 - (i) configurational near-degeneracies and/or
 - (ii) gross deficiencies in the RHF wave function
- Includes near-degenerate orbitals to account for **static correlation**
- **Will in general not describe the complete correlation energy!**

CASSCF: concepts,
optimisation and limitations

CASSCF - concepts



- Definition of the orbital spaces follows from CASCI: **inactive**, **active** and **secondary**
- The **active orbital space** should include:
 - all orbitals where the occupation number η changes significantly during a process (reaction, excitation, ionisation, ...)
 - orbitals where $0 \ll \eta \ll 2$
 - can be **automated** (overlap, orbital entropy, perturbative estimates, ...) but do not underestimate “**chemical intuition**”

CASSCF - scaling

2	4
4	36
6	400
8	4.900
10	63.504
12	853.776
14	11.778.896
16	165.636.896
18	2.363.904.260
20	34.134.777.856
24	7.312.459.672.336

- The number of Slater determinant (or ONVs) $\{\Phi\}$ scales for $2k$ electrons in $2k$ orbitals as

$$\{\Phi\} = \binom{2k}{k}^2$$

- Largest calculation with standard CI: CAS(24,24), practical limit about (20,20)!
- Larger CAS spaces require more advanced approaches (—> [see The Present!](#))

CASSCF - active orbital spaces

Simple diatomics

- Sometimes simple and intuitive like for H₂: $(\sigma_g, \sigma_u)^2 \rightarrow \text{CAS}(2,2)$
- Ground state of N₂ requires 2p orbitals: $(\sigma_g, \pi_u, \pi_g, \sigma_u)^6 \rightarrow \text{CAS}(6,6)$
- C₂/Be₂: require inclusion of 2s/2p shells because of near-degeneracies!
- Picking CAS for main-group dimers can be straightforward... but does not necessarily have to be the case
- Transition metal dimers are far from trivial! (\rightarrow see “[The Present](#)”)

CASSCF - active orbital spaces

Polyatomic molecules

- In general, including the full valence space is not an option (too many e-/o)
- Simple guidelines:
 - Breaking a C-H or C-C bond in a hydrocarbon \rightarrow include $(\sigma, \sigma^*)^2$
 - Spectroscopy/reaction of aromatic/conjugated π -systems \rightarrow include (π, π^*)
- If even the minimal CAS reaches beyond (20,20), consider alternative approaches like DMRG, HCI, FCIQMC, selective CI, ...

CASSCF - targeting individual states

State-specific approach

- Goal: target individual excited states which are not the lowest states wrt spin and/or spatial symmetry
- Challenges:
 - Requires convergence of optimisation algorithm to a saddle point
 - *Root flipping*: excited state may become the lowest state in CI along a path
 - Converged MCSCF/CASSCF wave functions for two roots of the same symmetry (spatial/spin) are in general **NOT** orthogonal!
 - > use *state-interaction* to calculate properties: SOC, NAC, ...

CASSCF - targeting an ensemble of states

State-average approach

- Goal: target an ensemble of states **simultaneously** wrt spin and/or spatial symmetry

- Introduce a weighted ensemble $\{M\}_\omega$ of the energies of M states:

$$E^{SA} = \sum_{i=1}^M \omega_i E_i$$

- Each state in $\{M\}_\omega$ will have identical MOs but different CI coefficients
- Challenge: MOs in different states may be **very** different
—> may require larger CAS to ensure smooth convergence

CASSCF - targeting an ensemble of states

State-average approach

- Example: consider an SA CAS(2,2)SCF calculation of ethylene (C_2H_4) for the singlet ($S=0$) ground (“ N state”) and lowest excited state (“ V state”):
 - CAS: $(\pi_u, \pi_g)^2$
 - Character of N state: $|\Psi_0\rangle = c_1(\pi_u)^2 + c_2(\pi_g)^2 + \dots$
 - Character of V state: $|\Psi_1\rangle = (\pi_u\pi_g) + \dots$
- N and V state \rightarrow different spatial extents ($\langle z^2 \rangle = 1.7 / 9.1$)
- Cannot be described by a single set of π orbitals!

CASSCF - Optimisation of the wave function

Concepts

- Wave function *ansatz* (note change of notation $|\tilde{0}\rangle \equiv |\tilde{\Psi}\rangle$):

$$|\tilde{0}\rangle = \sum_{\zeta} c_{\zeta} |\tilde{\Phi}_{\zeta}\rangle$$

Determine the MO and CI coefficients using the variational principle (normalisation!):

$$\delta E = \delta \left(\frac{\langle \tilde{0} | \hat{H} | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle} \right) = 0$$

- Indices: i, j, k, \dots v, w, x, \dots a, b, c, \dots p, q, r, \dots

CASSCF - Optimisation of the wave function

Energy

- Total CASSCF energy:
$$E = \langle \tilde{0} | \hat{H} | \tilde{0} \rangle$$
$$= \sum_{pq} h_{pq} D_{pq} + \sum_{pqrs} g_{pqrs} P_{pqrs} + h_{nuc}$$

with

$$D_{pq} = \langle \tilde{0} | \hat{E}_{pq} | \tilde{0} \rangle \text{ (first-order RDM)}$$

$$P_{pqrs} = \frac{1}{2} \langle \tilde{0} | \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} | \tilde{0} \rangle \text{ (second-order RDM)}$$

- MO coefficients $\{\tilde{\varphi}\}$ appear in h_{pq} and g_{pqrs} , CI coefficients $\{\tilde{\Phi}\}$ in \mathbf{D} and \mathbf{P}

CASSCF - Optimisation of the wave function

Unitary transformations of MOs

- MOs $\{\tilde{\varphi}\}$ are orthonormal \rightarrow unitary transformation U ensures orthonormality

$$\tilde{\varphi} = \varphi U \text{ with } U^\dagger U = \mathbf{1}$$

- Write U as $U = \exp(T)$ with $T^\dagger = -T$, that is T is **anti-hermitian**

$$\hat{T} = \sum_{pq} T_{pq} \hat{E}_{pq} = \sum_{p>q} T_{pq} (\hat{E}_{pq} - \hat{E}_{qp})$$

- Transformation of creation operators:

$$\hat{a}_{\tilde{p}} = \exp(\hat{T}) \hat{a}_p^\dagger \exp(-\hat{T})$$

- CAS \rightarrow we only need the following rotation parameters: $\{pq\}$, $\{pq\}$, $\{pq\}$

CASSCF - Optimisation of the wave function

Unitary transformations of CI vectors

- CI vector(s) $\{\Phi\}$ are normalised:

$$|0\rangle = \sum_{\zeta} c_{\zeta} |\Phi_{\zeta}\rangle \quad \text{with} \quad \sum_{\zeta} |c_{\zeta}|^2 = 1$$

- Complementary space $|K\rangle$ orthogonal to $|0\rangle$: $\langle 0 | K \rangle = 0$

- Define anti-hermitian operator $\hat{S}^{\dagger} = -\hat{S}$:

$$\hat{S} = \sum_{K \neq 0} S_{K0} \left(|K\rangle \langle 0| - |0\rangle \langle K| \right)$$

- Unitary transformation of $|0\rangle$ such that $|\tilde{0}\rangle$ remains normalised

$$|\tilde{0}\rangle = \exp(\hat{S}) |0\rangle$$

CASSCF - Optimisation of the wave function

Concepts

- Resulting wave function ansatz:

$$|\tilde{0}\rangle = \exp(\hat{T})\exp(\hat{S})|0\rangle$$

- “Double”-exponential parametrisation with parameters T_{pq} ($p > q$) and S_{K0}
- Energy function with parameter space $\{\mathbf{p}\} \equiv \{\{T_{pq}\}_{p>q}, \{S_{K0}\}\}$

$$E(\mathbf{p}) = E(\mathbf{T}, \mathbf{S}) = \langle \tilde{0} | \hat{H} | \tilde{0} \rangle = \langle 0 | \exp(-\hat{S})\exp(-\hat{T})\hat{H}\exp(\hat{T})\exp(\hat{S}) | 0 \rangle$$

CASSCF - Optimisation of the wave function

Optimal energy

- Vary parameters \mathbf{T} and \mathbf{S} such that energy $E(\mathbf{T}, \mathbf{S}) = \langle 0 | e^{-\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} e^{\hat{S}} | 0 \rangle$

becomes stationary:

$$\frac{\partial E}{\partial T_{pq}} = 0 \quad \frac{\partial E}{\partial S_{K0}} = 0$$

- Leads to a set of nonlinear equations that must be solved iteratively
- In the following, we examine the Newton-Raphson method for CASSCF optimisation

CASSCF - Optimisation of the wave function

Newton-Raphson method - concepts I

- Find stationary point of $E(\mathbf{p})$ where \mathbf{p} is a set of parameters to be freely varied
- Requires start guess, for example with $\mathbf{p}_0 = 0$
- Expand E through second-order around this point

$$\begin{aligned} E(\mathbf{p}) &\approx E^{(2)} = E(0) + \sum_i \left(\frac{\partial E}{\partial p_i} \right)_0 p_i + \frac{1}{2} \sum_{ij} p_i \left(\frac{\partial^2 E}{\partial p_i \partial p_j} \right)_0 p_j \\ &= E(0) + \mathbf{g}^\dagger \mathbf{p} + \frac{1}{2} \mathbf{p}^\dagger \mathbf{H} \mathbf{p} \end{aligned}$$

- \mathbf{g} is the **gradient vector** & \mathbf{H} is the **Hessian matrix**

CASSCF - Optimisation of the wave function

Newton-Raphson method - concepts II

- Approximation to stationary point by finding stationary point of $E^{(2)}$:

$$\frac{\partial E^{(2)}}{\partial p_i} = 0 \rightarrow \mathbf{g} + \mathbf{H}\mathbf{p} = \mathbf{0} \rightarrow \mathbf{p} = -\mathbf{H}^{-1}\mathbf{g}$$

- For the current \mathbf{p} , compute new gradient and Hessian
- Continue iterative procedure until $|\mathbf{g}| \approx 0$
- **Note:**
 - Approximating E with $E^{(2)}$ is only valid for small \mathbf{p}
 - Quadratic convergence for small \mathbf{p}

CASSCF - Optimisation of the wave function

Taylor expansion of the energy

- **Recall:** BCH expansion for operators

$$\exp(-\hat{A})\hat{B}\exp(\hat{A}) = \hat{B} + [\hat{B}, \hat{A}] + \frac{1}{2} [[\hat{B}, \hat{A}], \hat{A}] + \dots$$

- Expand E through second order in \hat{T} , \hat{S} with $E(0)$, \mathbf{g} and \mathbf{H} parts

$$E^{(2)}(\mathbf{T}, \mathbf{S}) = \langle 0 | \hat{H} | 0 \rangle + \langle 0 | [\hat{H}, \hat{T}] + [\hat{H}, \hat{S}] | 0 \rangle \\ + \langle 0 | \frac{1}{2} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{2} [[\hat{H}, \hat{S}], \hat{S}] + [[\hat{H}, \hat{T}], \hat{S}] | 0 \rangle$$

CASSCF - Optimisation of the wave function

Newton-Raphson equations

- After some straightforward math, Newton-Raphson equations assume the form

$$\begin{pmatrix} \mathbf{H}^{cc} & \mathbf{H}^{co} \\ \mathbf{H}^{oc} & \mathbf{H}^{oo} \end{pmatrix} \begin{pmatrix} \mathbf{S} \\ \mathbf{T} \end{pmatrix} = - \begin{pmatrix} \mathbf{g}^c \\ \mathbf{g}^o \end{pmatrix}$$

comprising orbital (o) and configurational (c) parts as well as mixed terms

- Common approximations:
 - Neglect oc/co parts in H
 - Approximate H^{oo} \rightarrow super-CI approach

CASSCF - Optimisation of the wave function

Code availability and capabilities

- DALTON: NR and other optimization techniques → state-specific MCSCF
- OpenMolcas: no *co/oc* couplings → state-specific + state-average MCSCF
- MOLPRO: second-order optimisation → state-specific + state-average MCSCF
- ORCA: second-order optimisation → state-specific + state-average MCSCF
- pySCF: quasi-second order → state-specific + state-average MCSCF
- ...

Dynamical electron correlation
combined with static correlation

Dynamical correlation combined with MCSCF

Wishlist

- **GOAL:** treat dynamical correlation in combination with MCSCF wave function
 - simultaneously (**diagonalize-and-perturb**)
 - *a posteriori* (**diagonalize-then-perturb**)
- Should preferably be both size-extensive and size-consistent
 - size-extensive: energy scales linearly with number of particles N
 - size-consistent: $E_{AB} = E_A + E_B$ at $r(A - B) \rightarrow \infty$
- Should allow to treat an ensemble of states on an equal footing

Dynamical correlation combined with MCSCF

A not-so-complete summary ...

- **Multi-reference CI:**
 - Based on excitations out of a MC state
 - Variational but not size-consistent/size-extensive
- Multi-reference perturbation (**MRPT2**) theories: **CASPT2**, **NEVPT2**, ...
 - Based on (internally contracted) excitations out of a MC state
 - Differ in form of \hat{H}_0 and form of wave function corrections
 - (Nearly) size-extensive
- **MRCC**: less developed but most rigorous!
- post-MCSCF on-top pair-DFT correction (**MC-pDFT**)
 - Requires specialised DFAs
 - Works for SS and SA MC reference wave functions
- **srDFT-IrMCSCF**:
 - Requires specialised DFAs
 - Allows a simultaneous treatment of static and dynamic correlation

The Present ...



Second example: the Cr₂ puzzle resolved

H. R. Larsson, H. Zhai, C. J. Umrigar, G. K.-L. Chan, arXiv: 2206.10738

Cr₂ potential energy curve...

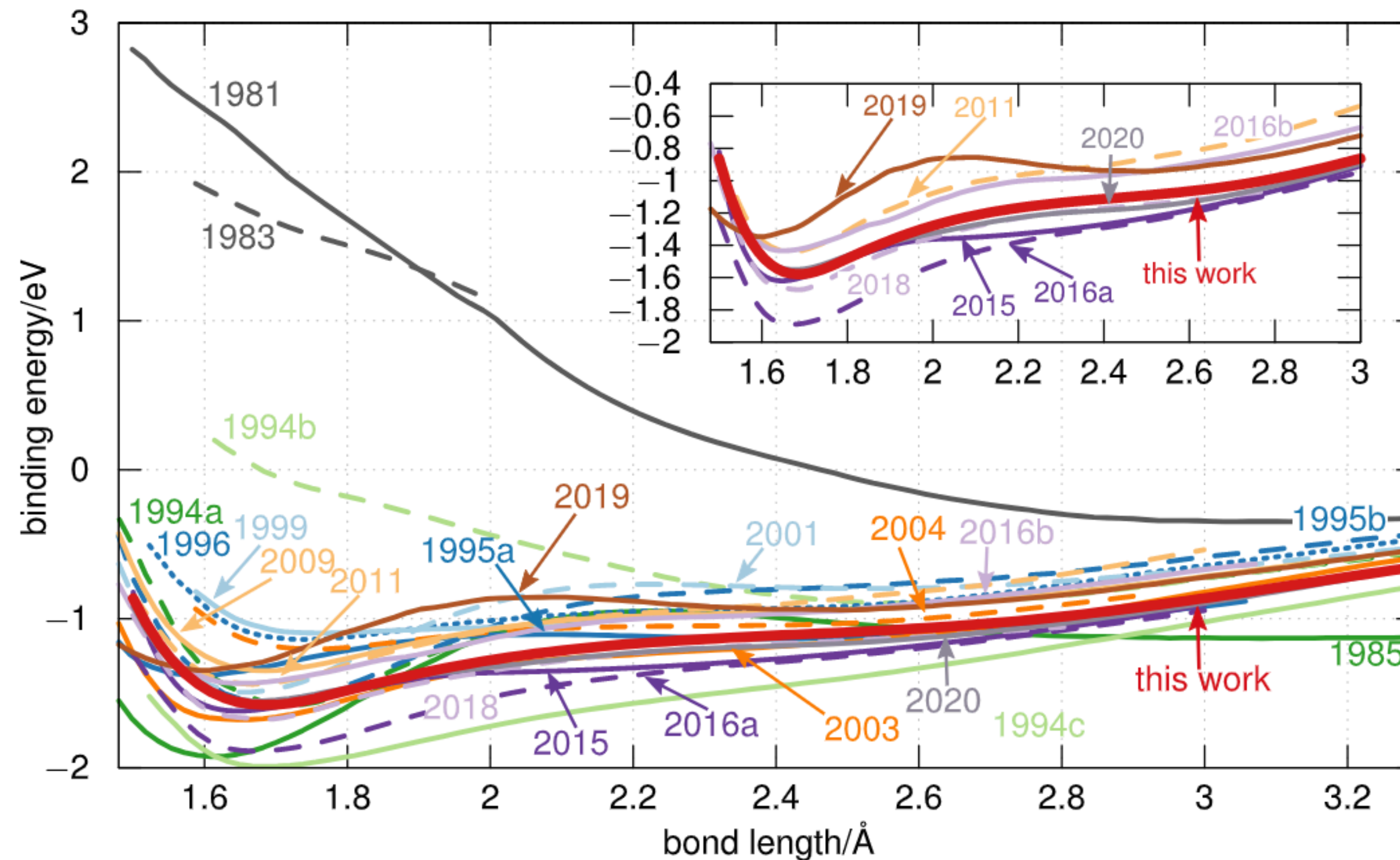


FIG. 1. Some of the simulated potential energy curves (PECs) of the chromium dimer that are available in the literature. The PECs are labeled by the study's year. The red curve marks the PEC from this work. The inset shows selected PECs from 2011 onwards. (List of references in SI).

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 (3d + 4s 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 3d-3d bonds requires the 3p electrons to move out of the same spatial region by exciting to higher lying orbitals

- **Challenge:**

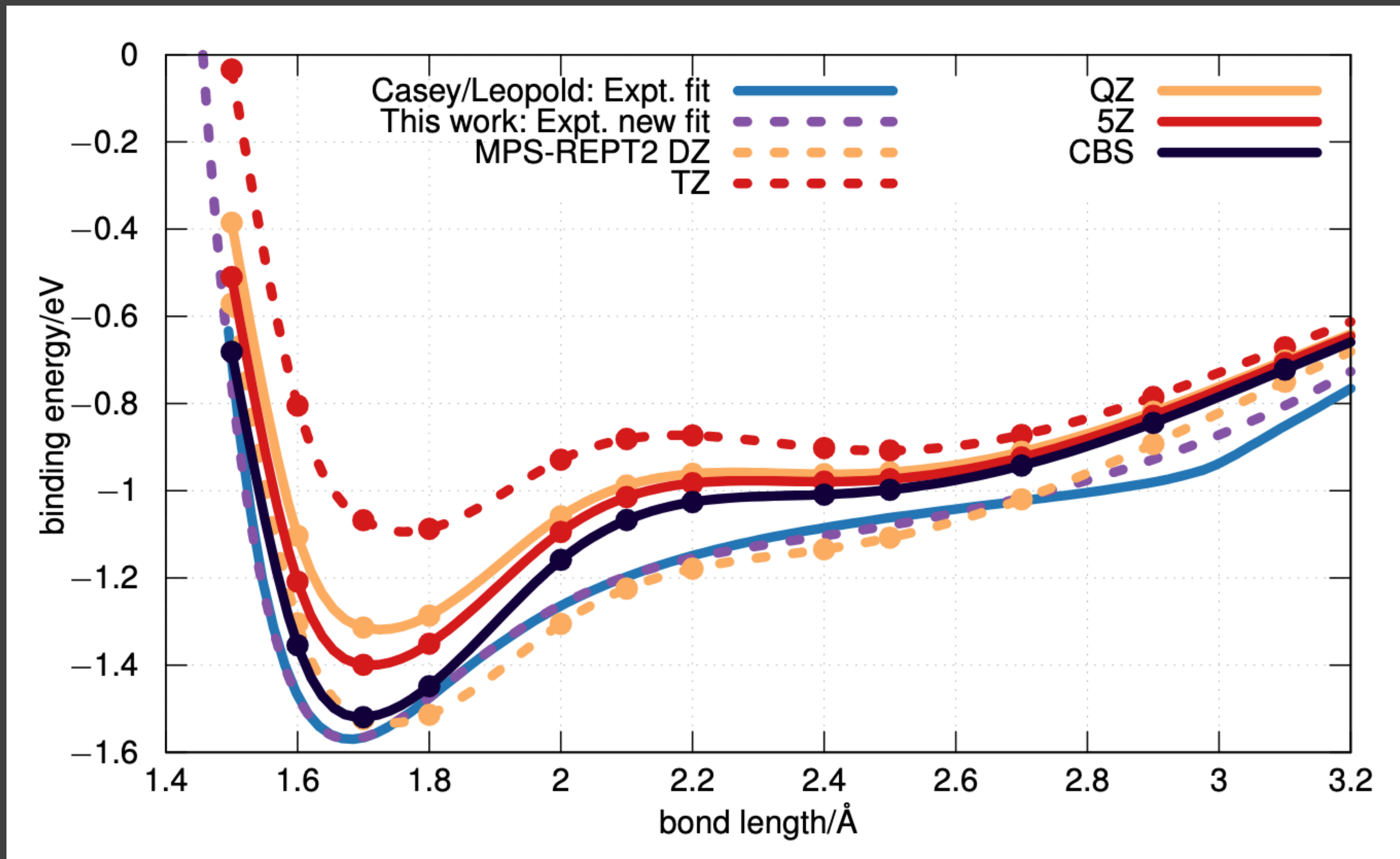
“The problem is computationally challenging because **both the static and dynamic correlation** must be computed sufficiently well even for a qualitatively reasonable description.”

Computational approach I

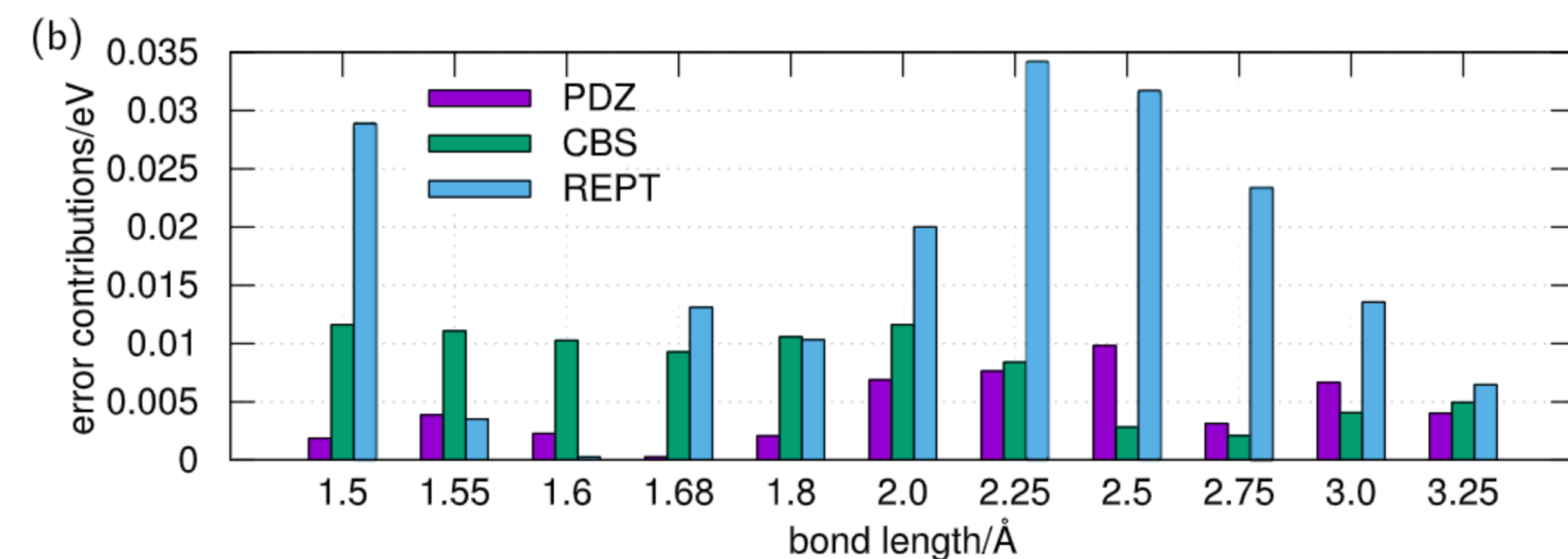
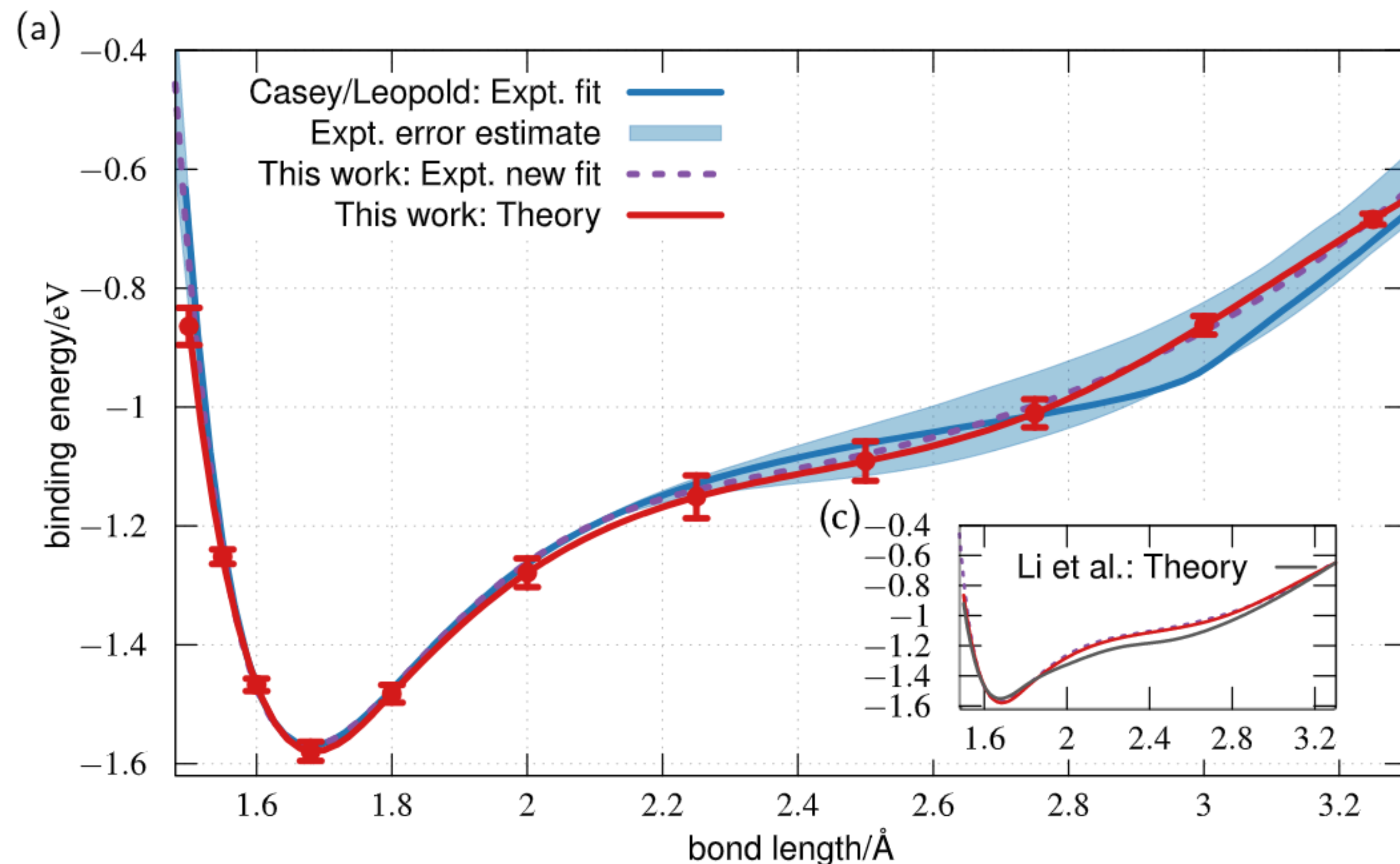
$$\Delta E = \Delta E_{\text{PDZ}}(\text{"exact"}) + \Delta E_{\text{CBS}}(\text{MPS-REPT2}) - \Delta E_{\text{DZ}}(\text{MPS-REPT2})$$

- 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 3s and 3p inner-valence shells
 - all secondary shells considered
- Basis set: MRPT2 with cc-pvNZ-DK (N=2,3,4,5) with extrapolation to CBS limit

Computational approach II



New state-of-the-art



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

with the individual error contributions as defined above,

$$\epsilon_{\text{PDZ}} = |\Delta E(\text{SHCI}) - \Delta E(\text{DMRG})|/2,$$

$$\epsilon_{\text{CBS}} = \sigma_{\text{CBS}},$$

$$\epsilon_{\text{REPT}} = |\Delta E(\text{MPS-REPT2}) - \Delta E[\text{UCCSD(T)}]|/2.$$

Thinking outside the box

Standard CI approach

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

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

DMRG

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

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

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

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

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

Very useful introductory reference:

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)
- G. K.-L. Chan and S. Sharma, Ann. Rev. Phys. Chem., 62, 465 (2011)
- K. Marti and M. Reiher, Phys. Chem. Chem. Phys., 13, 6750 (2011)
- U. Schollwöck, Ann. Phys., 326, 96 (2011)
- G. K.-L. Chan, WIREs, 2, 907 (2012)
- Y. Kurashige, Mol. Phys., 112, 1485 (2013)
- S. Wouters and D. van Neck, Eur. Phys. J. D, 68, 272 (2014)
- S. Szalay *et al.*, Int. J. Quantum Chem. 115, 1342 (2015)
- 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)

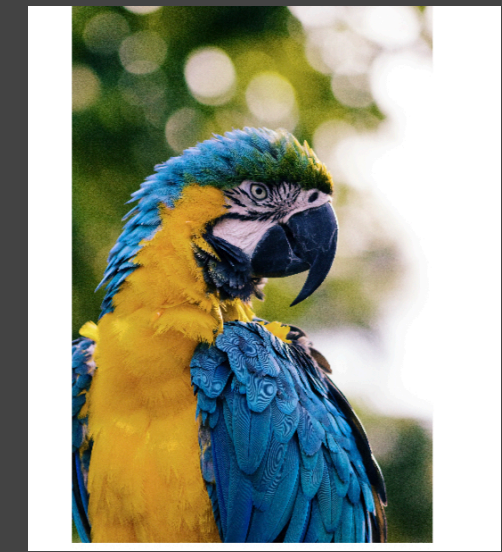
Intermission: singular value decomposition

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

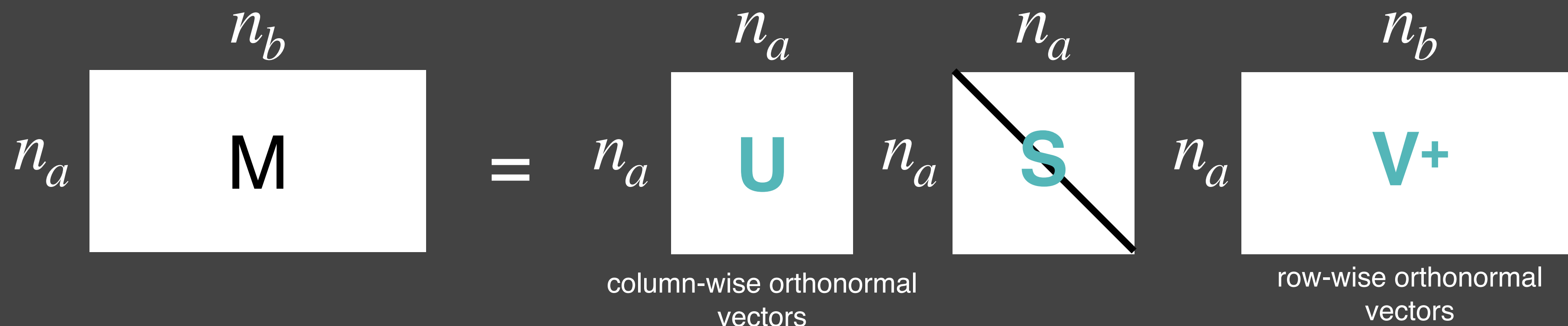
$$\mathbf{M} = \mathbf{U} \mathbf{S} \mathbf{V}^\dagger$$

yields:

- Left-singular matrix \mathbf{U} ($n_a \times \min(n_a, n_b)$) with $\mathbf{U}^\dagger \mathbf{U} = \mathbf{1}$
- Right-singular matrix \mathbf{V} ($\min(n_a, n_b) \times n_b$) with $\mathbf{V}^\dagger \mathbf{V} = \mathbf{1}$
- 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}

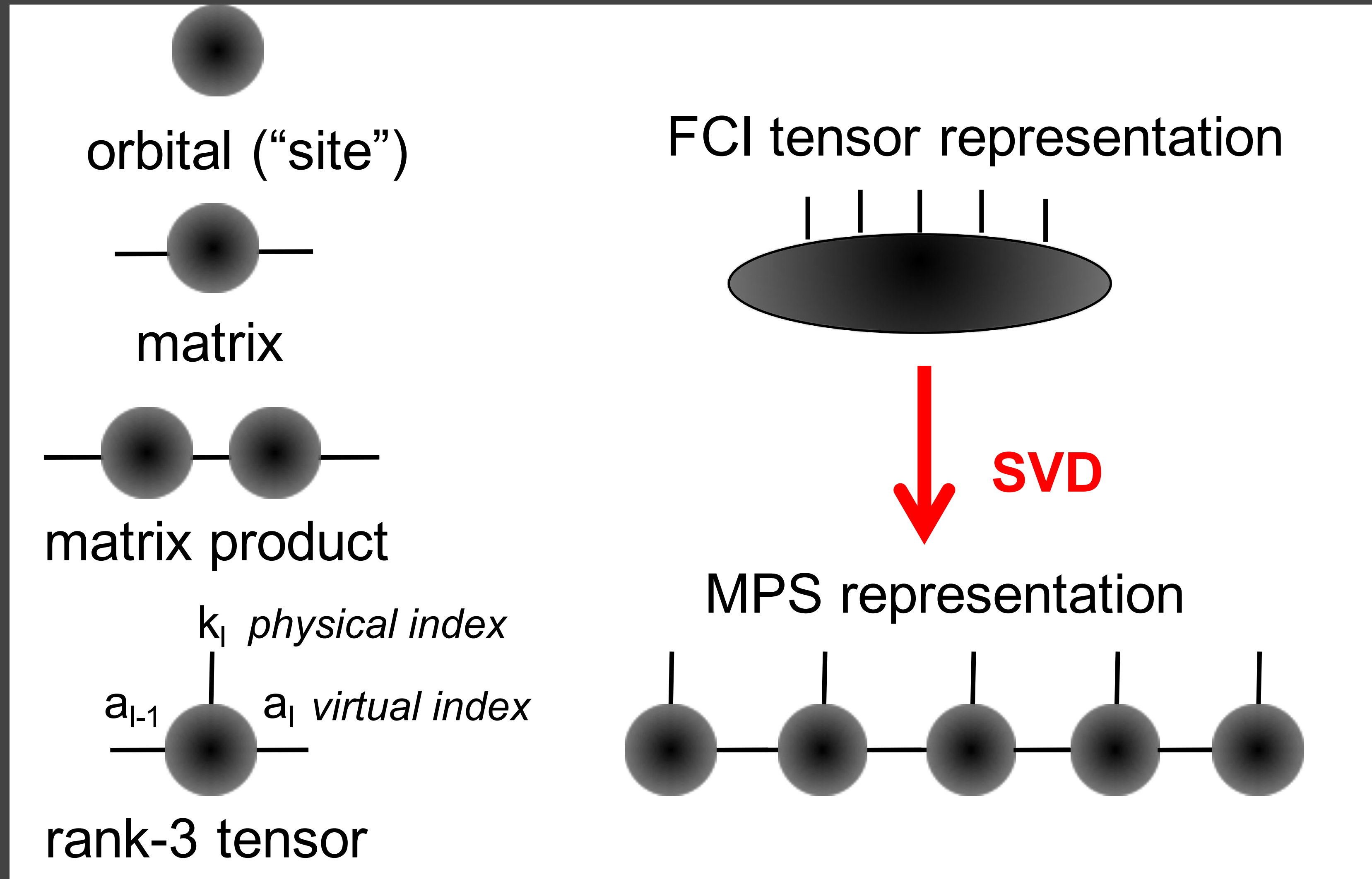


Remember?



From a CI to an MPS parametrisation I

- Successive application of SVD to CI tensor \rightarrow MPS wave function



From a CI to an MPS parametrisation II

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

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

- SVD of $\Gamma_{k_1, (k_2, \dots, k_L)}$ yields

$$\begin{aligned}\Gamma_{k_1, (k_2, \dots, k_L)} &= \sum_{a_1}^{r_1} U_{k_1, a_1} S_{a_1, a_1} (V^\dagger)_{a_1, (k_2, \dots, k_L)} \\ &\equiv \sum_{a_1}^{r_1} A_{1, a_1}^{k_1} c_{a_1, (k_2, \dots, k_L)}\end{aligned}$$

with

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

From a CI to an MPS parametrisation III

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

$$c_{k_1, k_2, \dots, k_L} = \sum_{a_1}^{r_1} A_{1, a_1}^{k_1} \Gamma_{(a_1 k_2), (k_3, \dots, k_L)}$$

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

$$\stackrel{\text{reshape}}{\equiv} \sum_{a_1}^{r_1} \sum_{a_2}^{r_2} A_{1, a_1}^{k_1} A_{a_1, a_2}^{k_2} \Gamma_{(a_2 k_3), (k_4, \dots, k_L)}$$

with

- S and V^\dagger multiplied and reshaped into coefficient tensor $c_{a_1, (k_2, \dots, k_L)}$

- $r_2 \leq r_1 d \leq d^2$

- collection of d matrices A^{k_2} with entries $A_{a_1, a_2}^{k_2} = U_{(a_1 k_2), a_2}$

From a CI to an MPS parametrisation IV

- Continue with SVDs until last site which then gives

$$\begin{aligned} c_{k_1, k_2, \dots, k_L} &= \sum_{a_1, a_2, \dots, a_{L-1}} A_{1, a_1}^{k_1} A_{a_1, a_2}^{k_2} \dots A_{a_{L-2}, a_{L-1}}^{k_{L-1}} A_{a_{L-1}, 1}^{k_L} \\ &\equiv A^{k_1} A^{k_2} \dots A^{k_{L-1}} A^{k_L} \end{aligned}$$

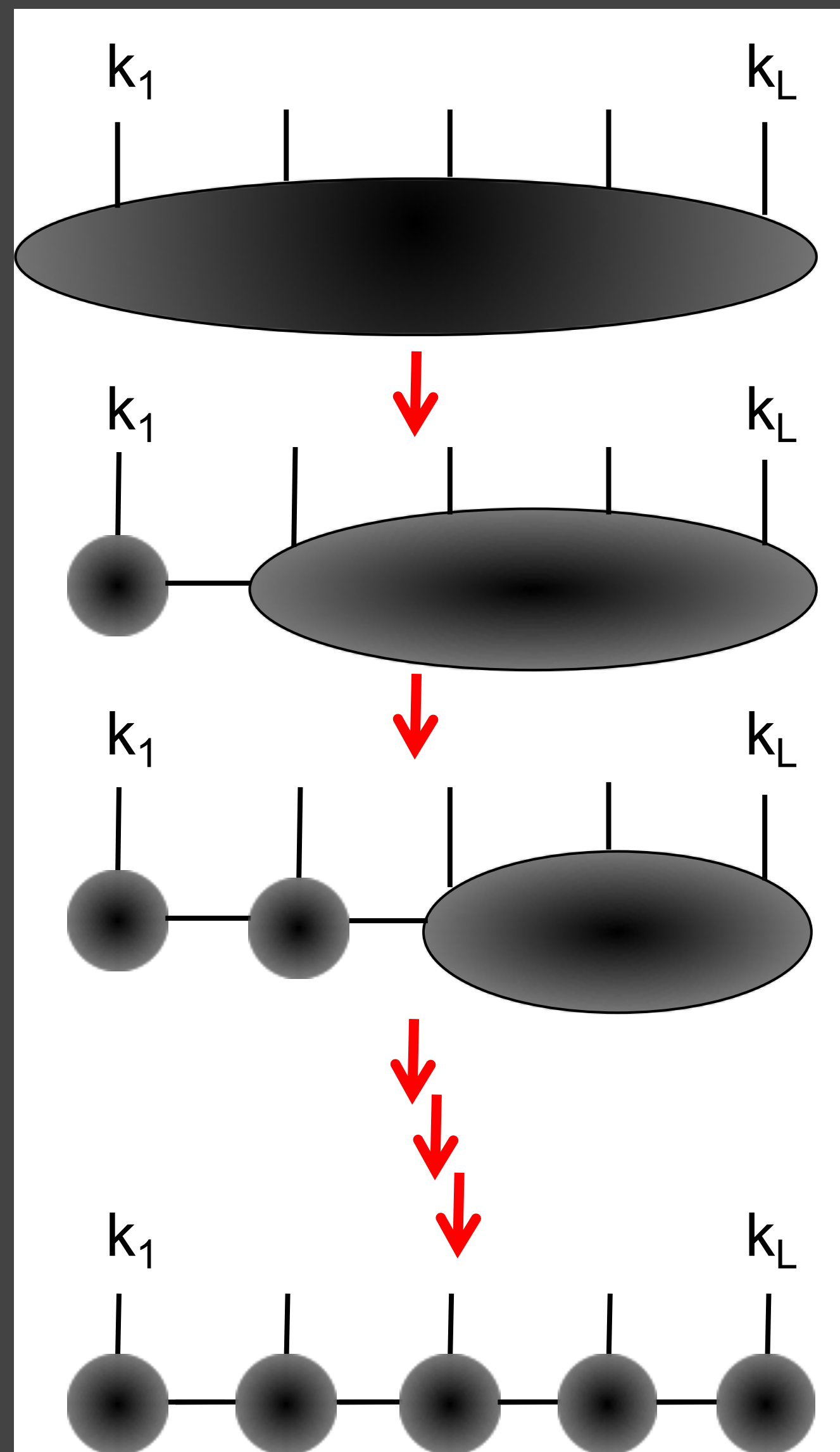
with

- interpretation of sums as matrix-matrix multiplications
- first and last **matrices** are row- and column vectors!
- CI wave function rewritten as MPS wave function:

$$|\Psi\rangle = \sum_k c_k |\mathbf{k}\rangle = \sum_{k_1, k_2, \dots, k_L} A^{k_1} A^{k_2} \dots A^{k_{L-1}} A^{k_L} |\mathbf{k}\rangle$$

From a CI to an MPS parametrisation V

schematically...

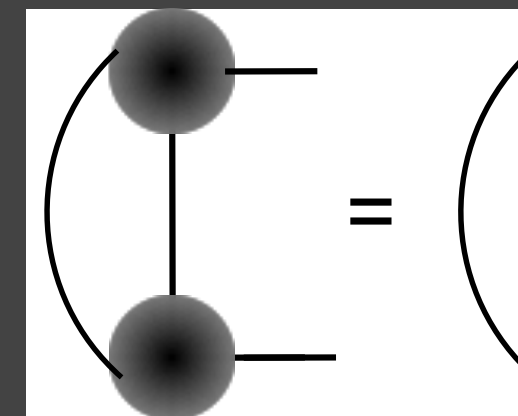


Properties of the MPS I

- 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 $1, \dots, l$

$$|a_l\rangle_{\mathcal{L}} = \sum_{k_1, k_2, \dots, k_l} (A^{k_1} \dots A^{k_l})_{1, a_l} |k_1, \dots, k_l\rangle$$

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

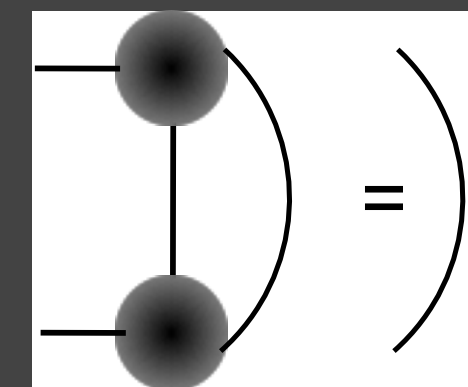
Properties of the MPS II

- Starting SVD on coefficient tensor from right-hand side

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

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 $l + 1 \dots, L$

$$|a_{l+1}\rangle_{\mathcal{R}} = \sum_{k_{l+1}, k_{l+2}, \dots, k_L} (B^{k_{l+1}} \dots B^{k_L})_{a_{l+1}} |k_{l+1}, \dots, k_L\rangle$$

span a right subsystem \mathcal{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

$$M^{k_l} \rightarrow M^{k_l} X; \quad M^{k_{l+1}} \rightarrow X^{-1} M^{k_{l+1}}$$

since

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

Mixed-canonical MPS representation

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

$$|\Psi\rangle = \sum_k A^{k_1} \dots A^{k_{l-1}} M^{k_l k_{l+1}} B^{k_{l+2}} \dots B^{k_L} |k\rangle$$

by starting from a general MPS wave function

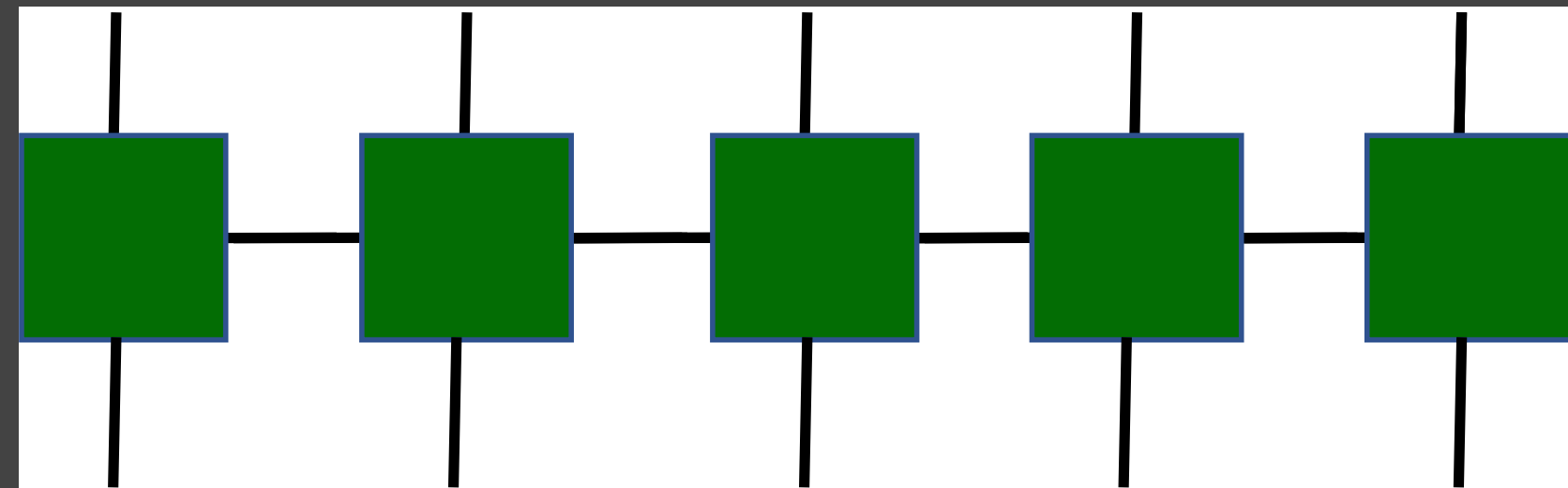
$$|\Psi\rangle = \sum_k M^{k_1} M^{k_2} \dots M^{k_L} |k\rangle$$

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

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

Matrix product operators I

- MPS concept applied to operators \rightarrow matrix product operators (MPOs)



- N -electron operator $\widehat{\mathcal{W}}$ in MPO form

$$\begin{aligned} \widehat{\mathcal{W}} &= \sum_{kk'} \sum_{b_1, \dots, b_{L-1}} W_{1,b_1}^{k_1 k'_1} W_{b_1, b_2}^{k_2 k'_2} \dots W_{b_{L-1}, 1}^{k_L k'_L} |k\rangle \langle k'| \\ &= \sum_{kk'} W^{k_1 k'_1} W^{k_2 k'_2} \dots W^{k_L k'_L} |k\rangle \langle k'| \\ &\equiv \sum_{kk'} w_{kk'} |k\rangle \langle k'| \end{aligned}$$

Matrix product operators II

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

$$\widehat{W}_{b_{l-1}, b_l}^l = \sum_{k_l k'_l} W_{b_{l-1}, b_l}^{k_l k'_l} |k_l\rangle \langle k'_l|$$

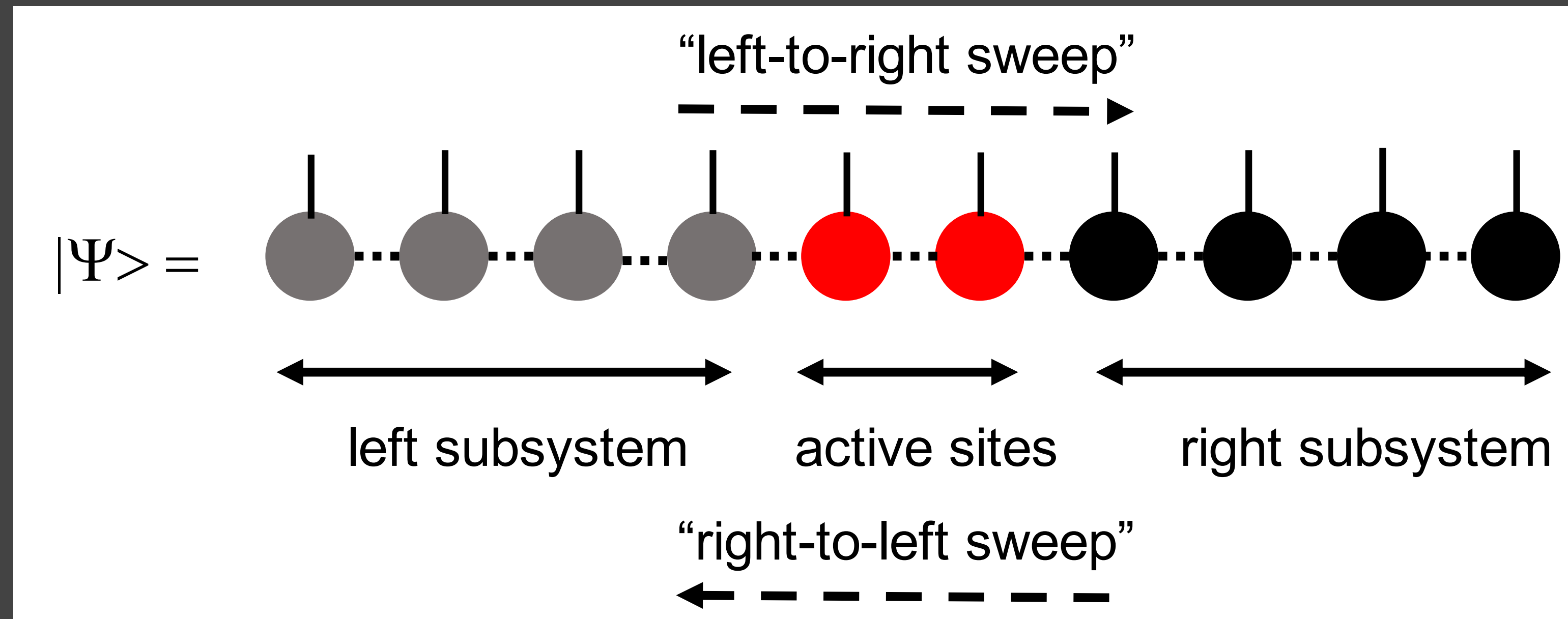
- This allows us to write the equation on previous slide as

$$\widehat{\mathcal{M}} = \sum_{b_1, \dots, b_{L-1}} \widehat{W}_{1, b_1}^1 \cdots \widehat{W}_{b_{l-1}, b_l}^l \cdots \widehat{W}_{b_{L-1}, 1}^L$$

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

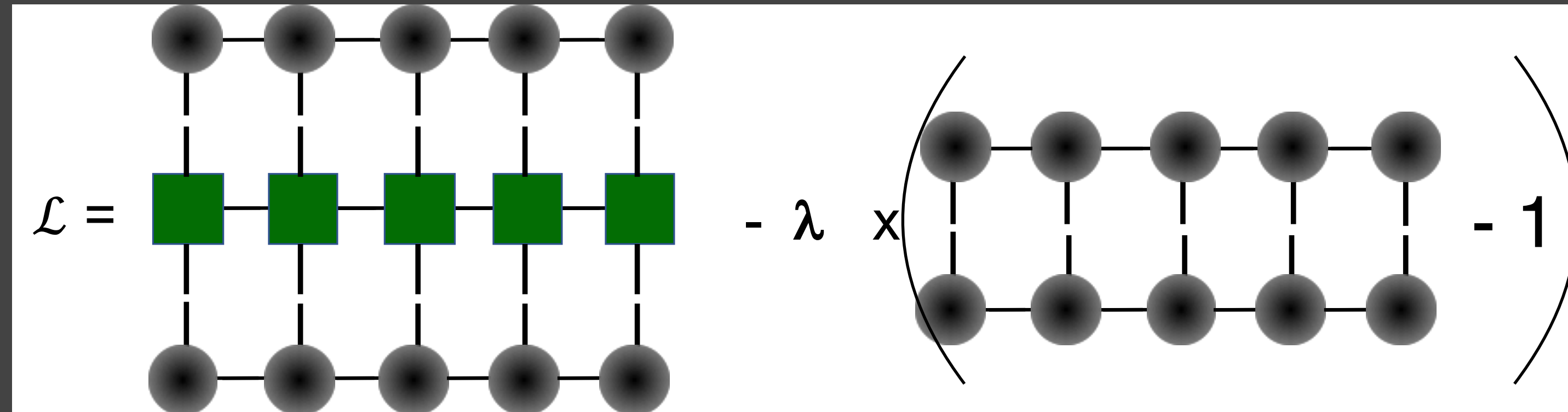
$$\tilde{a}_{\uparrow_l}^\dagger = |\uparrow \downarrow\rangle \langle \downarrow| + |\uparrow\rangle \langle 0|$$

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 by Ö. Legeza, ...
- assume normalisation, i.e., $\langle\Psi|\Psi\rangle = 1$

Variational MPS optimisation II



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

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

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 \mathcal{L} with respect to complex conjugate of

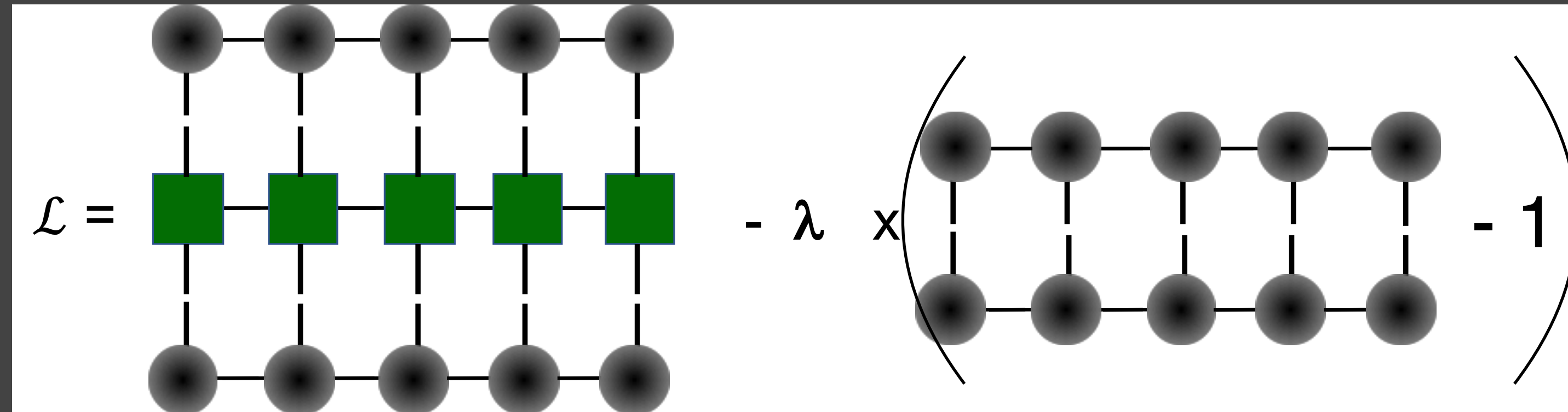
$$M^{k_l, k_{l+1}} \frac{\partial}{\partial M^{k_l, k_{l+1}*}} \left(\langle \Psi | \hat{H} | \Psi \rangle - \lambda \left[\langle \Psi | \Psi \rangle - 1 \right] \right) = 0$$

which then yields

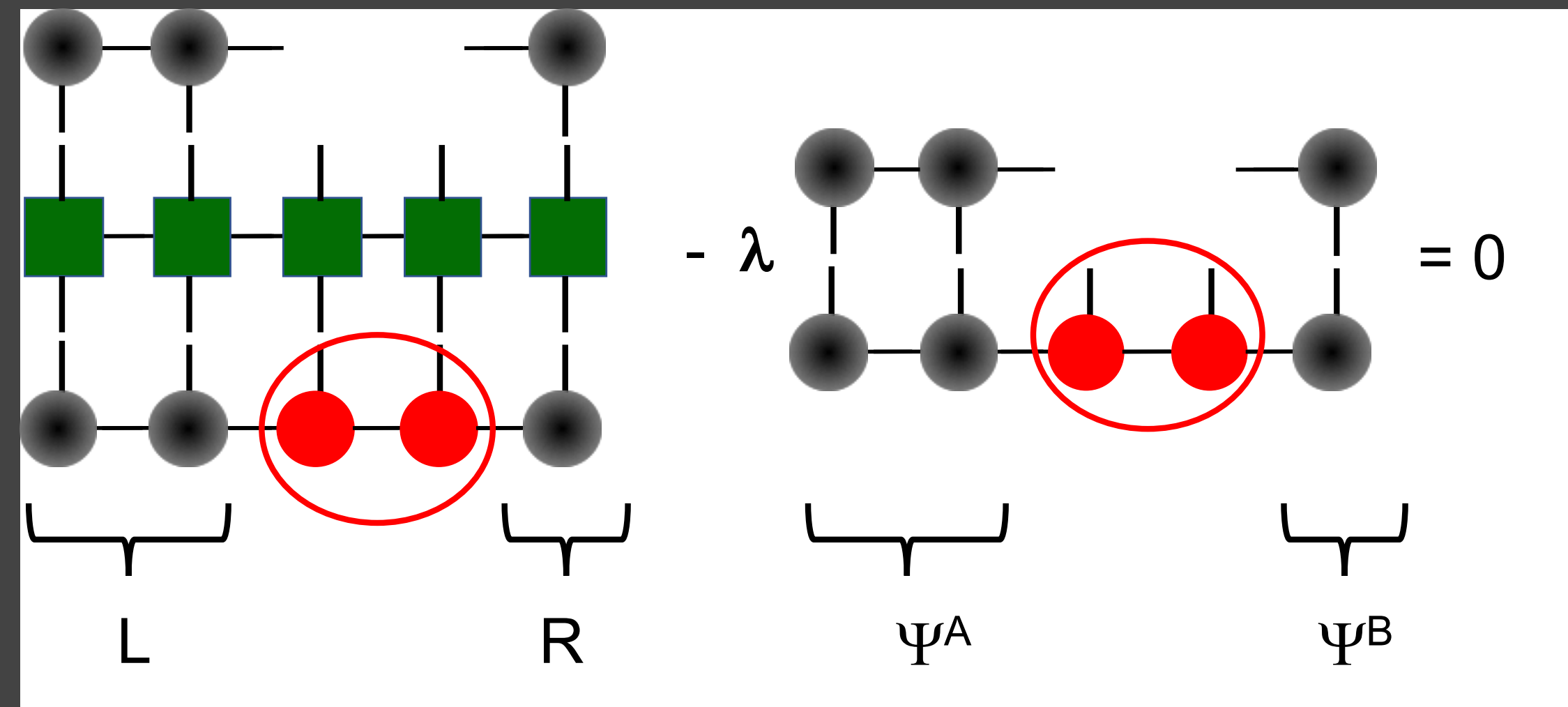
$$\sum_{\substack{a'_{l-1} a'_l \\ b_{l-1} b_{l+1}}} \sum_{k'_l k'_{l+1}} L^{b_{l-1}}_{a_{l-1}, a'_{l-1}} W^{k_l k_{l+1}, k'_l k'_{l+1}}_{b_{l-1}, b_{l+1}} R^{b_{l+1}}_{a'_{l+1}, a_{l+1}} M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}} = \lambda \sum_{a'_{l-1} a'_l} \Psi^A_{a'_{l-1}, a_{l-1}} \times M^{k'_l k'_{l+1}}_{a'_{l-1},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

- 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



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

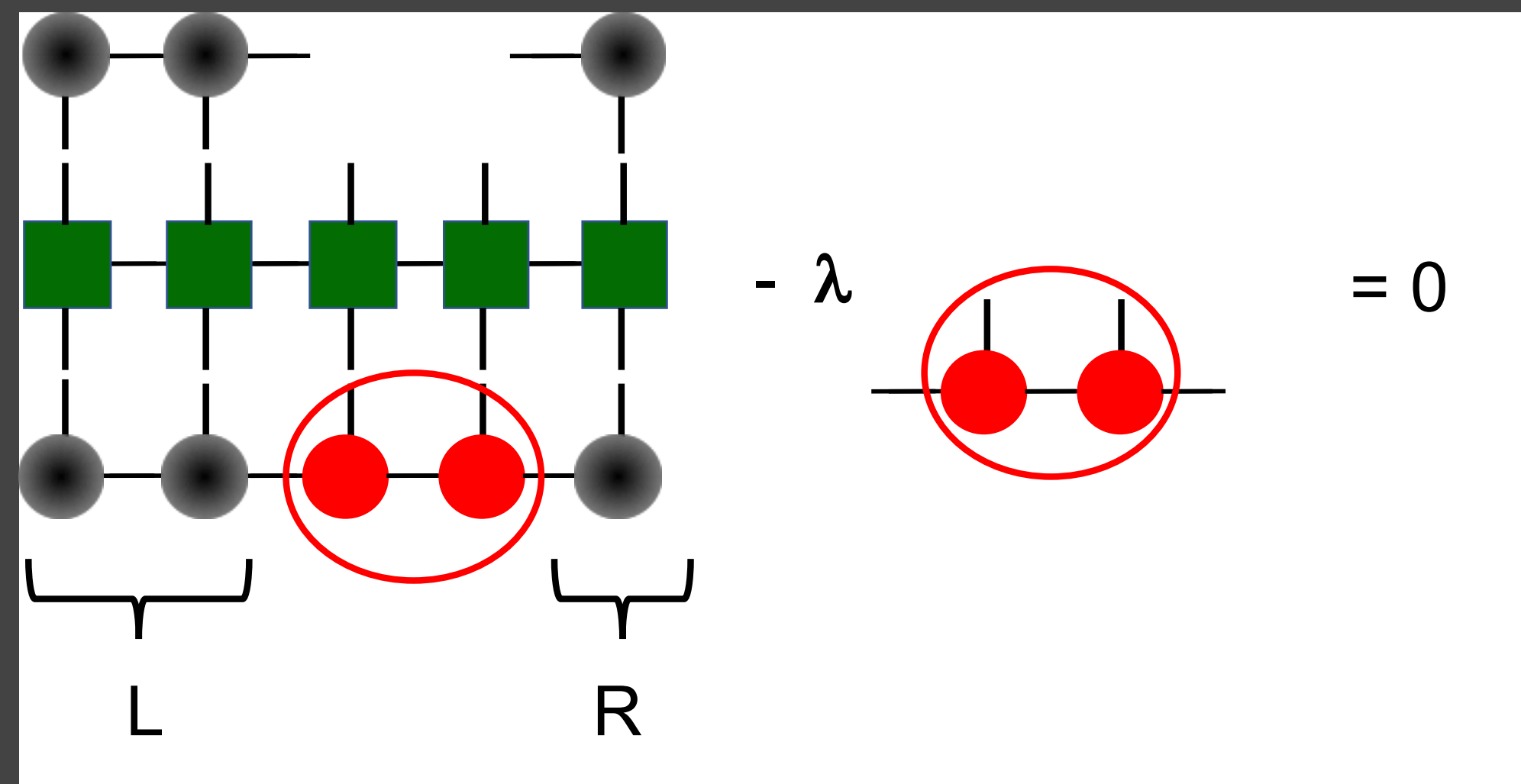


Variational MPS optimisation V

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

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

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

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

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

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

- and a vector v

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

- Solving EV problem \rightarrow eigenvalue λ^0 and corresponding eigenvector $v_{k'_l k'_{l+1} a'_{l-1} a'_{l+1}}^0$

Variational MPS optimisation VII

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

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

- 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

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

- Energy calculated as a function of the truncation error ϵ

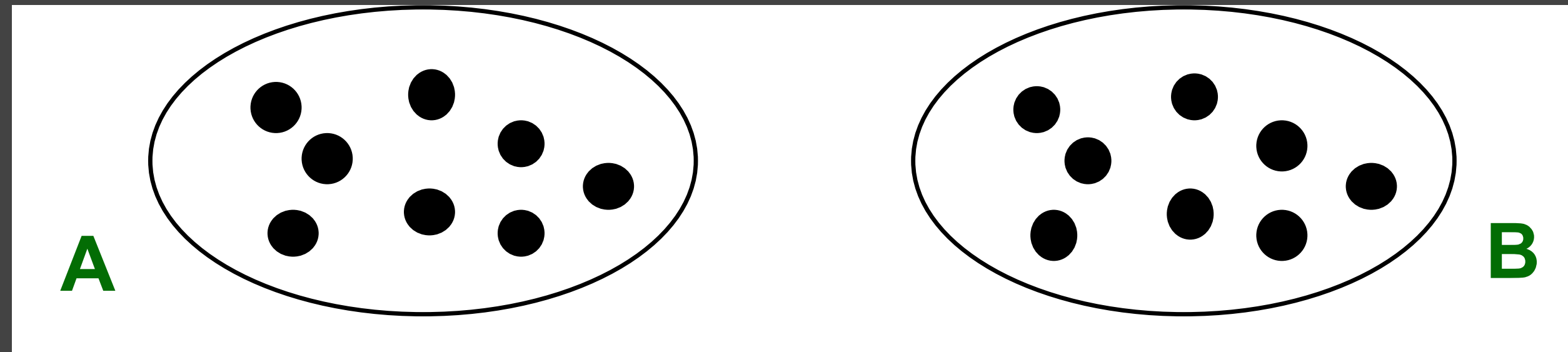
$$\epsilon = \sum_{s_l=m+1}^{4m} S_{s_l s_l} = ||\Psi_{16m^2} - \Psi_{4m^2}||$$

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
- **BUT:** Is the chosen approximation optimal in a least-square sense?

Optimal bipartition in a least square sense I

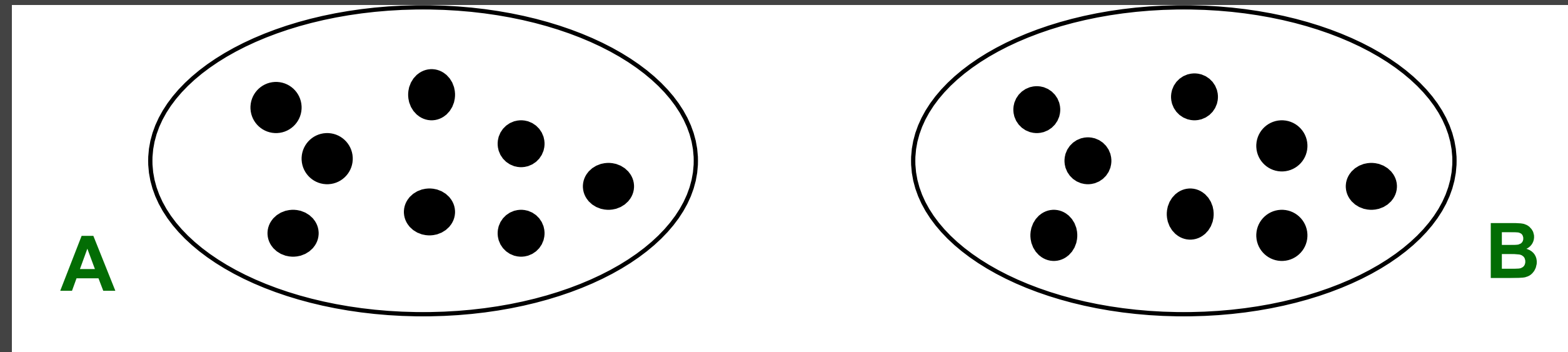


- **Given:** many-body state $|\Psi\rangle$ of composite system **AB**

$$|\Psi\rangle = \sum_{ij} C_{ij} |i\rangle_A \otimes |j\rangle_B$$

- $\{|i\rangle_A\}$ ($\{|j\rangle_B\}$) are orthonormal bases of **A** (**B**) with dimension N_A (N_B)

Optimal bipartition in a least square sense II



- SVD of $|\Psi\rangle = \sum_{ij} \sum_{a=1}^{\min(N_A, N_B)} U_{ia} S_{aa} V_{ja}^* |i\rangle_A |j\rangle_B$
 $= \sum_{a=1}^{\min(N_A, N_B)} \left(\sum_i U_{ia} |i\rangle_A \right) s_a \left(\sum_j V_{ja}^* |j\rangle_B \right)$
 $= \sum_{a=1}^{\min(N_A, N_B)} s_a |a\rangle_A |a\rangle_B$

Optimal bipartition in a least square sense III

- Restricting the sum in last equation to some value $m' \leq \min(N_A, N_B)$ yields the *Schmidt decomposition*

$$|\Psi\rangle = \sum_{a=1}^{m'} s_a |a\rangle_A |a\rangle_B$$

where $m' = 1$ corresponds to (classical) product states and $m' > 1$ to entangled (quantum) states

- For orthonormal states in **A** and **B**, the two-norm $||\Psi||_2^2$ is identical to the Frobenius norm of the matrix $\{C_{ij}\}$

$$||\Psi||_2^2 = ||C||_F^2 = \sum_{a=1}^{\min(N_A, N_B)} s_a^2$$

Optimal bipartition in a least square sense IV

- Hence, an optimal approximation $|\tilde{\Psi}\rangle$ to $|\Psi\rangle$ with respect to the 2-norm immediately follows from optimal approximation of \mathbf{C} by $\tilde{\mathbf{C}}$ in the Frobenius norm, with $\tilde{\mathbf{C}}$ being a matrix of rank $m \leq m'$

$$|\tilde{\Psi}\rangle = \sum_{a=1}^m s_a |a\rangle_A |a\rangle_B$$

- **BUT:** how does this relate to the truncation (dimensionality reduction) in the variational MPS optimization?

Optimal bipartition in a least square sense V

- SVD of MPS in mixed-canonical form at site l

$$\begin{aligned}
 |\Psi\rangle &= \sum_{\substack{k_1, \dots, k_L \\ a_1, \dots, a_{L-1}}} A_{1,a_1}^{k_1} \cdots A_{a_{l-1},a_l}^{k_l} S_{a_l,a_l} B_{a_l,a_{l+1}}^{k_{l+1}} \cdots B_{a_{L-1},1}^{k_L} |k_1, \dots, k_l, \dots, k_L\rangle \\
 &= \sum_{a_l} \left(\sum_{\substack{k_1, \dots, k_l \\ a_1, \dots, a_{l-1}}} A_{1,a_1}^{k_1} \cdots A_{a_{l-1},a_l}^{k_l} |k_1, \dots, k_l\rangle \right) \cdot S_{a_l,a_l} \cdot \\
 &\quad \left(\sum_{\substack{k_{l+1}, \dots, k_L \\ a_{l+1}, \dots, a_{L-1}}} B_{a_l,a_{l+1}}^{k_{l+1}} \cdots B_{a_{L-1},1}^{k_L} |k_{l+1}, \dots, k_L\rangle \right) \\
 &= \sum_{a_l} S_{a_l,a_l} |a_l\rangle_{\mathcal{L}} |a_l\rangle_{\mathcal{R}}
 \end{aligned}$$

Optimal bipartition in a least square sense VI

- Comparison of last equation and the **Schmidt decomposition** immediately reveals that *an optimal bipartition in a least square sense* can be obtained for $|\tilde{\Psi}\rangle$ from an SVD retaining the lowest m values with $m < \dim(|\Psi\rangle)$

$$|\tilde{\Psi}\rangle = \sum_{a_l=1}^r s_{a_l a_l} |a_l\rangle_{\mathcal{L}} |a_l\rangle_{\mathcal{R}}$$

Scaling of variational MPS optimisation

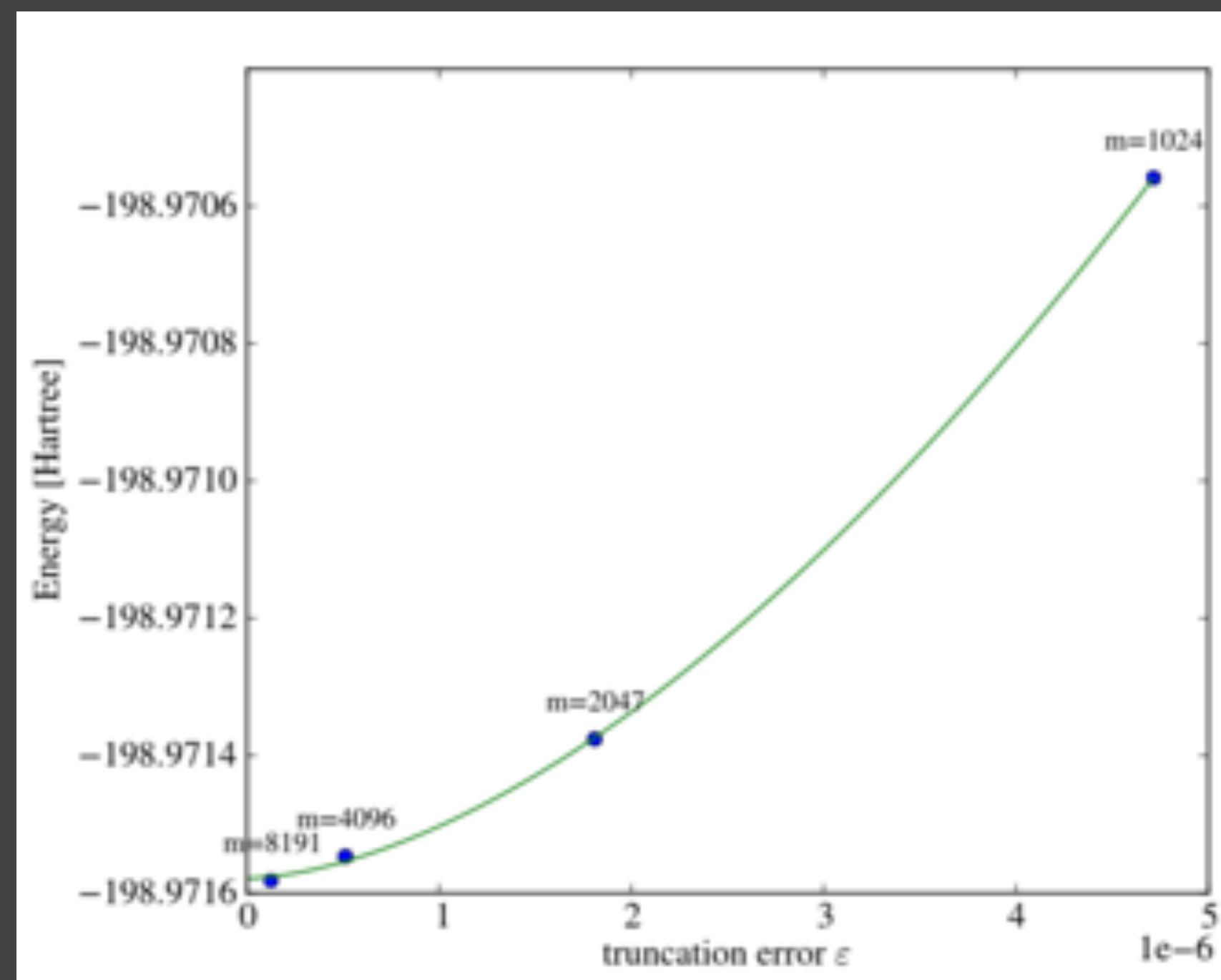
- **Scaling is dominated** by cost of contracting the operator with the MPS on one site and is proportional to the number of non-zero elements in the MPO matrices $\{\widehat{W}\}$
 - in a naïve MPO ansatz this step scales as $\mathcal{O}(L^5)$
 - in an optimized code scaling reduces to $\mathcal{O}(L^4)$
- 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

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

- 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

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

CASCI

- 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-Quantum Monte Carlo 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 ...



Quantum Chemistry on a Quantum Computer: Concepts and Challenges

Some important references

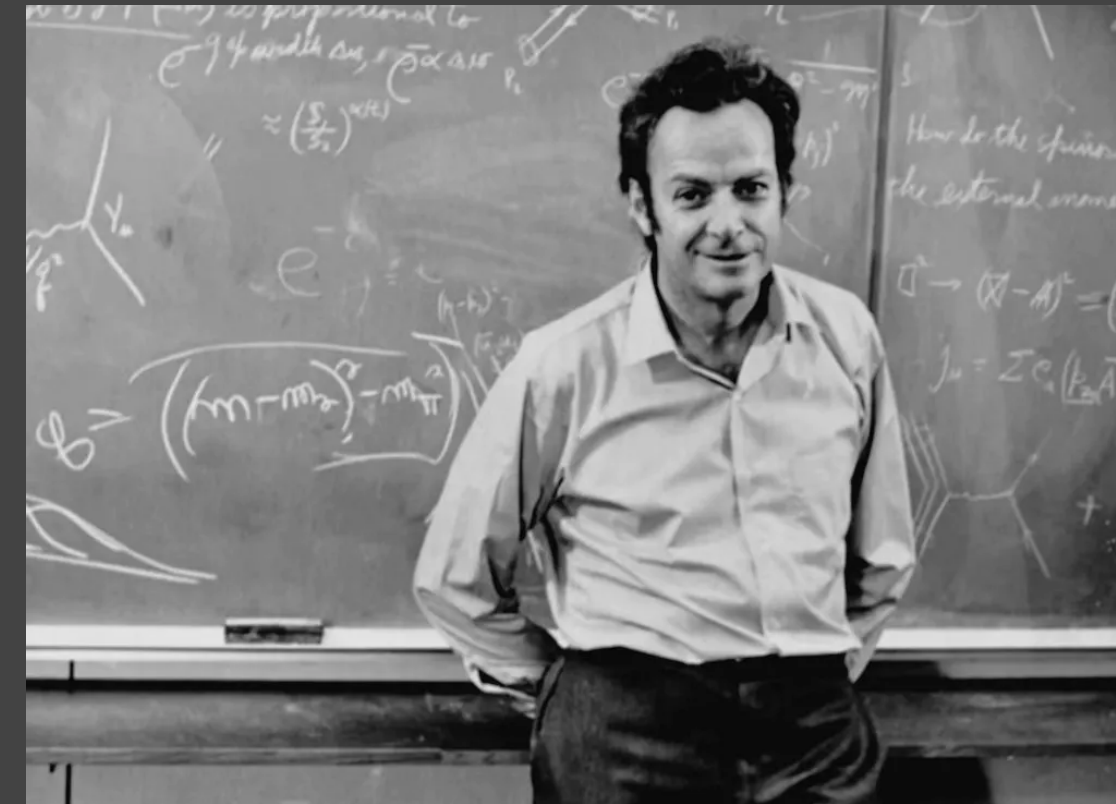
- Quantum computational chemistry
McArdle, Endo, Aspuru-Guzik, Benjamin, Yuan, Rev. Mod. Phys. **92**, 015003 (2020)
- An adaptive variational algorithm for exact molecular simulations on a quantum computer
Grimsley, Economou, Barnes, Mayhall, Nat. Comm. **10**, 3007 (2019)
- Learning to measure: adaptive informationally complete generalized measurements for quantum algorithms
García-Pérez, Rossi, Sokolov, Tacchino, Barkoutsos, Mazzola, Tavernelli, Maniscalco, PRX Quantum **2**, 040342 (2021)
- Optimal fermion-to-qubit mapping via ternary trees with applications to reduced quantum states learning
Jiang, Kalev, Mruczkiewicz, Neven, Quantum **4**, 276 (2020)
- Efficient and noise resilient measurements for quantum chemistry on near-term quantum computers
Huggins, McClean, Rubin, Jiang, Wiebe, Birgitta Whaley, Babbush, npj Quant. Inf. **7**, 23 (2021)
- Hybrid Quantum-Classical Algorithms and Quantum Error Mitigation
Endo, Cai, Benjamin, Yuan, J. Phys. Soc. Japan., **90**, 032001 (2021)

The origins of quantum computing

Simulating quantum physics



Yuri Manin
1980



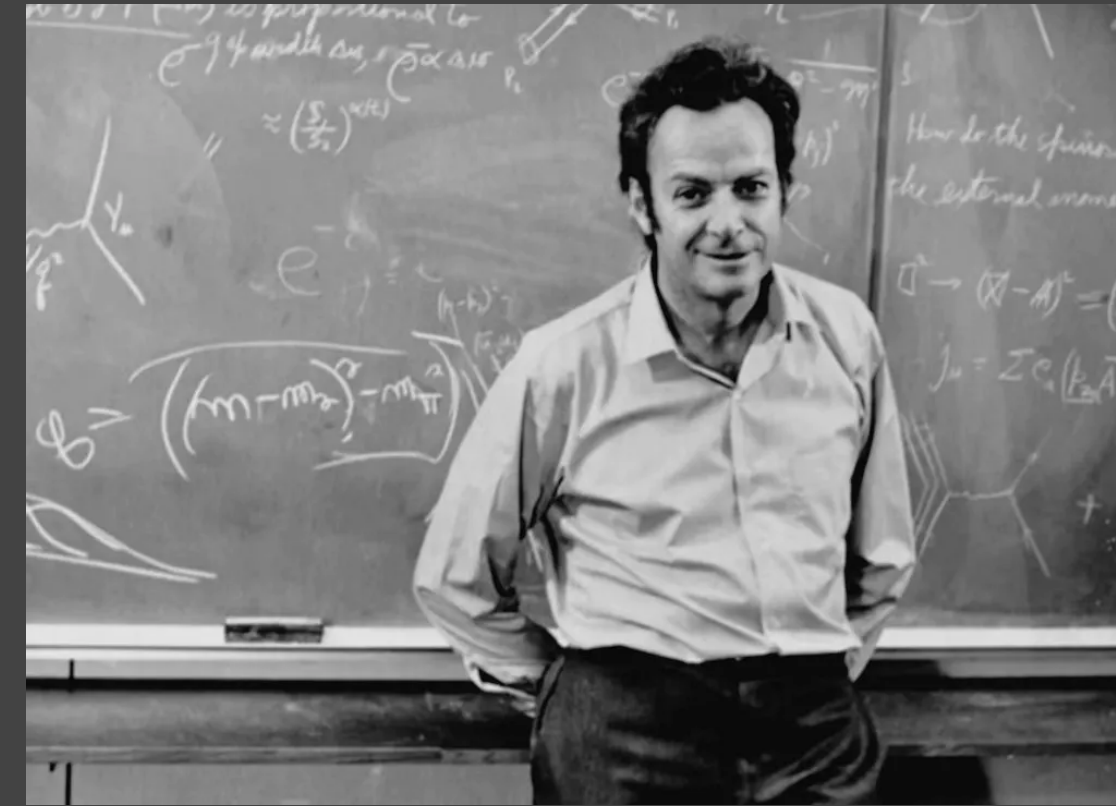
Richard Feynman
1982

The origins of quantum computing

Simulating quantum physics



Yuri Manin
1980



Richard Feynman
1982

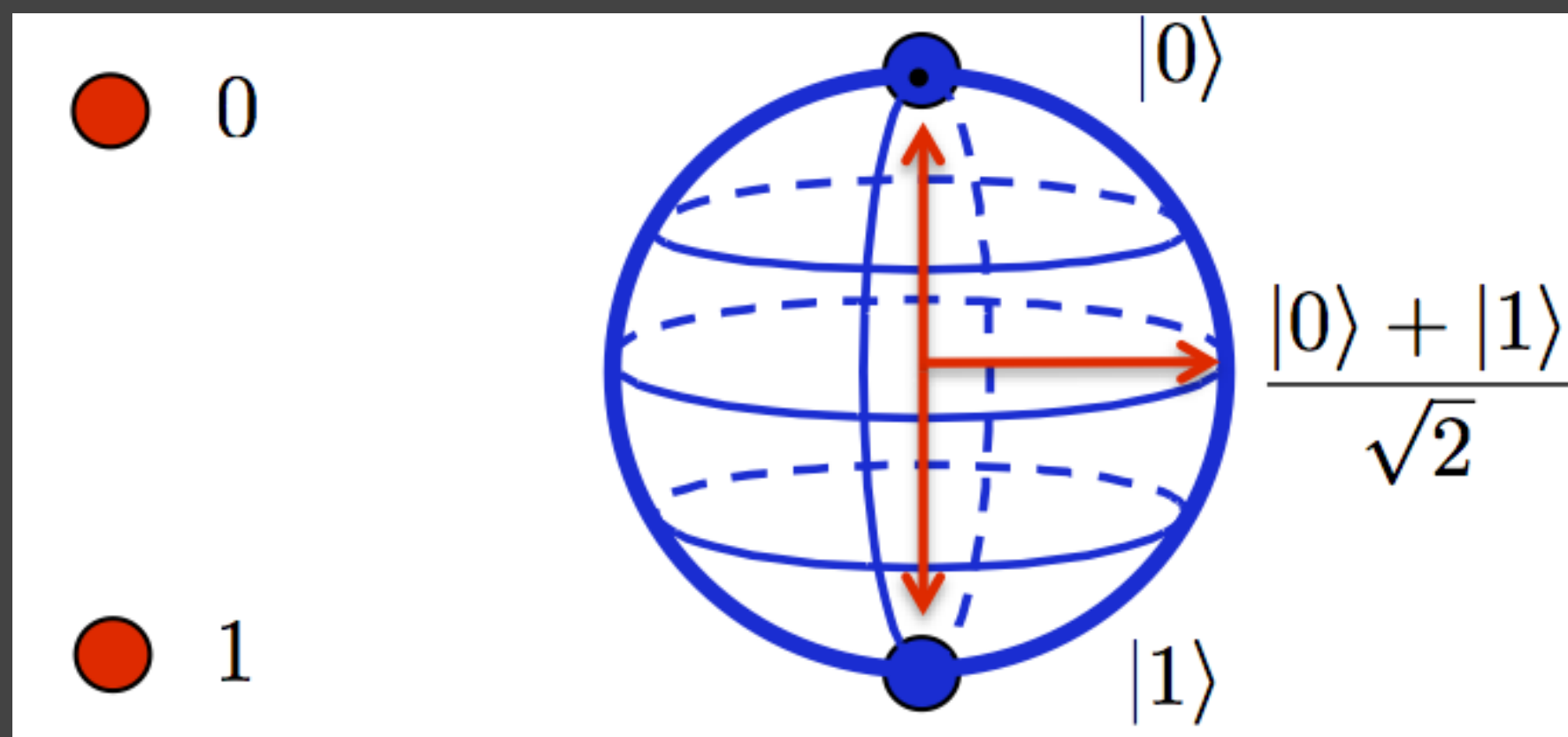
Simulating some quantum mechanical effects on a classical computer is unfeasible



Use a quantum one!

The origins of quantum computing

Simulating quantum physics



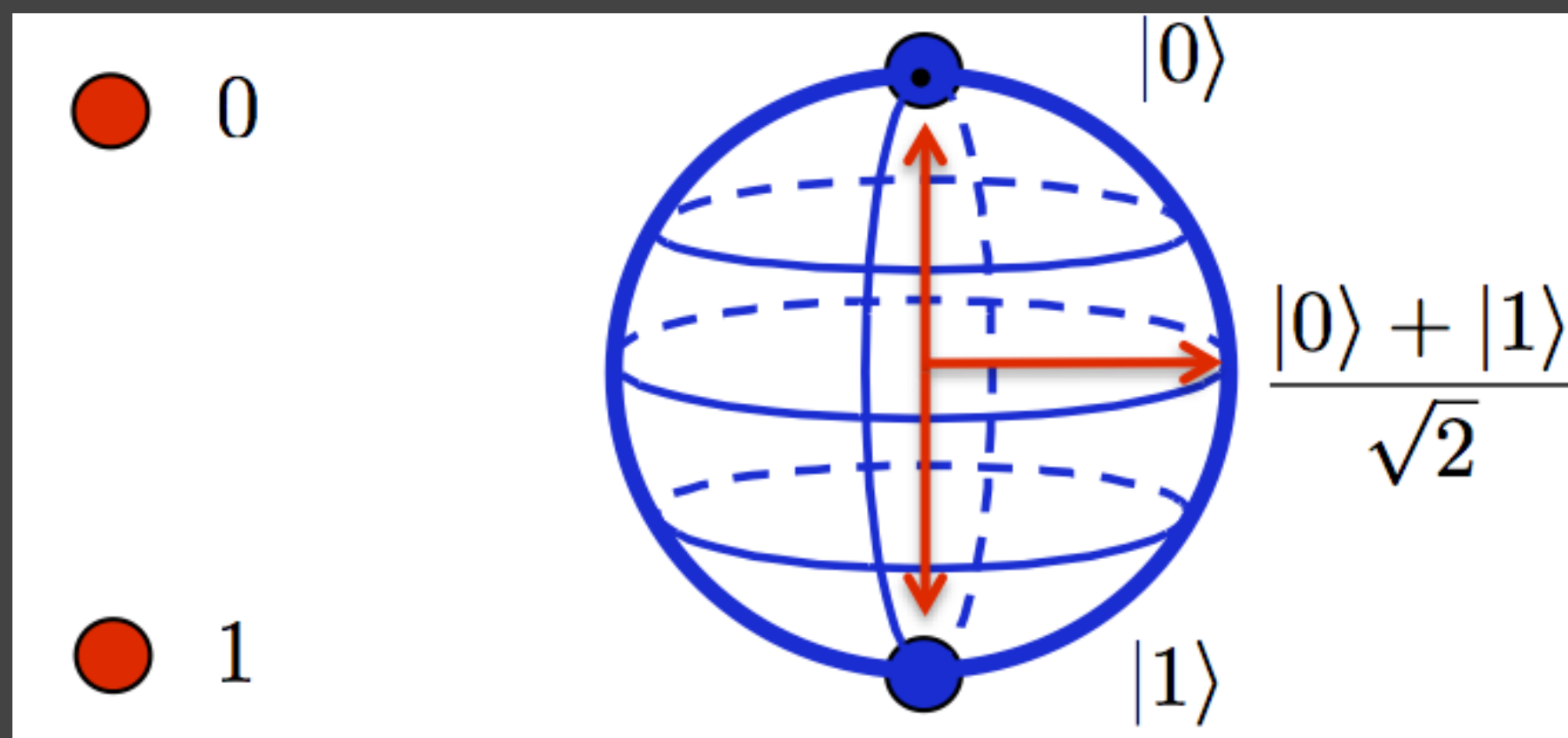
- Classical bit can be **either** in state $|0\rangle$ **or** state $|1\rangle$
- Qubit can be in a **superposition** of both states

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

From **bits** to ... \longrightarrow **qubits**

The origins of quantum computing

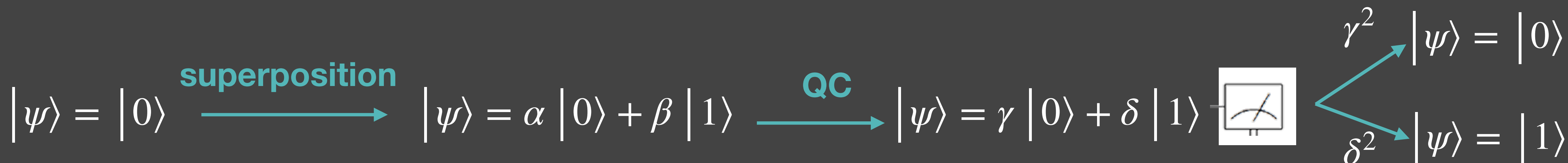
Simulating quantum physics



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

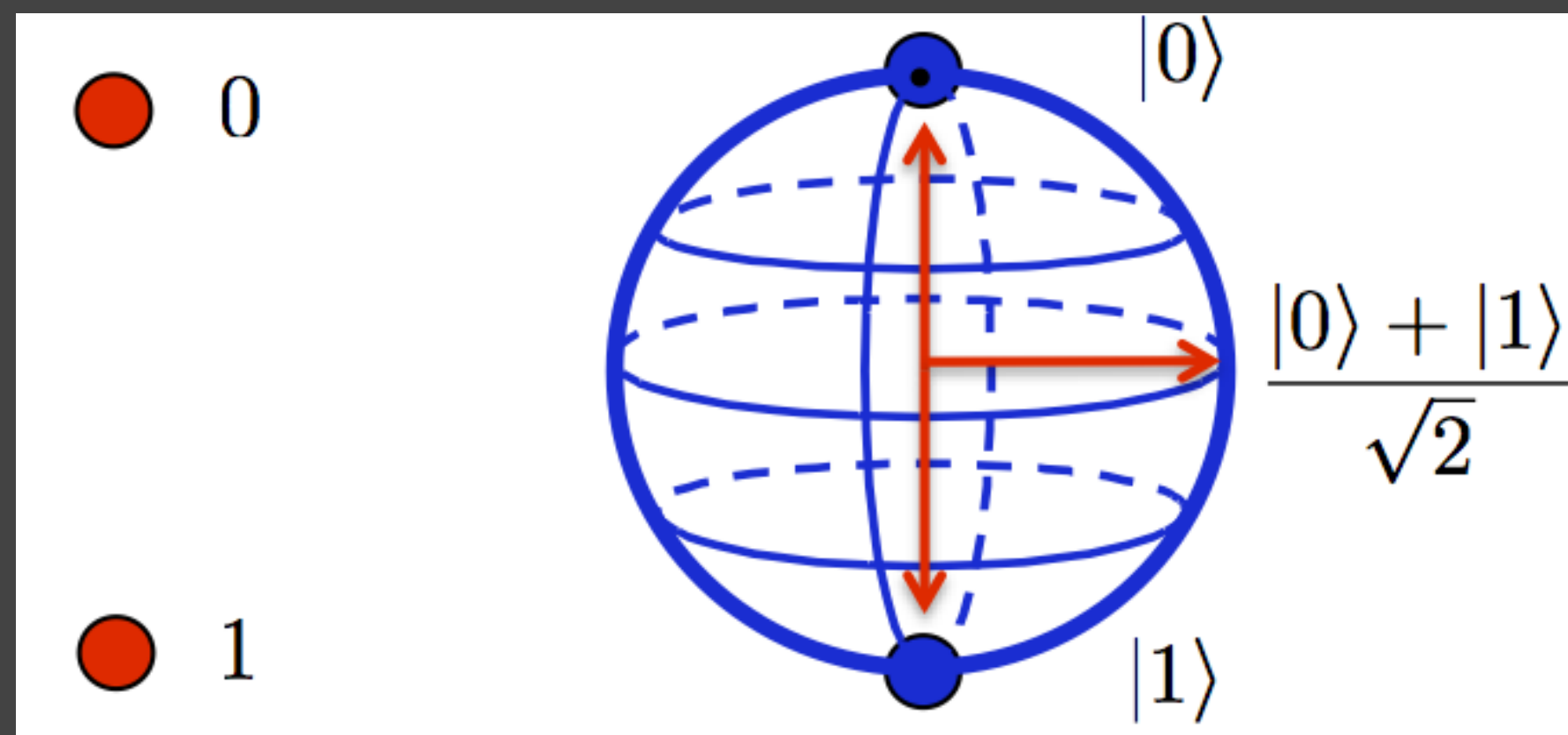
$$|\psi\rangle = \alpha |0\rangle + \beta |1\rangle \equiv \alpha \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \beta \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

From **bits** to ... \longrightarrow **qubits**



The origins of quantum computing

Simulating quantum physics



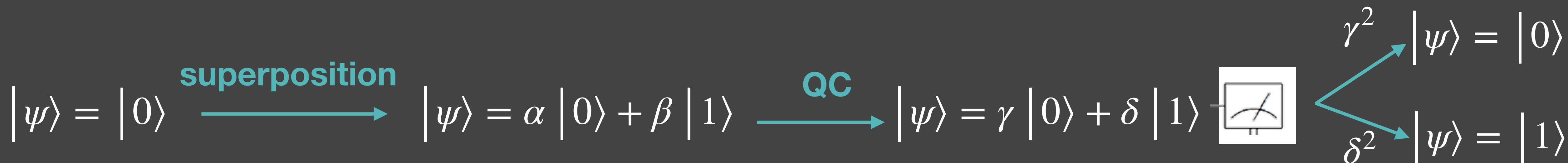
- Classical bit can be **either** in state $|0\rangle$ **or** state $|1\rangle$
- Qubit can be in a **superposition** of both states

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

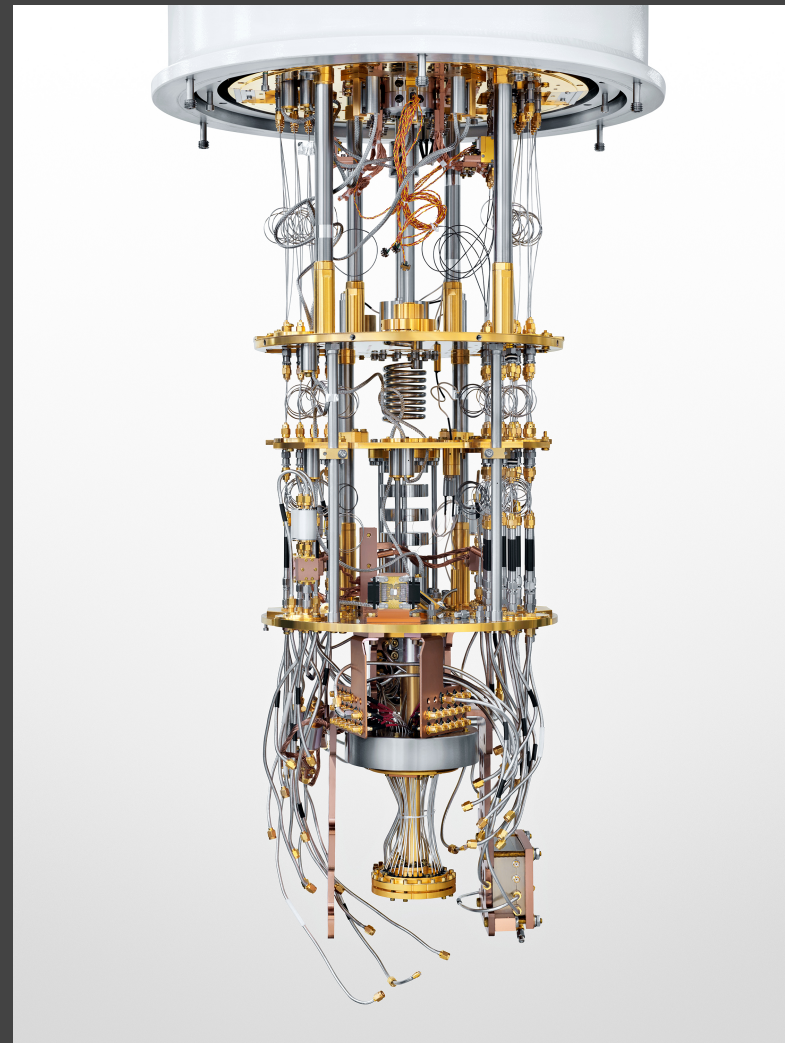
From **bits** to ... \longrightarrow **qubits**

- Measuring the state of the qubit with probability P

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



Using a quantum computer as a quantum physics simulator

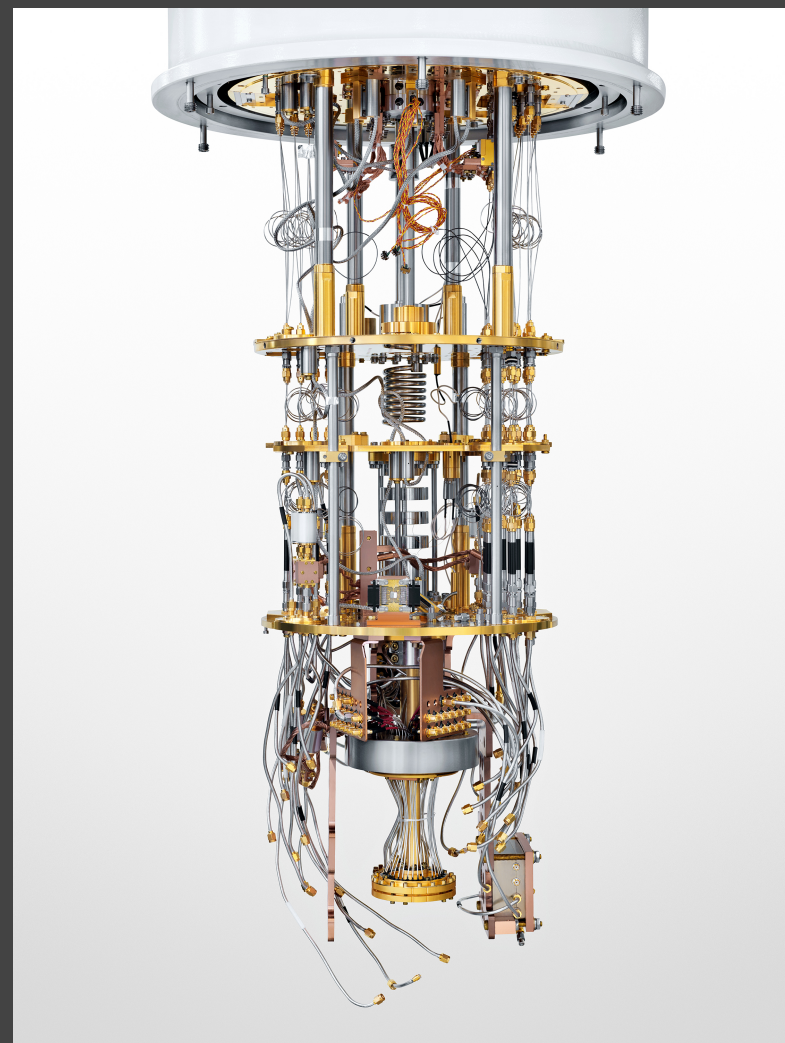


Arbitrary state of its qubits

→

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

Using a quantum computer as a quantum physics simulator

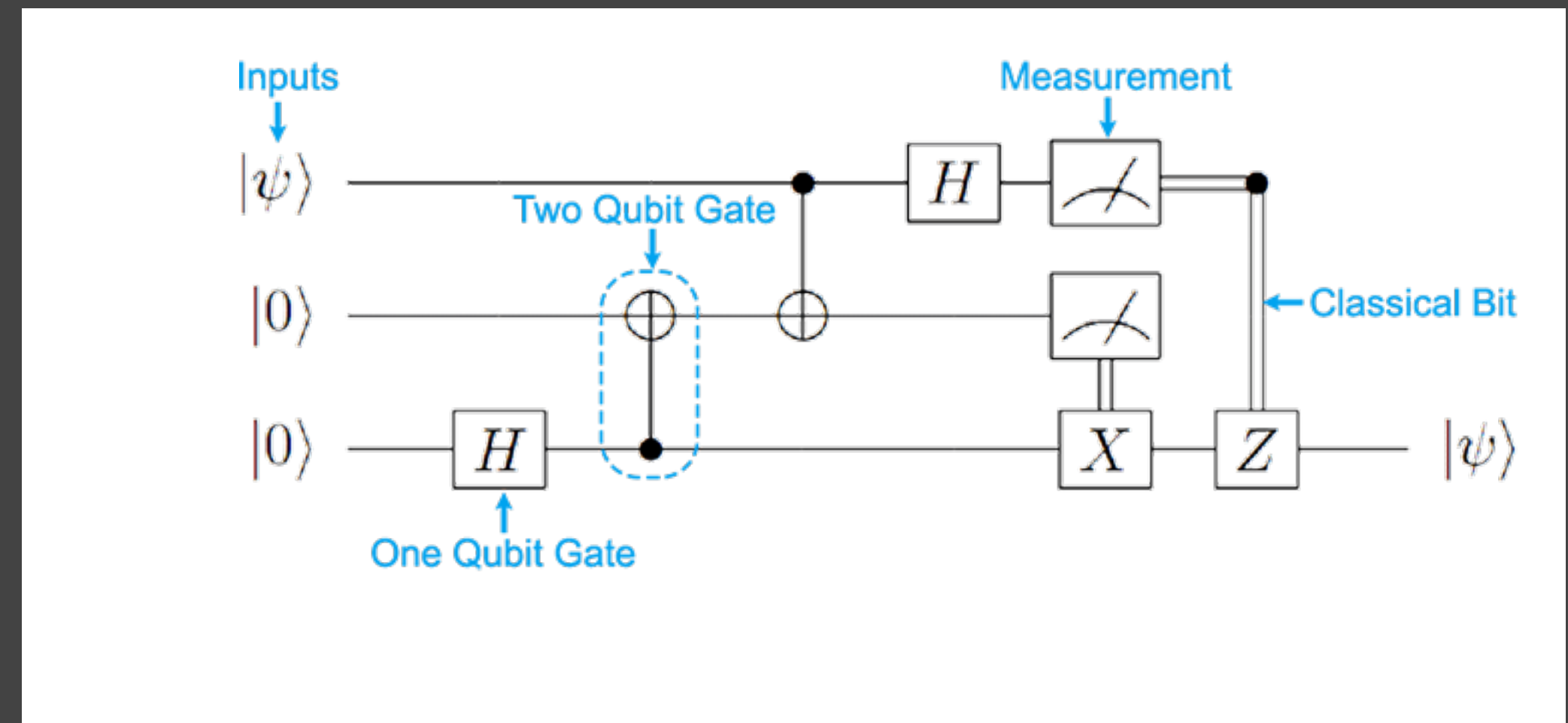


Arbitrary state of its qubits

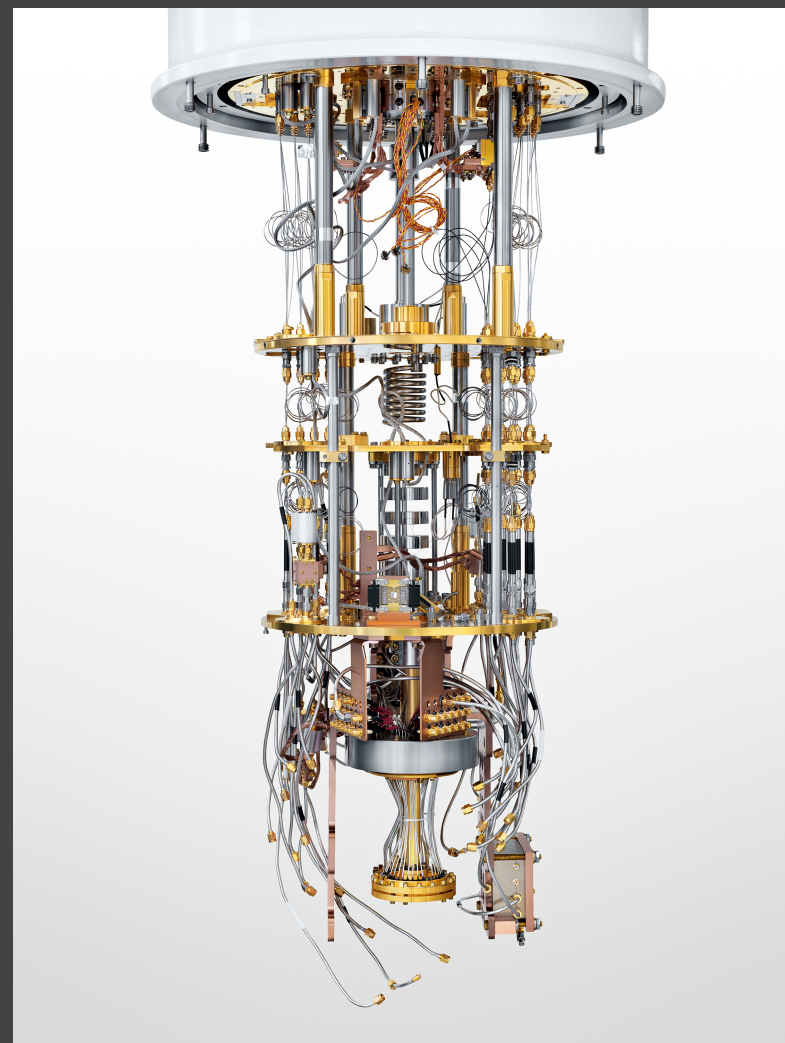
↓

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

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



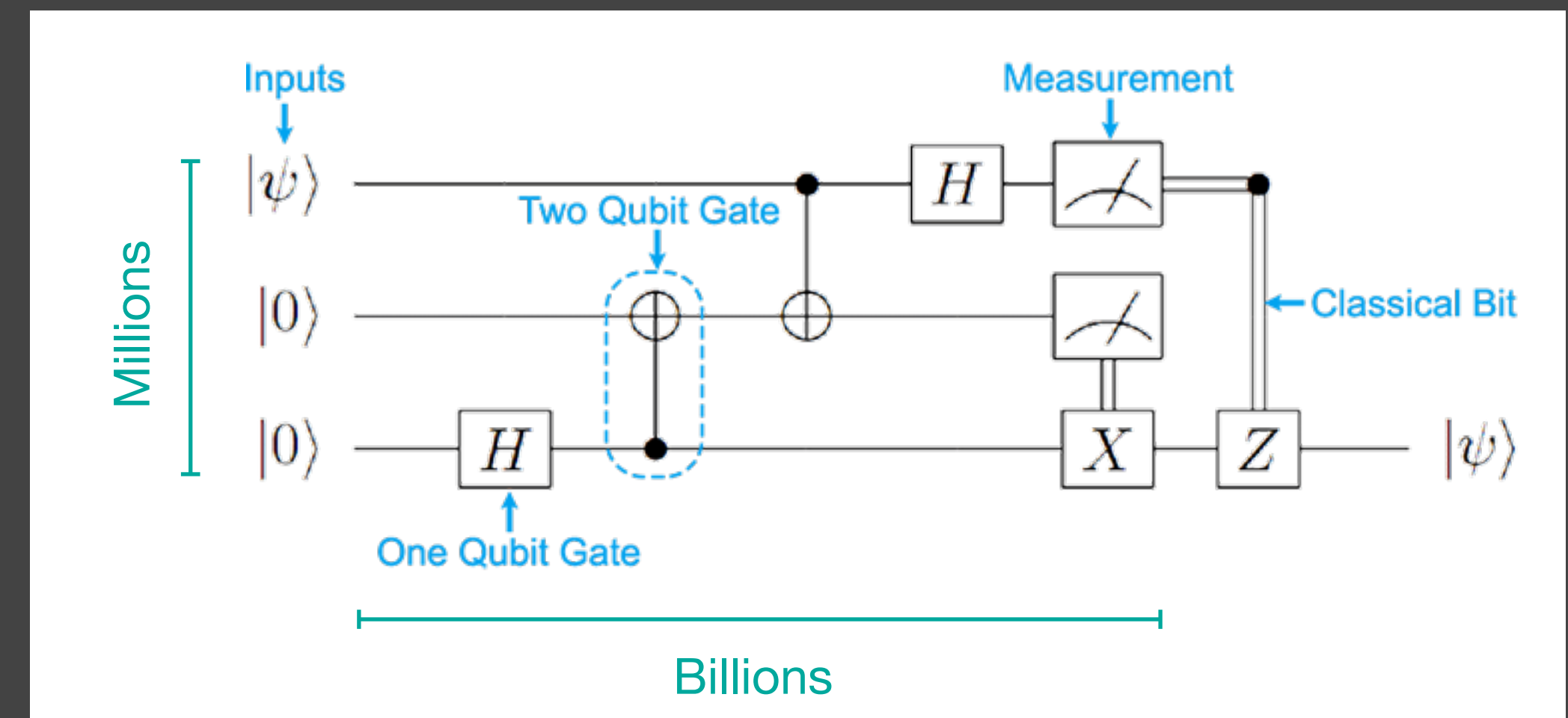
Using a quantum computer as a quantum physics simulator



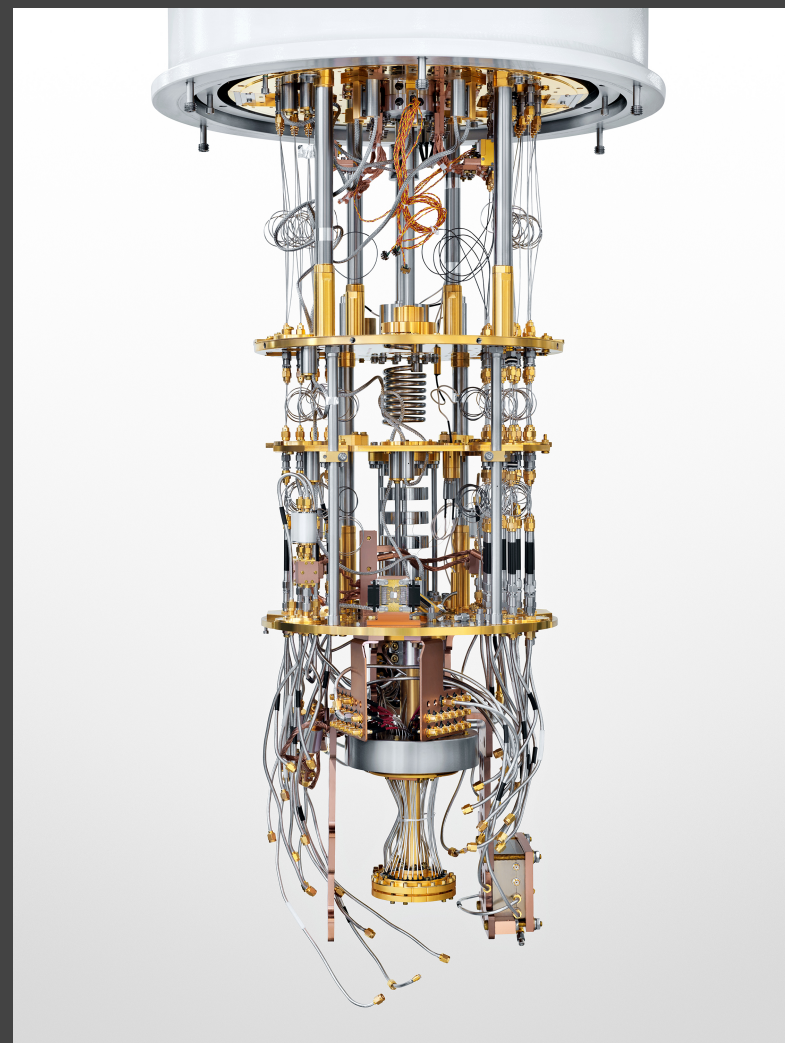
Arbitrary state of its qubits

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

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



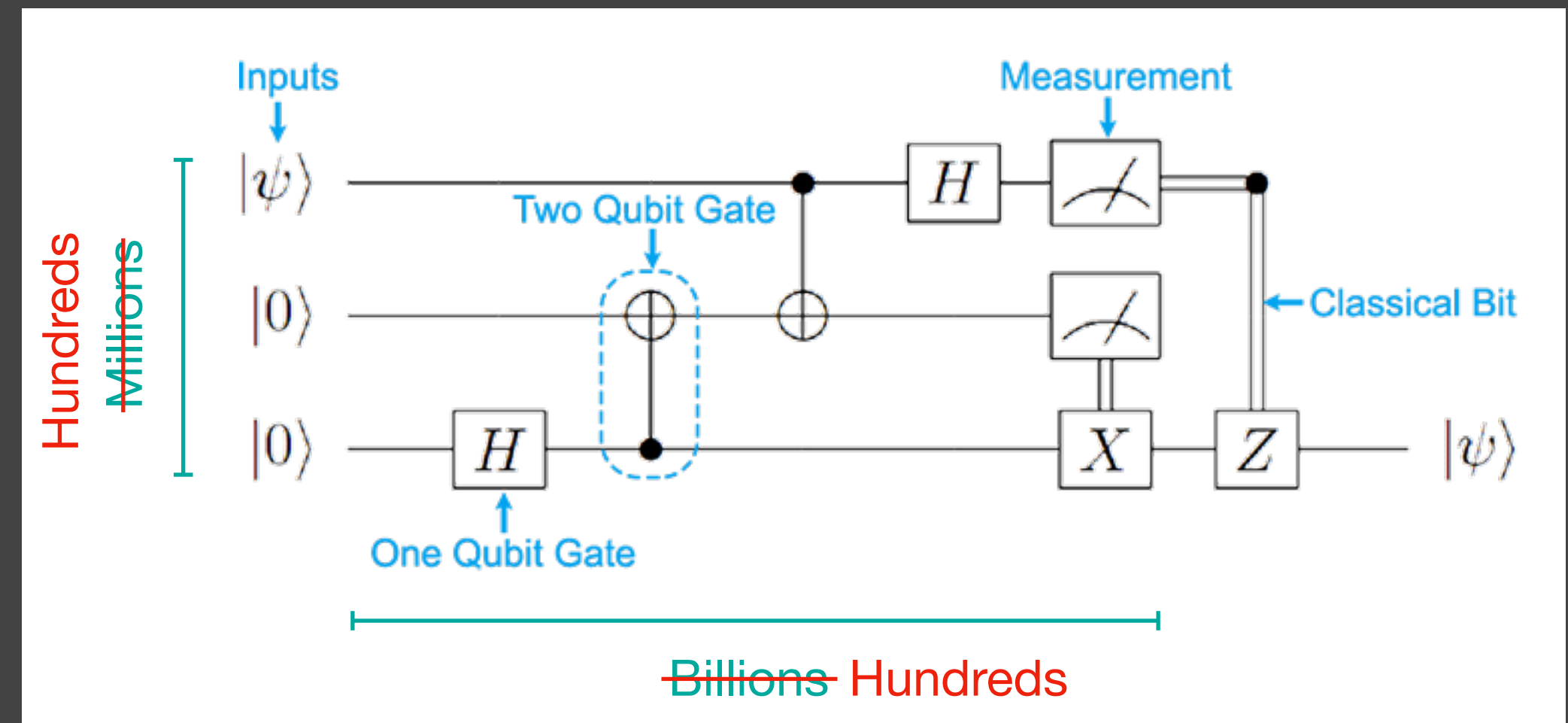
Using a quantum computer as a quantum physics simulator



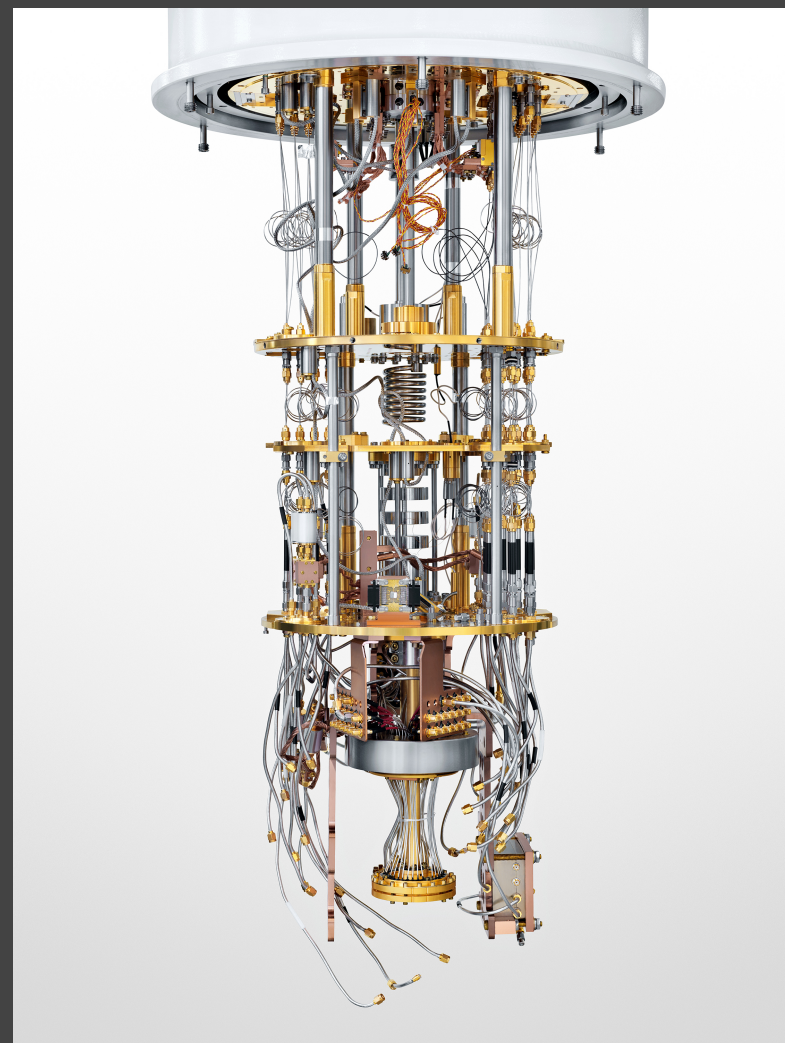
Arbitrary state of its qubits

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

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



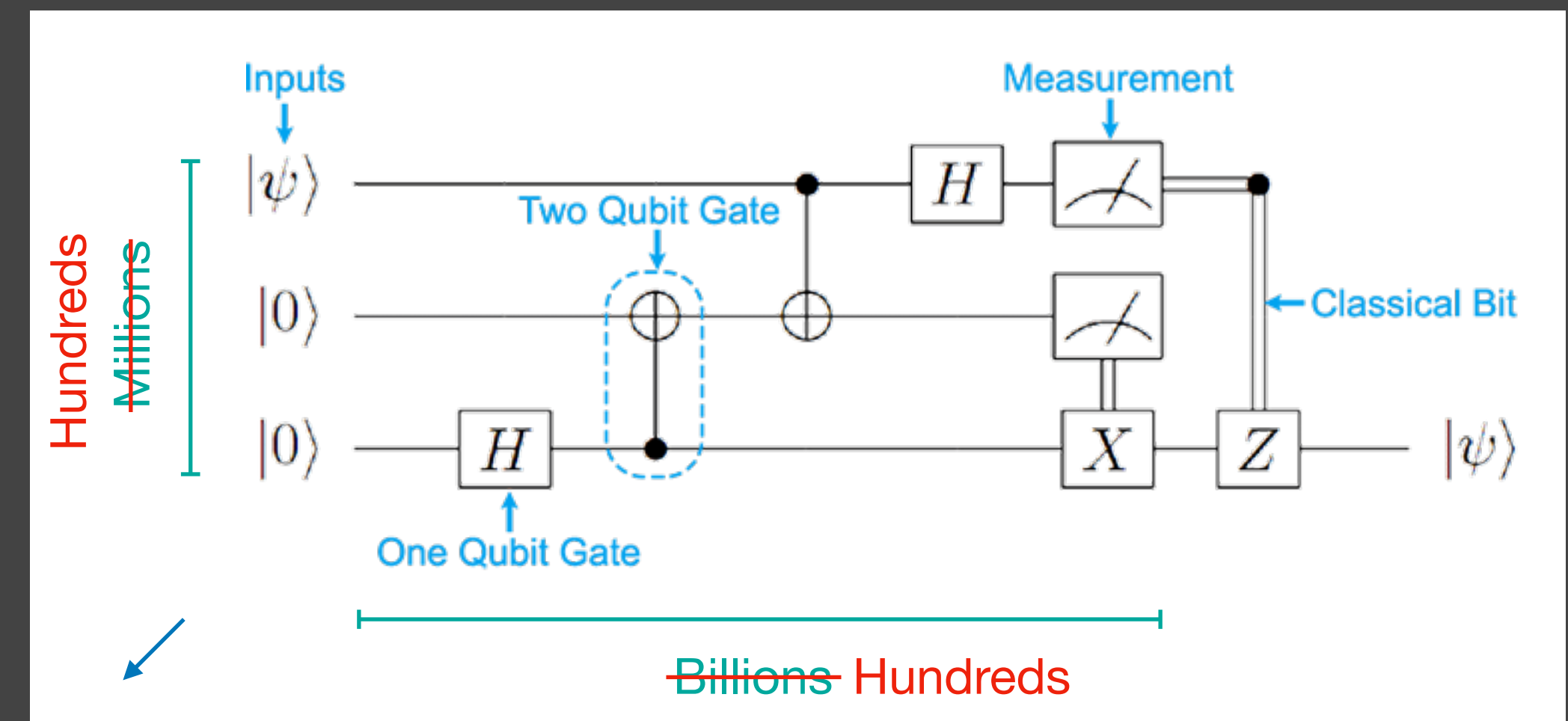
Using a quantum computer as a quantum physics simulator



Arbitrary state of its qubits

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

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

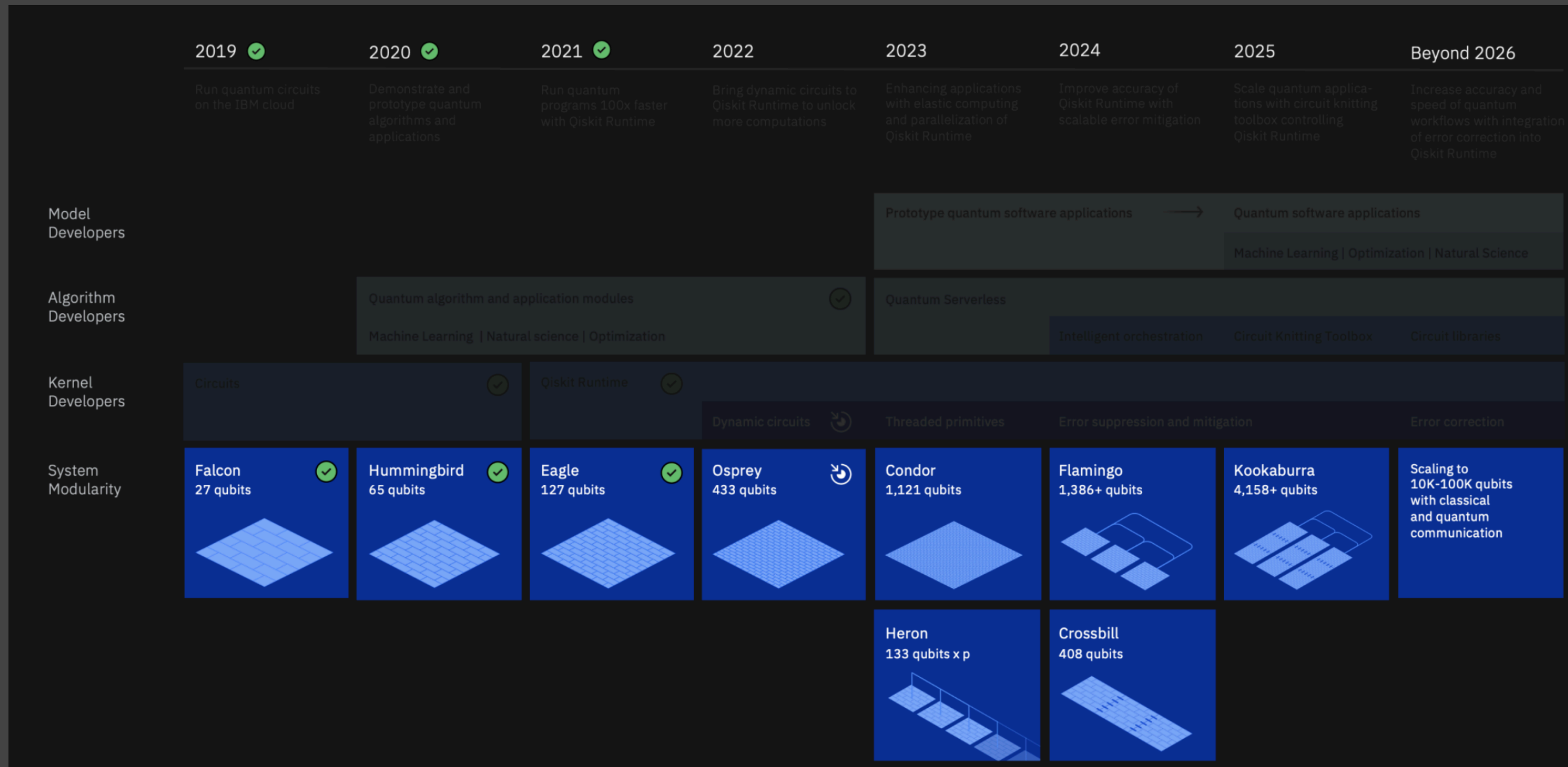


We are in the era of the Noisy Intermediate-Scale Quantum computers: soon useful for simulation!

Quantum 5, 433 (2021)

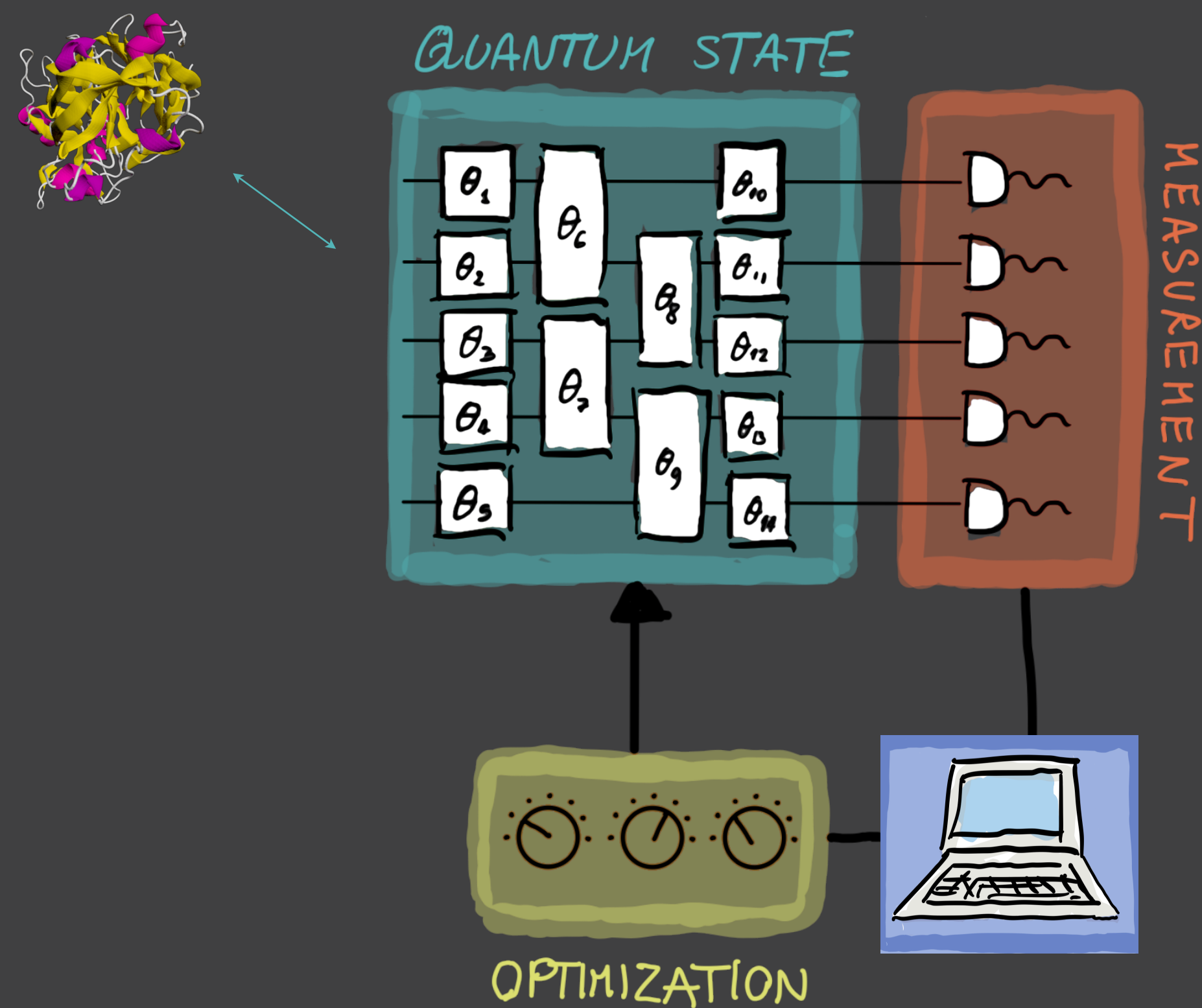
Ressource estimates

Roadmap of IBM (others have similar plans)



Quantum chemistry simulation

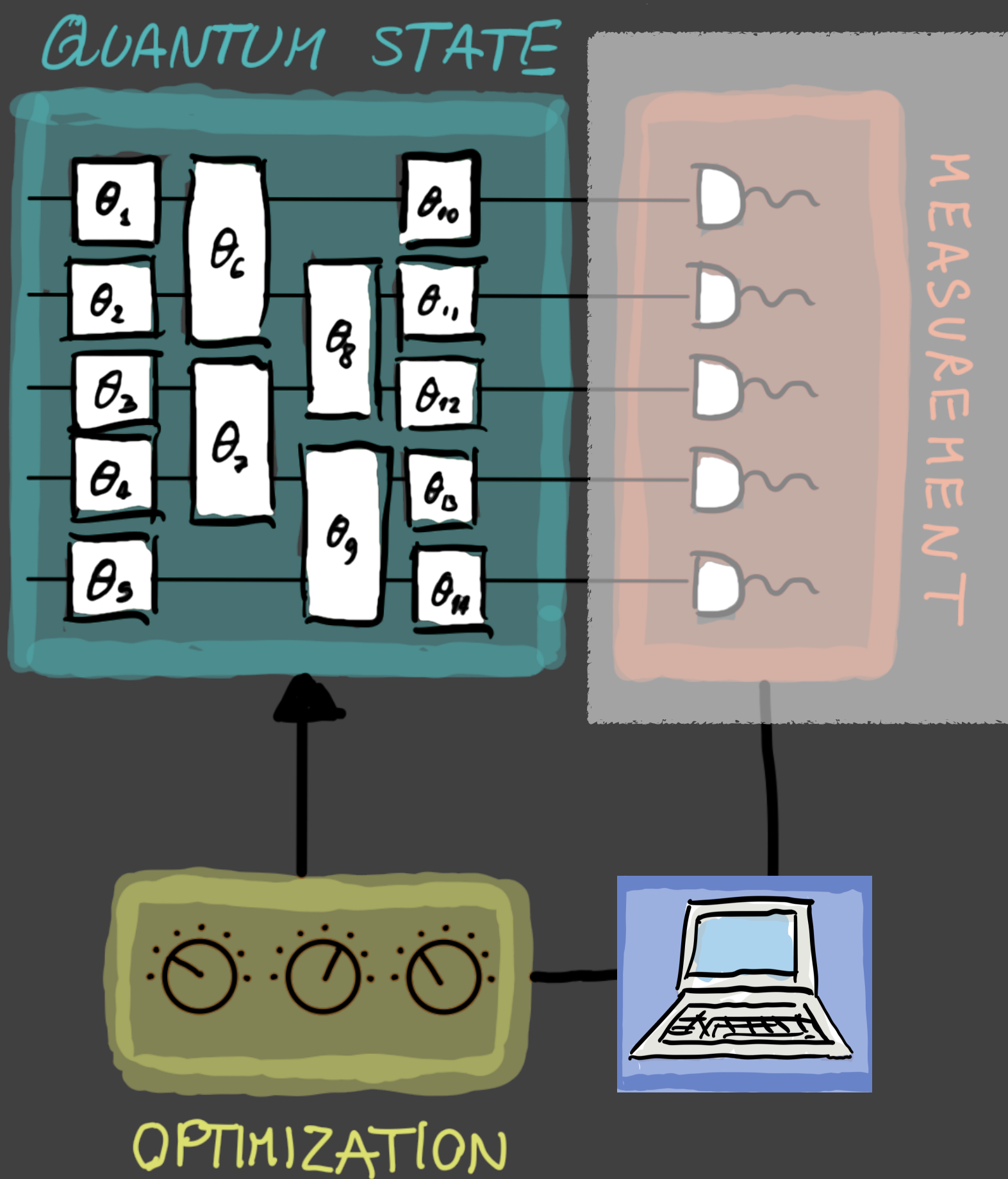
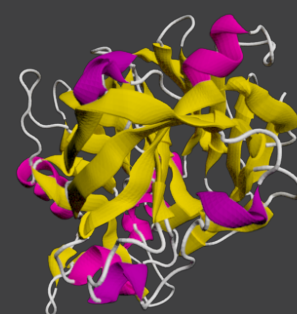
in a nutshell



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

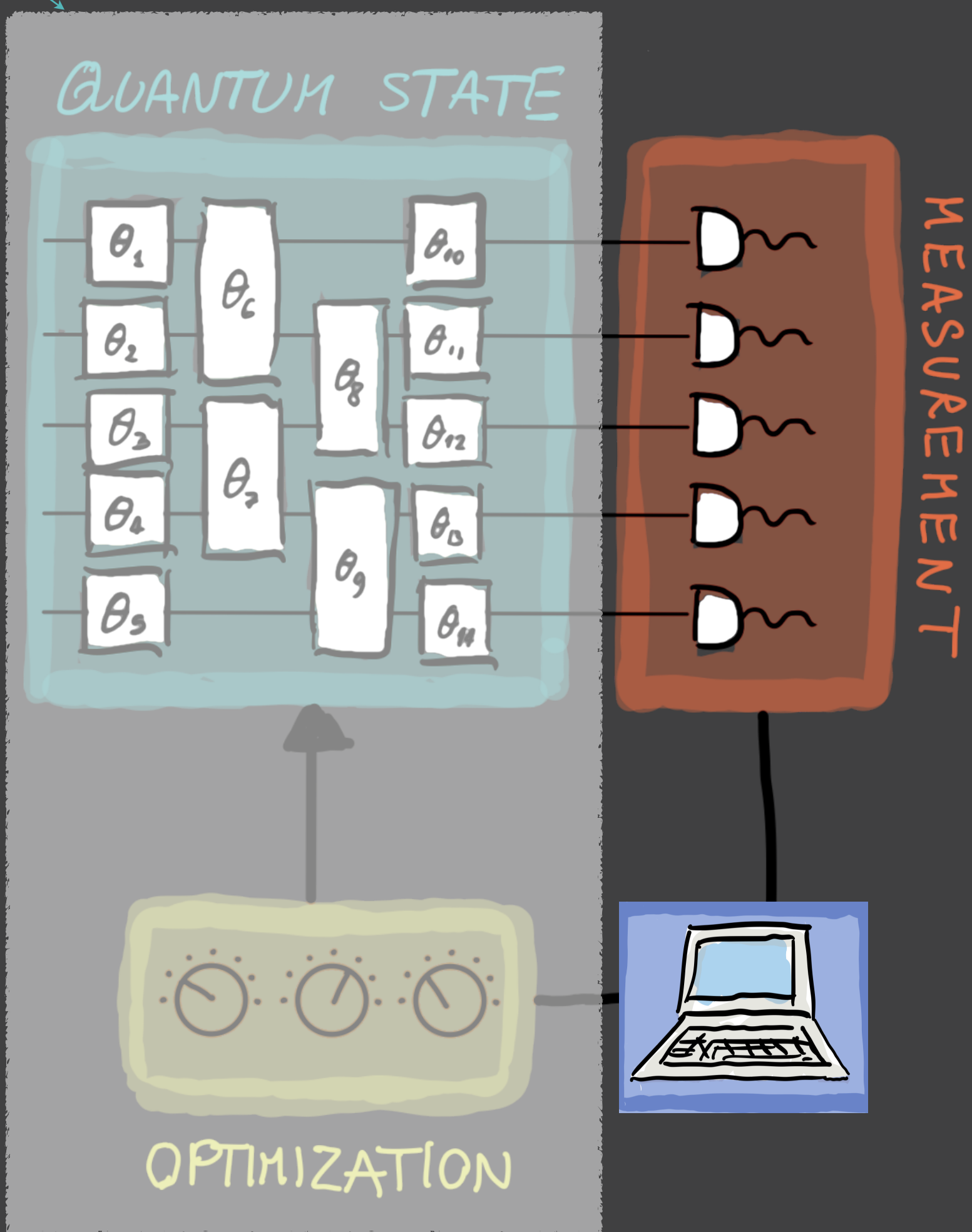
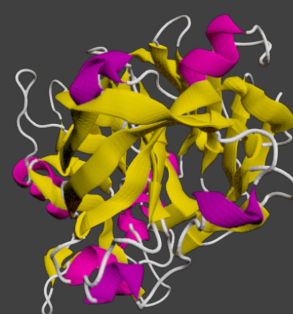
The goal is to find the state of the molecule for which the **energy is minimal**

The energy of the molecule needs to be **measured**



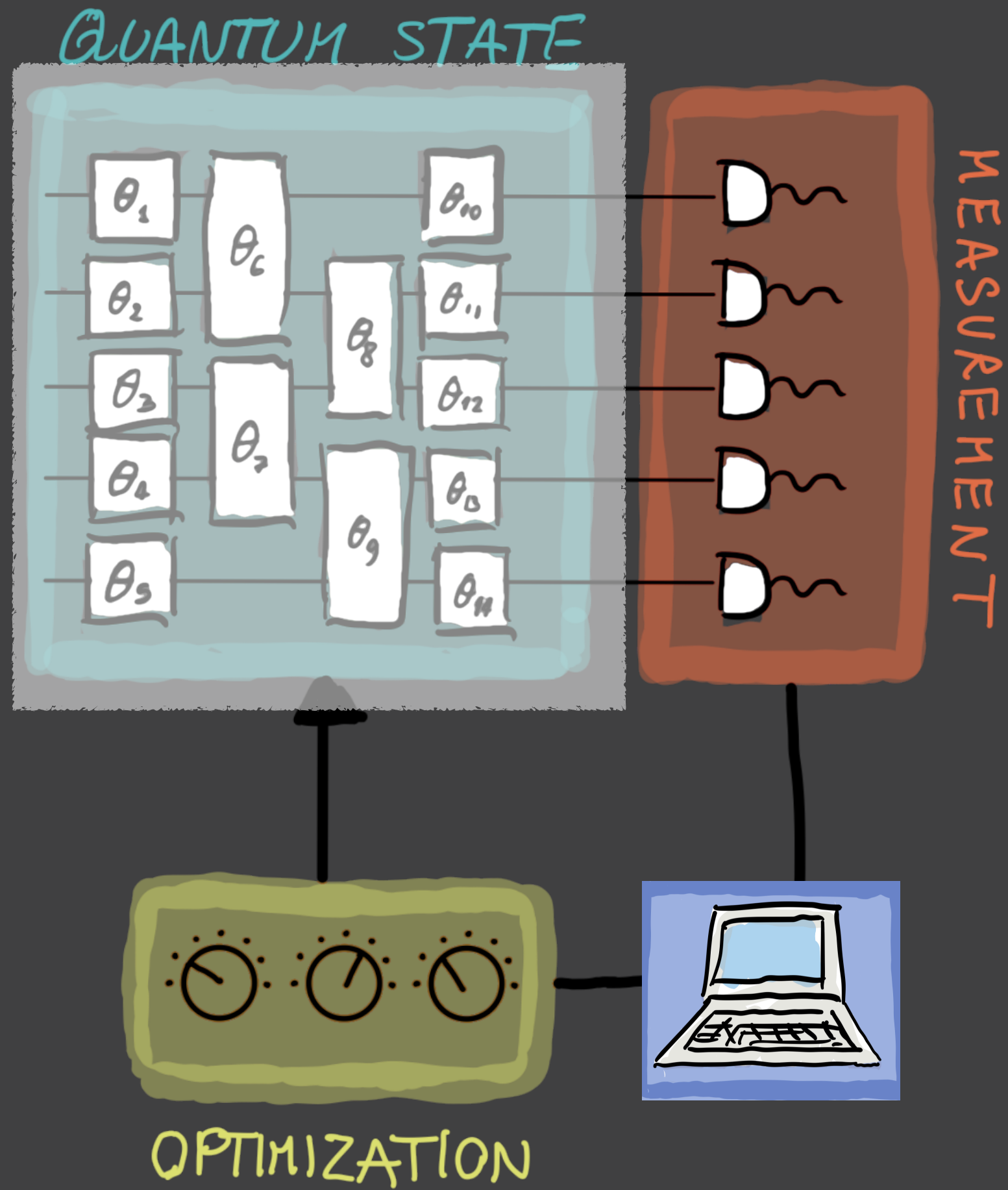
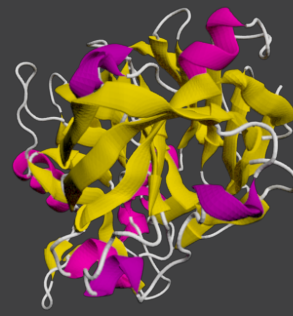
Challenges

- Measurement stage is time-consuming



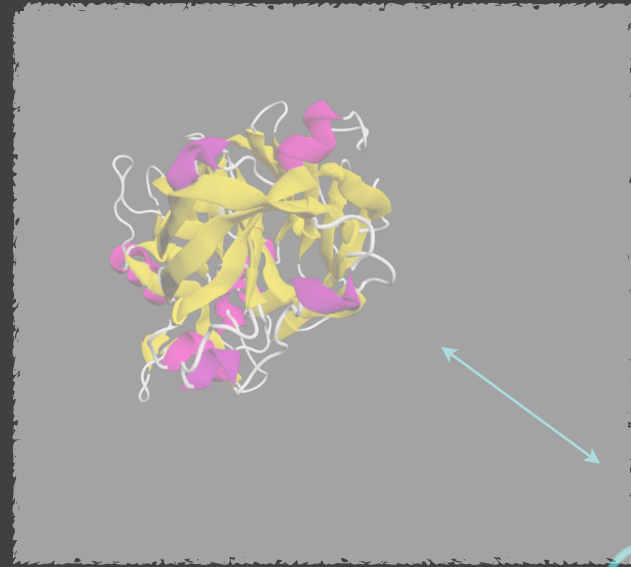
Challenges

- Measurement stage is time-consuming
- Hilbert space is a big space

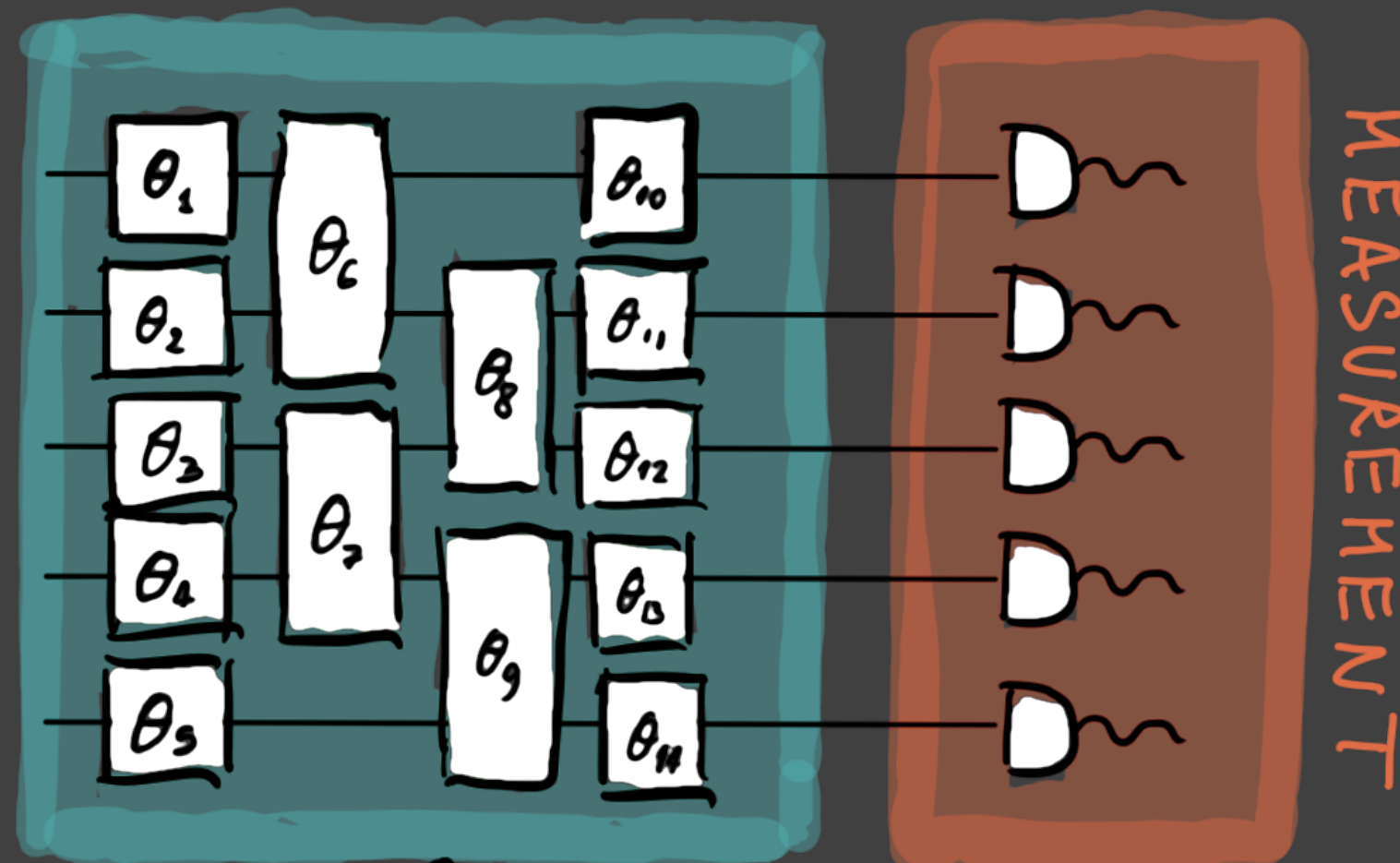


Challenges

- Measurement stage is time-consuming
- Hilbert space is a big space
- Noise biases the results



QUANTUM STATE



OPTIMIZATION

Challenges

- Measurement stage is time-consuming
- Hilbert space is a big space
- Noise biases the results
- Qubits are a scarce resource

Problem statement

Molecular ground-state energy

- Composition of the molecule is given
- Must determine ground-state energy as a function of positions of nuclei (potential energy surface)

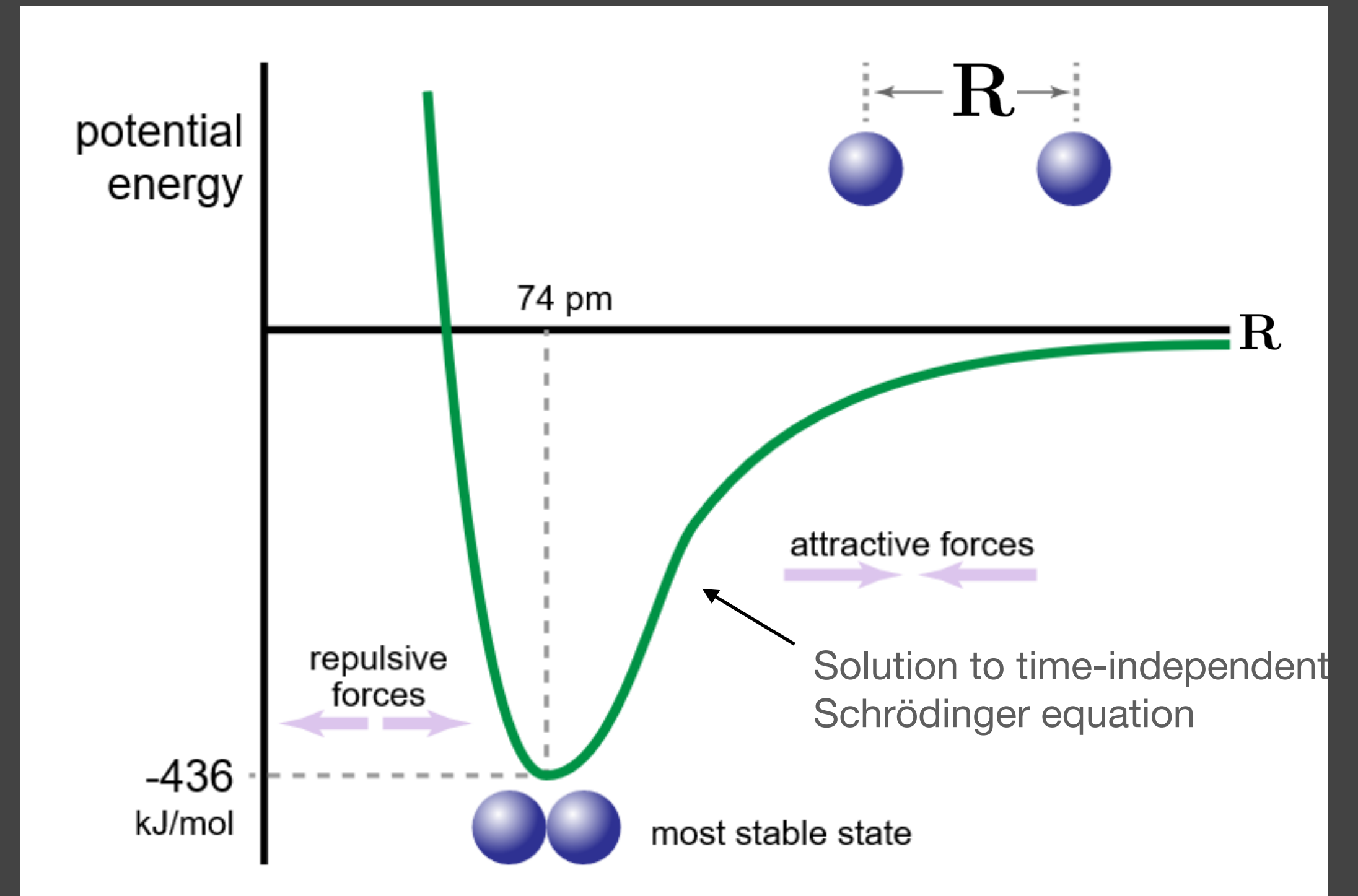
Well-known from QM theory
Efficient classical representation



$$\hat{H}_e |\Psi\rangle = E |\Psi\rangle$$



High-dimensional vector
in Hilbert space



Born-Oppenheimer approximation

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

Solving the problem

General considerations

- N -electron wave function

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

Solving the problem

General considerations

- N -electron wave function

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

→ Usually a dominant determinant (Hartree-Fock)

All terms considered in FCI
(usually classically intractable!)

Exact for infinite M

Solving the problem

General considerations

- N -electron wave function

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



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

Solving the problem

General considerations

- N -electron wave function

$$|\Psi\rangle = \sum_{\vec{f}} \alpha_{\vec{f}} |f_1 f_2 \dots f_M\rangle \quad \longleftrightarrow \quad H_e = - \sum_i \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Creation/annihilation (second quantisation) operators enforce antisymmetry

$$a_p^\dagger |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,0} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 1 \dots f_M\rangle$$

$$a_p |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,1} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 0 \dots f_M\rangle$$

$$\{a_p, a_q^\dagger\} = \delta_{p,q}$$

$$\{a_p, a_q\} = \{a_p^\dagger, a_q^\dagger\} = 0$$

Solving the problem

General considerations

- N -electron wave function

$$|\Psi\rangle = \sum_{\vec{f}} \alpha_{\vec{f}} |f_1 f_2 \dots f_M\rangle \longleftrightarrow H_e = -\sum_i \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Creation/annihilation (second quantisation) operators enforce antisymmetry

$$a_p^\dagger |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,0} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 1 \dots f_M\rangle$$

$$\{a_p, a_q^\dagger\} = \delta_{p,q}$$

$$a_p |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,1} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 0 \dots f_M\rangle$$

$$\{a_p, a_q\} = \{a_p^\dagger, a_q^\dagger\} = 0$$

- Requires Hamiltonian in second quantisation

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

Solving the problem

Mapping to quantum computer

- Find a qubit Hamiltonian equivalent to electronic one (Jordan-Wigner mapping)

$|f_1 \dots f_M\rangle \rightarrow |q_1 \dots q_M\rangle \rightarrow$ Mapping of state is straightforward

Solving the problem

Mapping to quantum computer

- Find a qubit Hamiltonian equivalent to electronic one (Jordan-Wigner mapping)

$|f_1 \dots f_M\rangle \rightarrow |q_1 \dots q_M\rangle \rightarrow$ Mapping of state is straightforward

$$a_p |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,1} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 0 \dots f_M\rangle$$



$$\tilde{a}_p |q_1 q_2 \dots q_p \dots q_M\rangle = \delta_{q_p,1} (-1)^{\sum_{k=1}^{p-1} q_k} |q_1 q_2 \dots 0 \dots q_M\rangle$$

Solving the problem

Mapping to quantum computer

- Find a qubit Hamiltonian equivalent to electronic one (Jordan-Wigner mapping)

$|f_1 \dots f_M\rangle \rightarrow |q_1 \dots q_M\rangle \rightarrow$ Mapping of state is straightforward

$$a_p |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,1} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 0 \dots f_M\rangle$$

$$\tilde{a}_p |q_1 q_2 \dots q_p \dots q_M\rangle = \delta_{q_p,1} (-1)^{\sum_{k=1}^{p-1} q_k} |q_1 q_2 \dots 0 \dots q_M\rangle$$

$$\tilde{a}_p = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_-^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_-^{(p)} = |0\rangle\langle 1| = \frac{1}{2}(\sigma_x^{(p)} + i\sigma_y^{(p)})$$

Solving the problem

Mapping to quantum computer

- Find a qubit Hamiltonian equivalent to electronic one (Jordan-Wigner mapping)

$|f_1 \dots f_M\rangle \rightarrow |q_1 \dots q_M\rangle \rightarrow$ Mapping of state is straightforward

$$a_p |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,1} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 0 \dots f_M\rangle$$

$$\tilde{a}_p |q_1 q_2 \dots q_p \dots q_M\rangle = \delta_{q_p,1} (-1)^{\sum_{k=1}^{p-1} q_k} |q_1 q_2 \dots 0 \dots q_M\rangle$$

$$\tilde{a}_p = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_-^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_-^{(p)} = |0\rangle\langle 1| = \frac{1}{2}(\sigma_x^{(p)} + i\sigma_y^{(p)})$$

$$\tilde{a}_p^\dagger = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_+^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_+^{(p)} = |1\rangle\langle 0| = \frac{1}{2}(\sigma_x^{(p)} - i\sigma_y^{(p)})$$

Solving the problem

Mapping to quantum computer

- Find a qubit Hamiltonian equivalent to electronic one (Jordan-Wigner mapping)

$|f_1 \dots f_M\rangle \rightarrow |q_1 \dots q_M\rangle \rightarrow$ Mapping of state is straightforward

$$a_p |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,1} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 0 \dots f_M\rangle$$

$$\tilde{a}_p |q_1 q_2 \dots q_p \dots q_M\rangle = \delta_{q_p,1} (-1)^{\sum_{k=1}^{p-1} q_k} |q_1 q_2 \dots 0 \dots q_M\rangle$$

$$\tilde{a}_p = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_-^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_-^{(p)} = |0\rangle\langle 1| = \frac{1}{2}(\sigma_x^{(p)} + i\sigma_y^{(p)})$$

$$\tilde{a}_p^\dagger = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_+^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_+^{(p)} = |1\rangle\langle 0| = \frac{1}{2}(\sigma_x^{(p)} - i\sigma_y^{(p)})$$

Why are Pauli matrices a suitable choice?

Solving the problem

Mapping to quantum computer

- Find a qubit Hamiltonian equivalent to electronic one (Jordan-Wigner mapping)

$|f_1 \dots f_M\rangle \rightarrow |q_1 \dots q_M\rangle \rightarrow$ Mapping of state is straightforward

$$a_p |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,1} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 0 \dots f_M\rangle$$

$$\tilde{a}_p |q_1 q_2 \dots q_p \dots q_M\rangle = \delta_{q_p,1} (-1)^{\sum_{k=1}^{p-1} q_k} |q_1 q_2 \dots 0 \dots q_M\rangle$$

$$\tilde{a}_p = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_-^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_-^{(p)} = |0\rangle\langle 1| = \frac{1}{2}(\sigma_x^{(p)} + i\sigma_y^{(p)})$$

$$\tilde{a}_p^\dagger = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_+^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_+^{(p)} = |1\rangle\langle 0| = \frac{1}{2}(\sigma_x^{(p)} - i\sigma_y^{(p)})$$

Why are Pauli matrices a suitable choice?

Single-qubit quantum gates are 2×2 unitary matrices
 \rightarrow Pauli matrices are 2×2 Hermitian (unitary) matrices

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

Solving the problem

Mapping to quantum computer

- Find a qubit Hamiltonian equivalent to electronic one (Jordan-Wigner mapping)

$|f_1 \dots f_M\rangle \rightarrow |q_1 \dots q_M\rangle \rightarrow$ Mapping of state is straightforward

$$a_p |f_1 f_2 \dots f_p \dots f_M\rangle = \delta_{f_p,1} (-1)^{\sum_{k=1}^{p-1} f_k} |f_1 f_2 \dots 0 \dots f_M\rangle$$

$$\tilde{a}_p |q_1 q_2 \dots q_p \dots q_M\rangle = \delta_{q_p,1} (-1)^{\sum_{k=1}^{p-1} q_k} |q_1 q_2 \dots 0 \dots q_M\rangle$$

$$\tilde{a}_p = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_-^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_-^{(p)} = |0\rangle\langle 1| = \frac{1}{2}(\sigma_x^{(p)} + i\sigma_y^{(p)})$$

$$\tilde{a}_p^\dagger = \sigma_z^{(1)} \otimes \sigma_z^{(2)} \otimes \dots \otimes \sigma_+^{(p)} \otimes \mathbb{I}^{(p+1)} \otimes \dots \otimes \mathbb{I}^{(M)} \rightarrow \sigma_+^{(p)} = |1\rangle\langle 0| = \frac{1}{2}(\sigma_x^{(p)} - i\sigma_y^{(p)})$$

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

$$\hat{H}_e = \sum_k c_k \hat{P}_k$$

Calculating the energy on a quantum computer

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

$$\hat{H}_e = \sum_k c_k \hat{P}_k$$

← Each term is a product of local operators

$$\hat{P}_k = \bigotimes_{i=1}^N \sigma_{k_i}^{(i)}$$

Calculating the energy on a quantum computer

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

$$\hat{H}_e = \sum_k c_k \hat{P}_k$$

← Each term is a product of local operators

$$\hat{P}_k = \bigotimes_{i=1}^N \sigma_{k_i}^{(i)}$$

- We can calculate expectation values on the quantum computer

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



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

Calculating the energy on a quantum computer

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

$$\hat{H}_e = \sum_k c_k \hat{P}_k$$

← Each term is a product of local operators

$$\hat{P}_k = \bigotimes_{i=1}^N \sigma_{k_i}^{(i)}$$

- We can calculate expectation values on the quantum computer

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

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

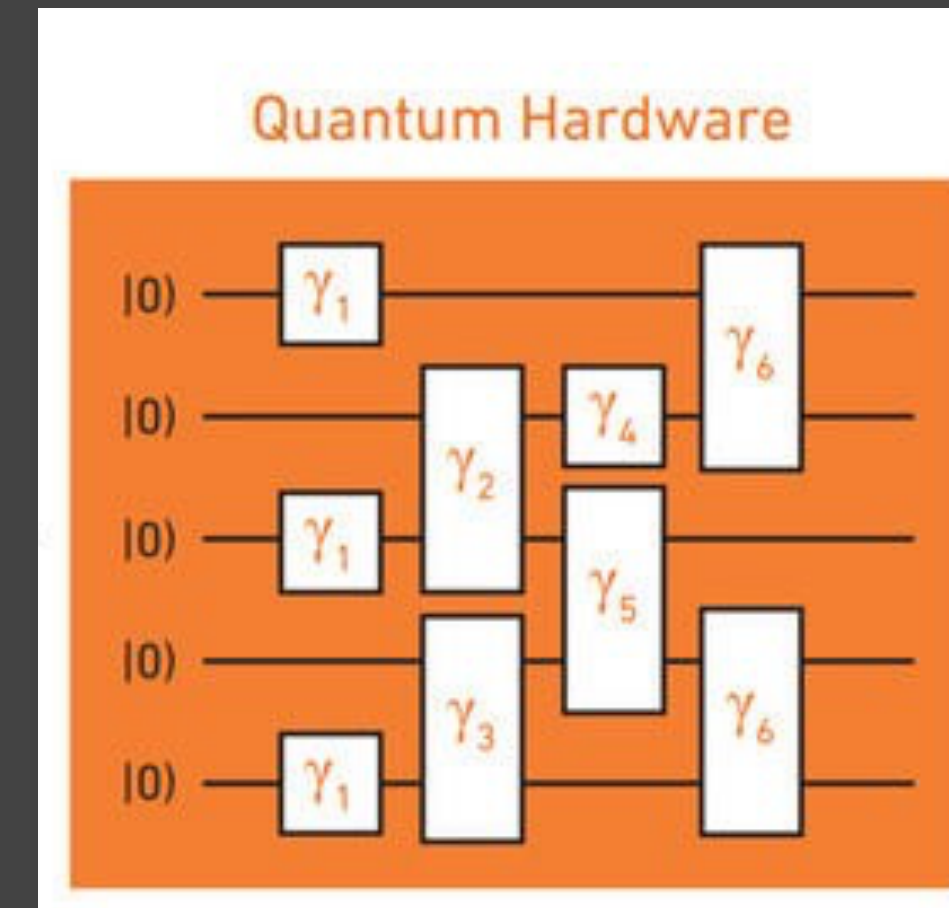
Cannot even be written
down on a classical
computer

Easy on a quantum computer: only
requires measuring Pauli strings

Solving the problem

The Variational Quantum Eigensolver

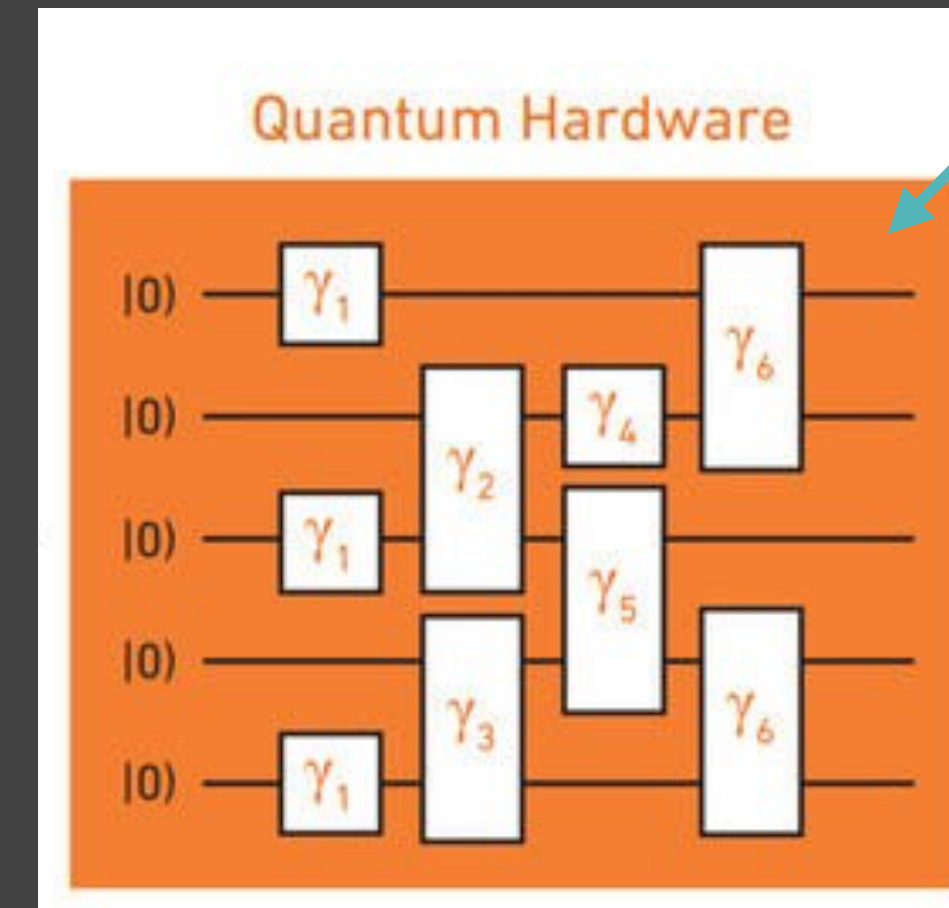
- Prepare *some* quantum state using a so-called variational form (ansatz)



Solving the problem

The Variational Quantum Eigensolver

- Prepare *some* quantum state using a so-called variational form (ansatz)
- Gates (unitary rotations) in the ansatz have free parameters $\{\vec{\theta}\}$

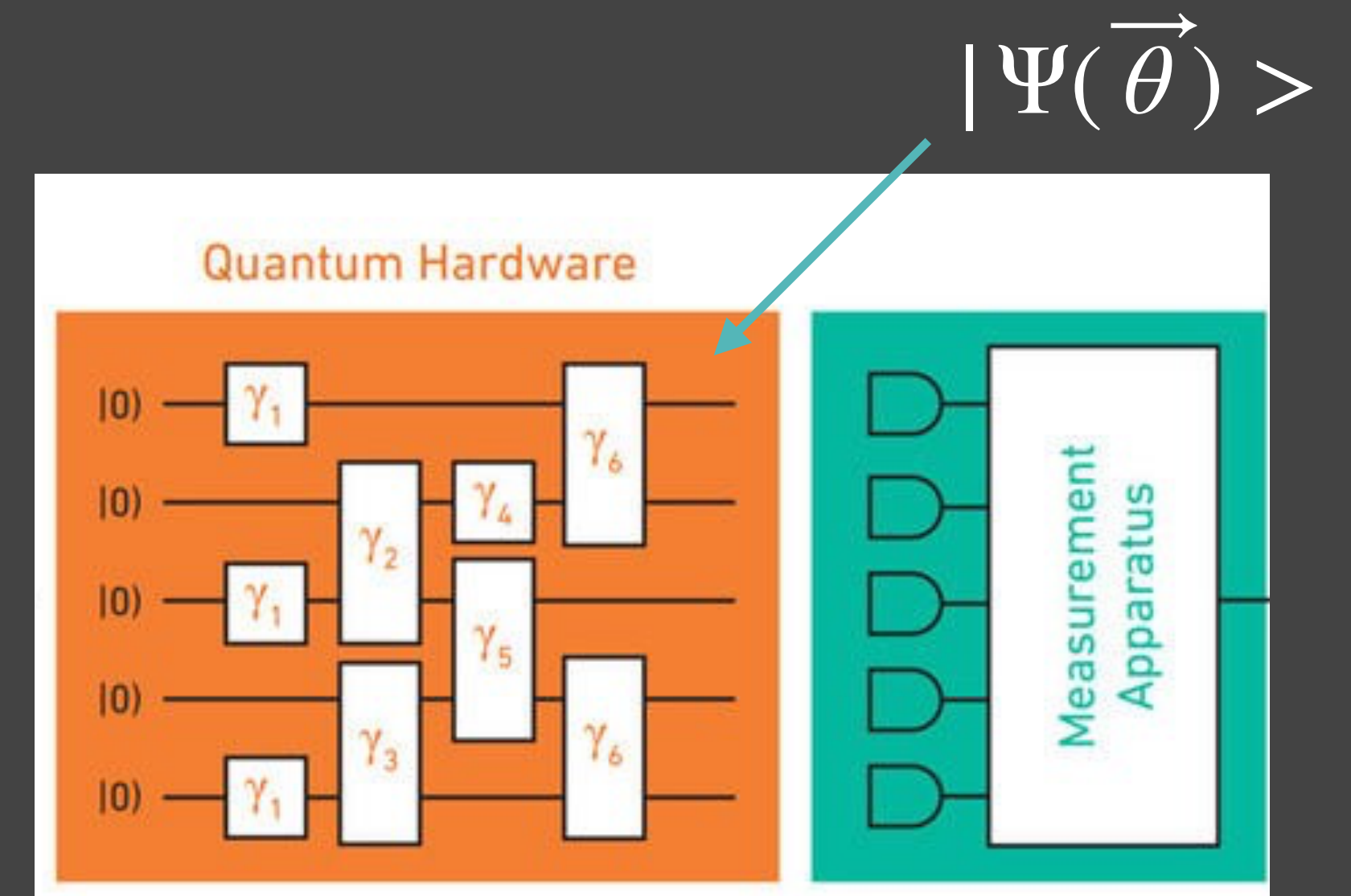


$$|\Psi(\vec{\theta})\rangle$$

Solving the problem

The Variational Quantum Eigensolver

- Prepare *some* quantum state using a so-called variational form (ansatz)
- Gates (unitary rotations) in the ansatz have free parameters $\{\vec{\theta}\}$
- For each value of the parameters the resulting state has some mean energy $\langle E \rangle$

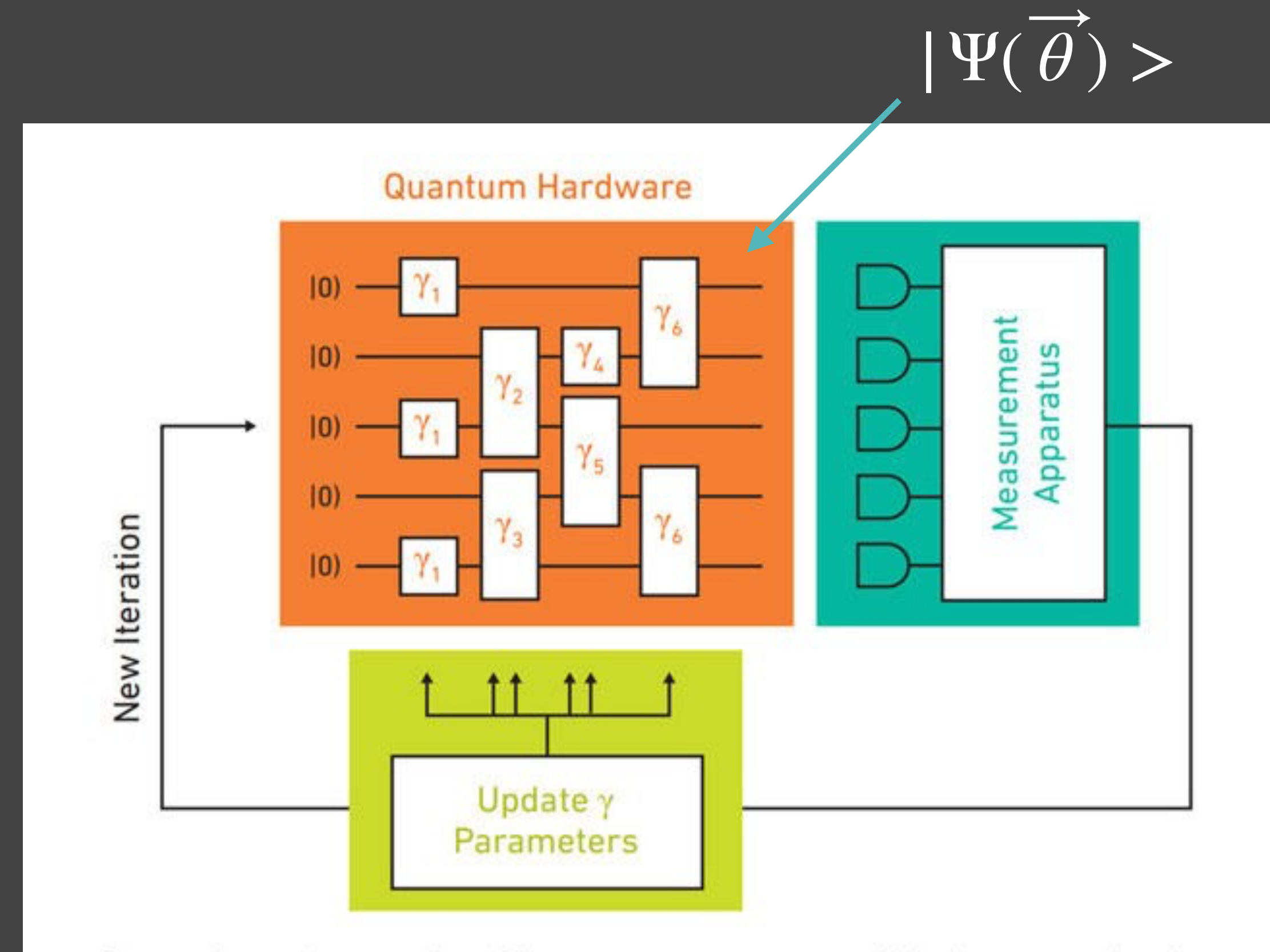


$$\langle E \rangle = \langle \Psi(\vec{\theta}) | \hat{H}_e | \Psi(\vec{\theta}) \rangle \geq E_{\text{ground}}$$

Solving the problem

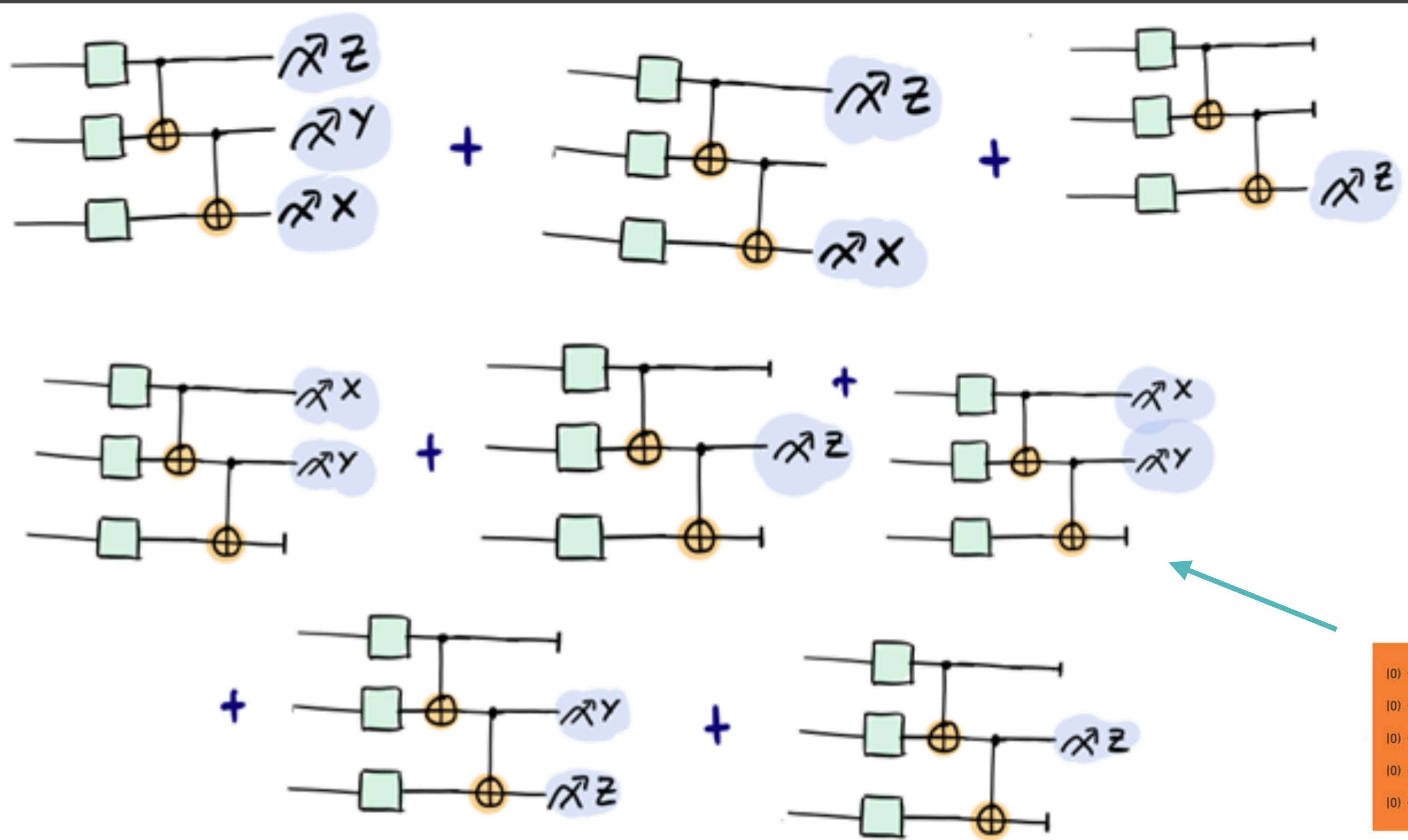
The Variational Quantum Eigensolver

- Prepare *some* quantum state using a so-called variational form (ansatz)
- Gates (unitary rotations) in the ansatz have free parameters $\{\vec{\theta}\}$
- For each value of the parameters the resulting state has some mean energy $\langle E \rangle$
- Find the ground state variationally: minimising over the parameters $\{\vec{\theta}\}$



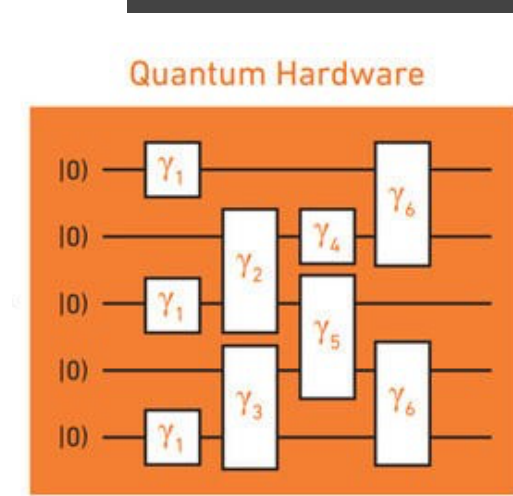
$$\langle E \rangle = \langle \Psi(\vec{\theta}) | \hat{H}_e | \Psi(\vec{\theta}) \rangle \geq E_{\text{ground}}$$

Measuring the energy in a VQE simulation

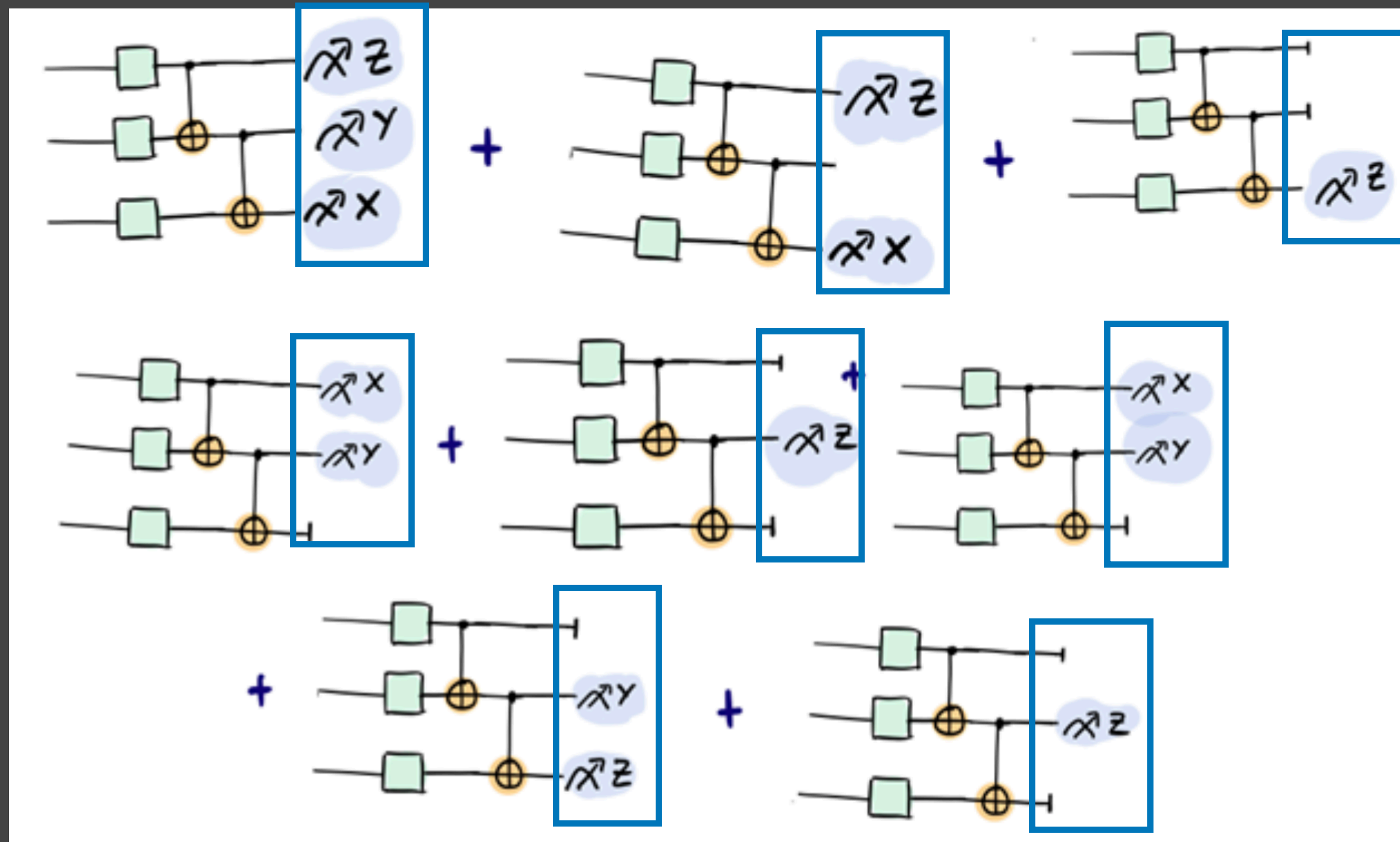


$$\langle \Psi | \hat{H}_e | \Psi \rangle = \sum_k c_k \langle \Psi | \hat{P}_k | \Psi \rangle$$

Every Pauli string evaluated independently through repeated measurements



Measuring the energy in a VQE simulation



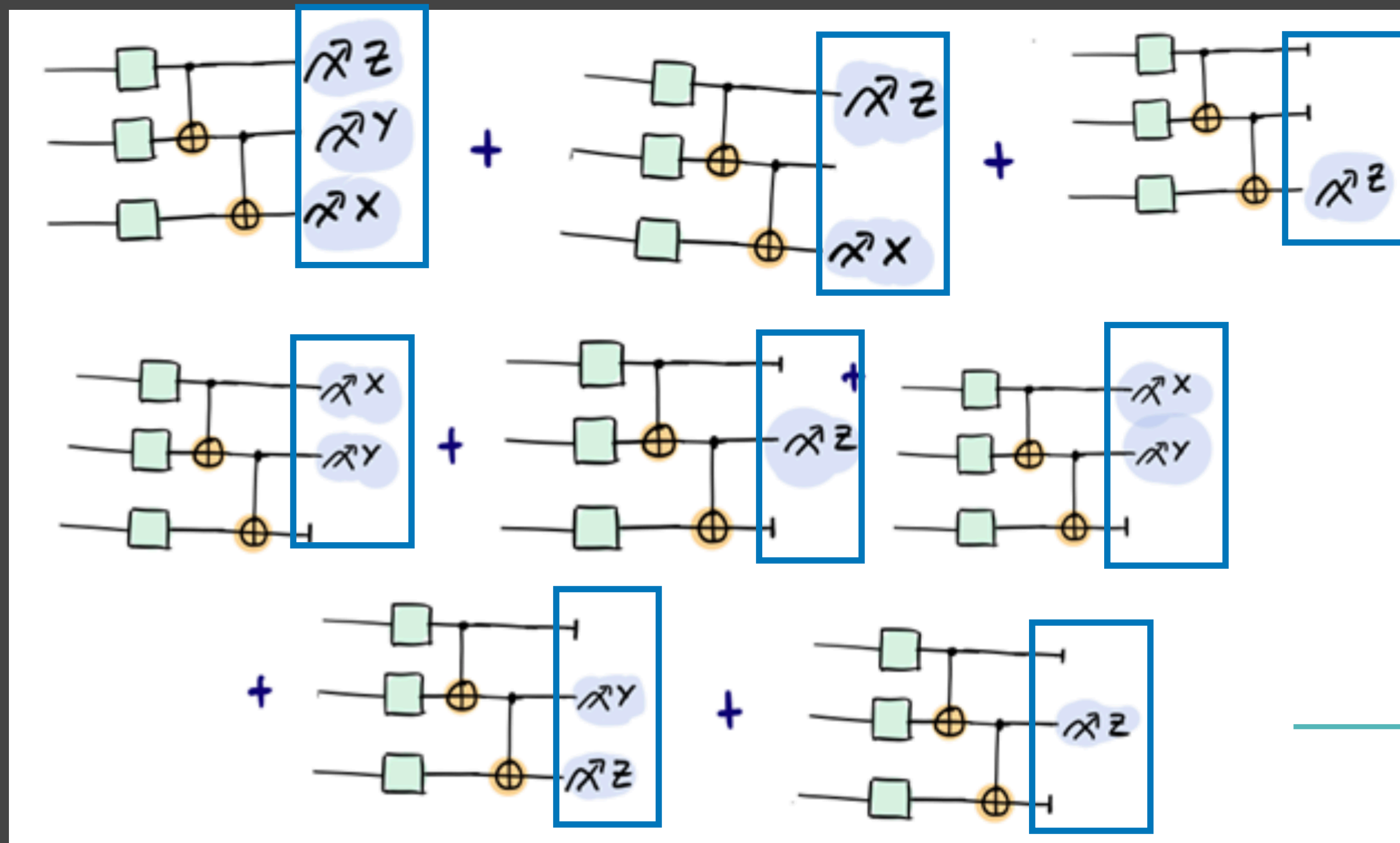
$$\langle \Psi | \hat{H}_e | \Psi \rangle = \sum_k c_k \langle \Psi | \hat{P}_k | \Psi \rangle$$



Every Pauli string evaluated independently through repeated measurements

Measuring the energy

in a VQE simulation



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



Every Pauli string evaluated independently through repeated measurements



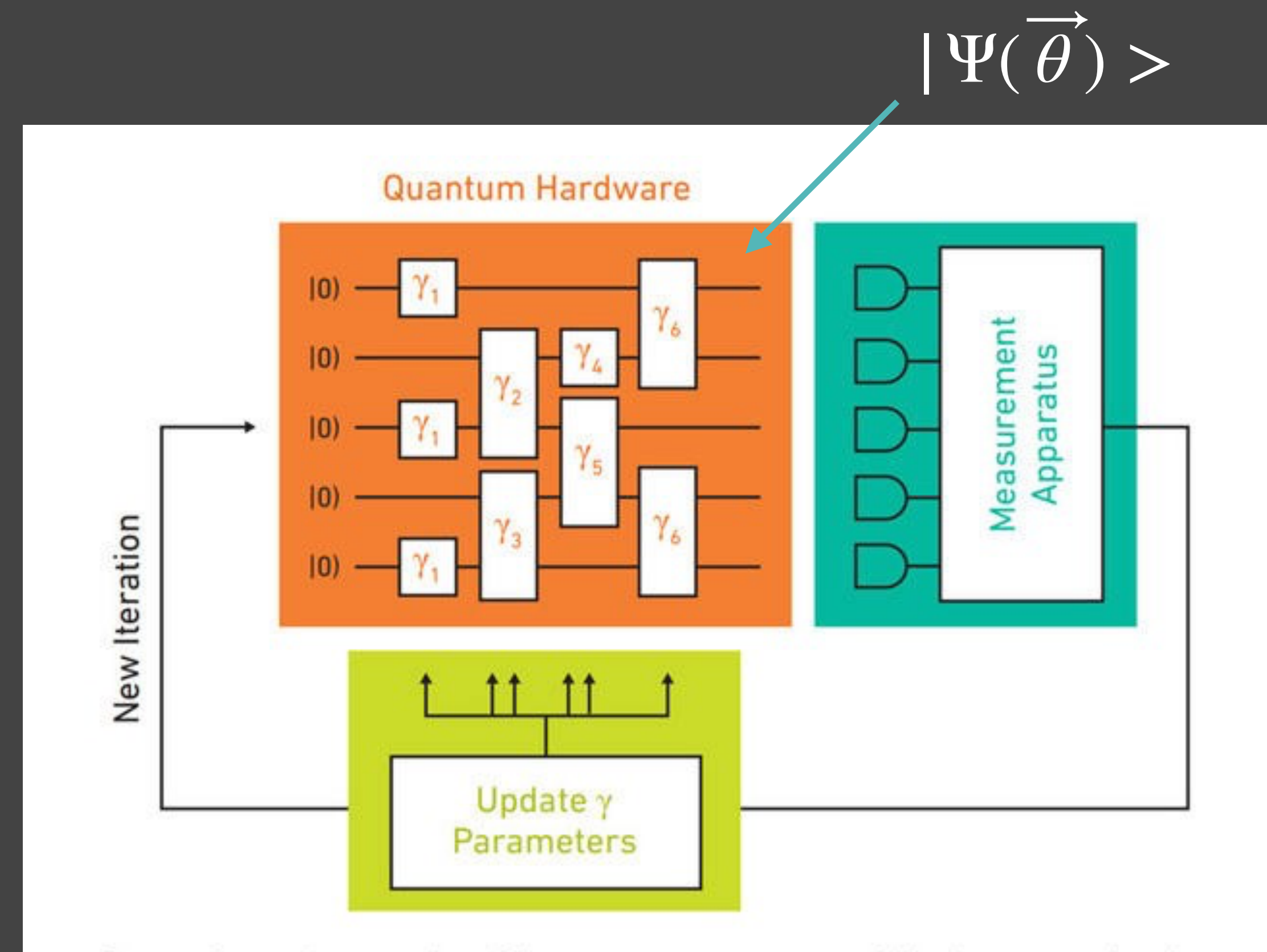
Repeat each many times to estimate the mean $\langle \Psi | \hat{P}_k | \Psi \rangle$

Solving the problem?

The Variational Quantum Eigensolver

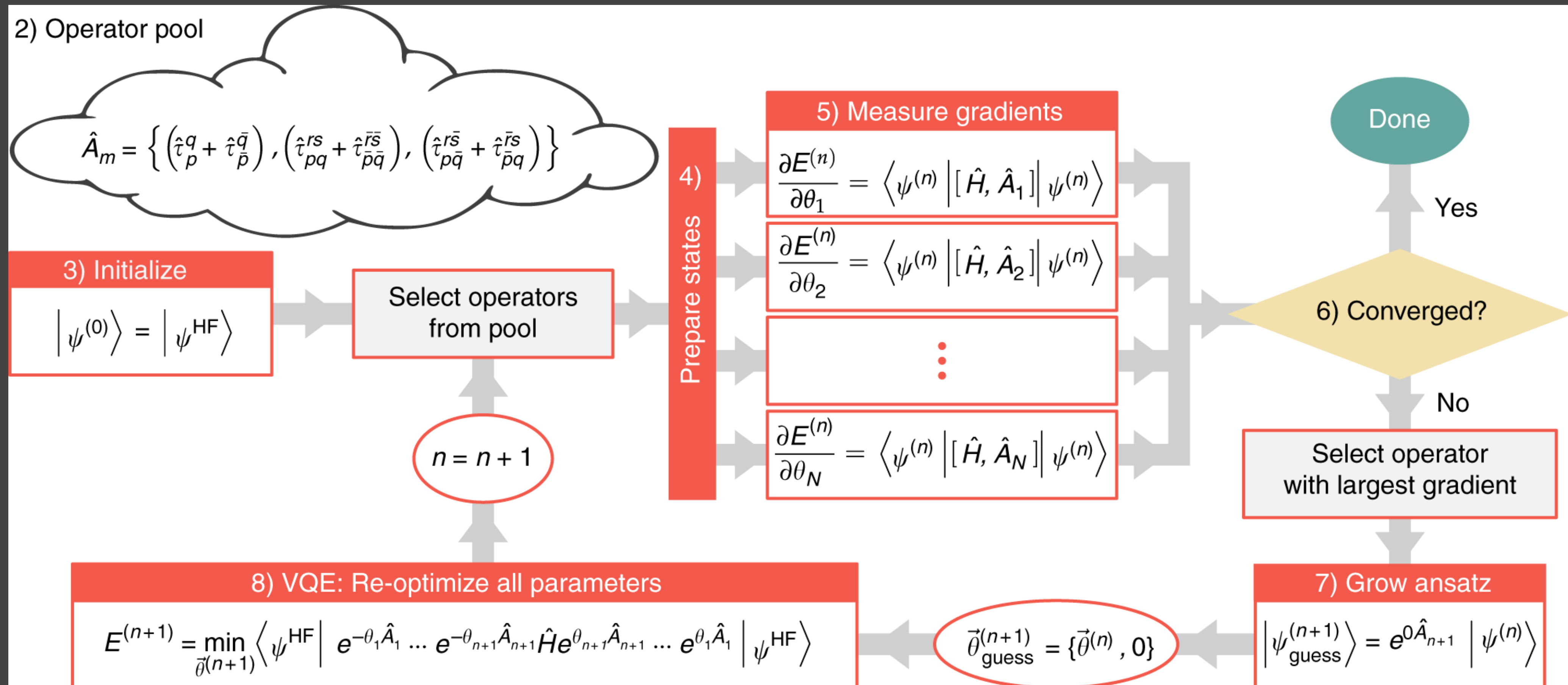
Sounds good, BUT

- 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?



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

Reliable state preparation with ADAPT-VQE

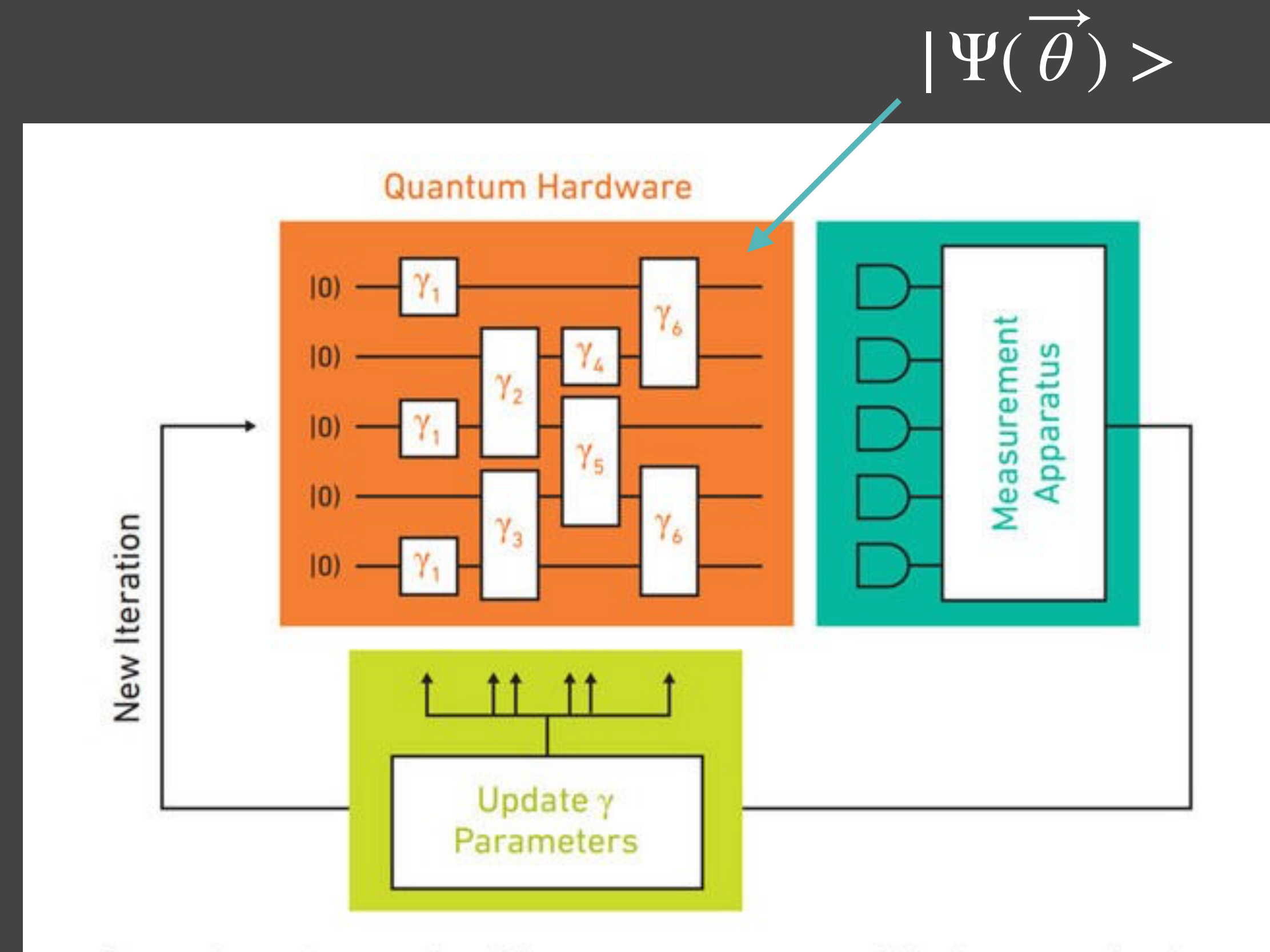


Solving the problem?

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?



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

Solving the problem?

The Variational Quantum Eigensolver

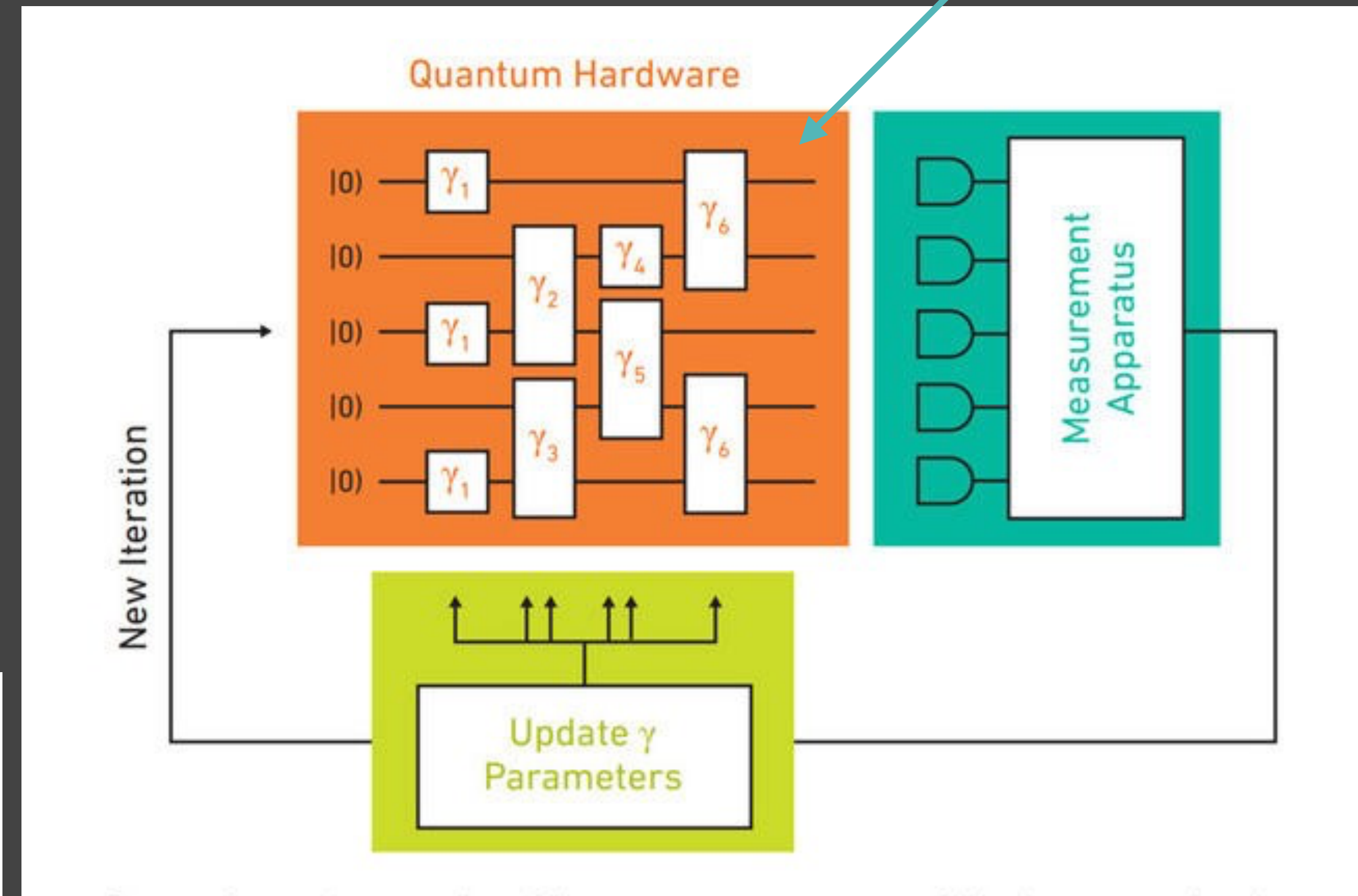
$$|\Psi(\vec{\theta})\rangle$$

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

Jérôme F. Gonthier,¹ Maxwell D. Radin,¹ Corneliu Buda,²
Eric J. Dosekocil,² Clena M. Abuan,³ and Jhonathan Romero¹
¹Zapata Computing, Inc., 100 Federal St., Boston, MA 02110, USA

Molecule	H ₂ O	CO ₂	CH ₄	CH ₄ O	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆ O	C ₃ H ₈	C ₃ H ₆	C ₃ H 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 · 10 ⁻³	1.9	16	1.6	8.4	8.5	6.6	3.1	24	16	23	18
M · 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



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

Solving the problem?

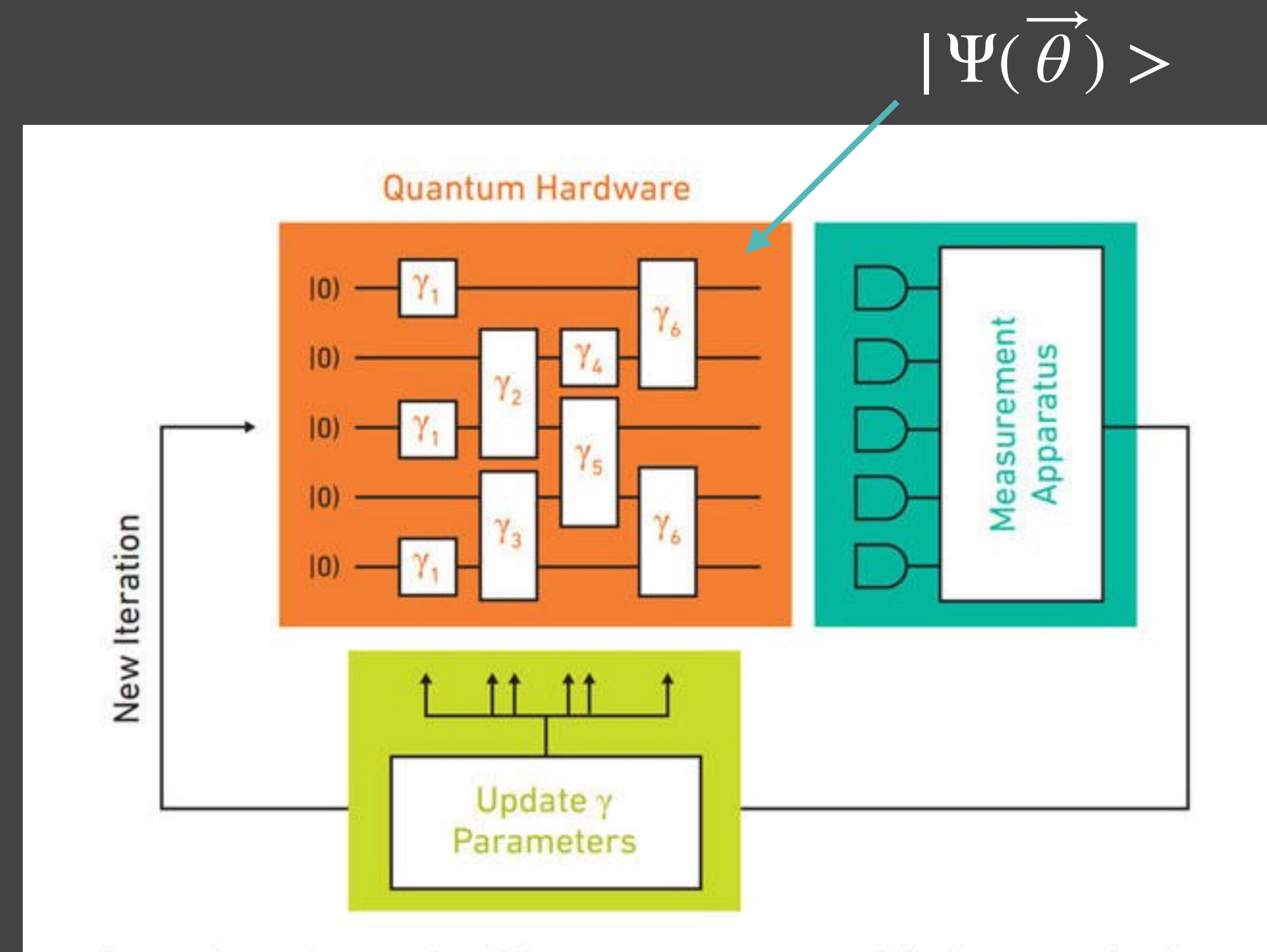
The Variational Quantum Eigensolver

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?

Efficient measurement strategies are required!

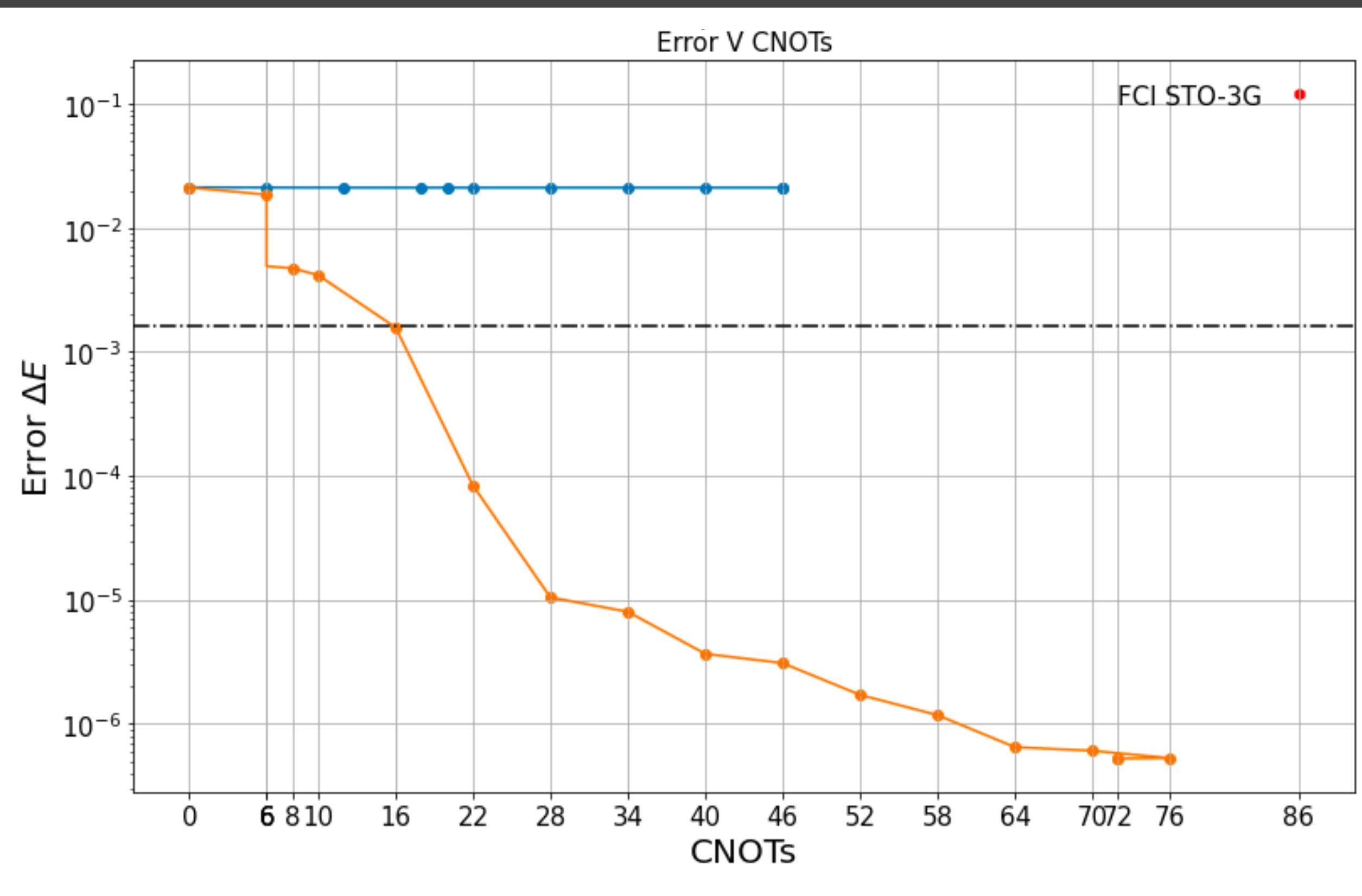
Noise mitigation is crucial!



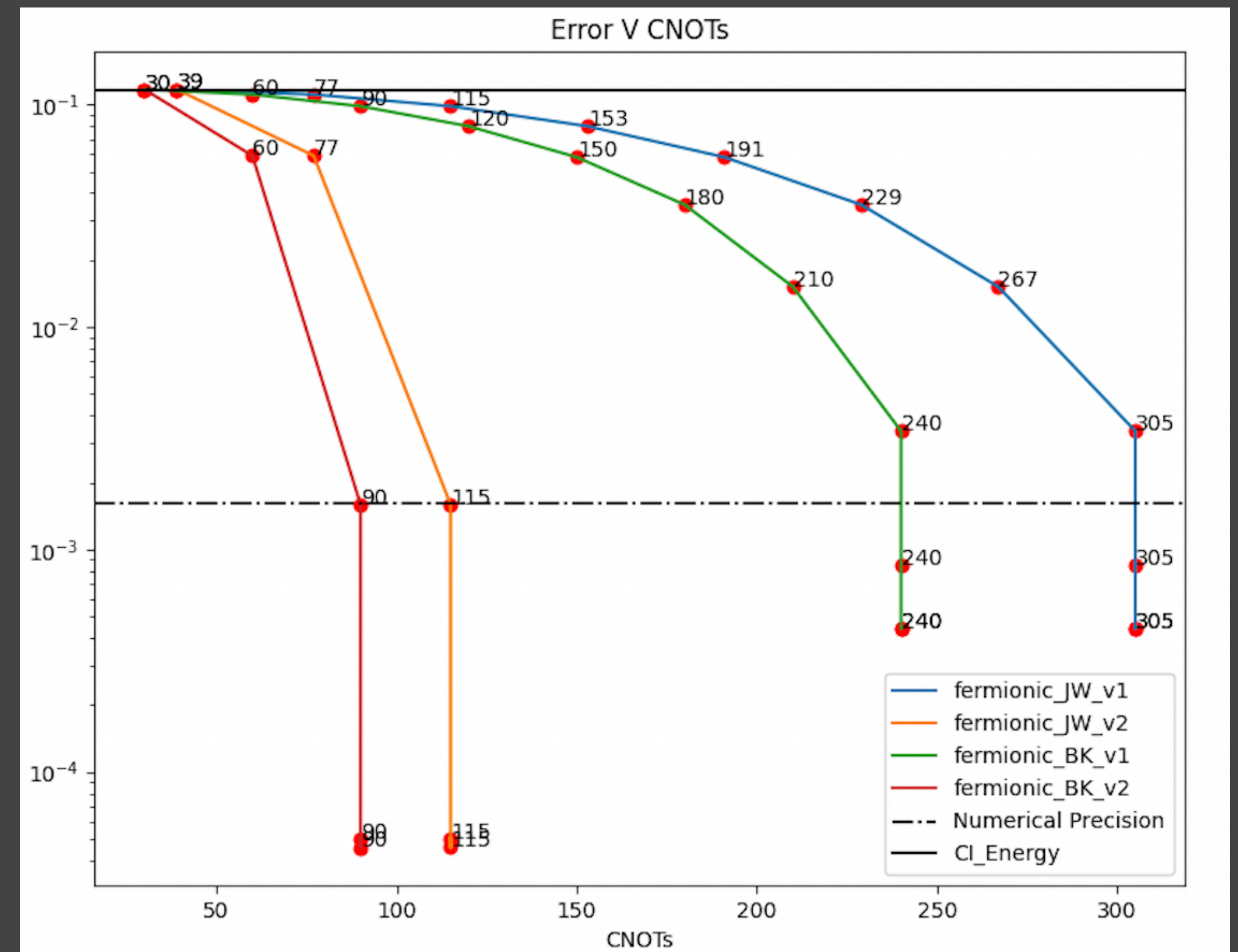
$$\langle E \rangle = \langle \Psi(\vec{\theta}) | \hat{H}_e | \Psi(\vec{\theta}) \rangle \geq E_{\text{ground}}$$

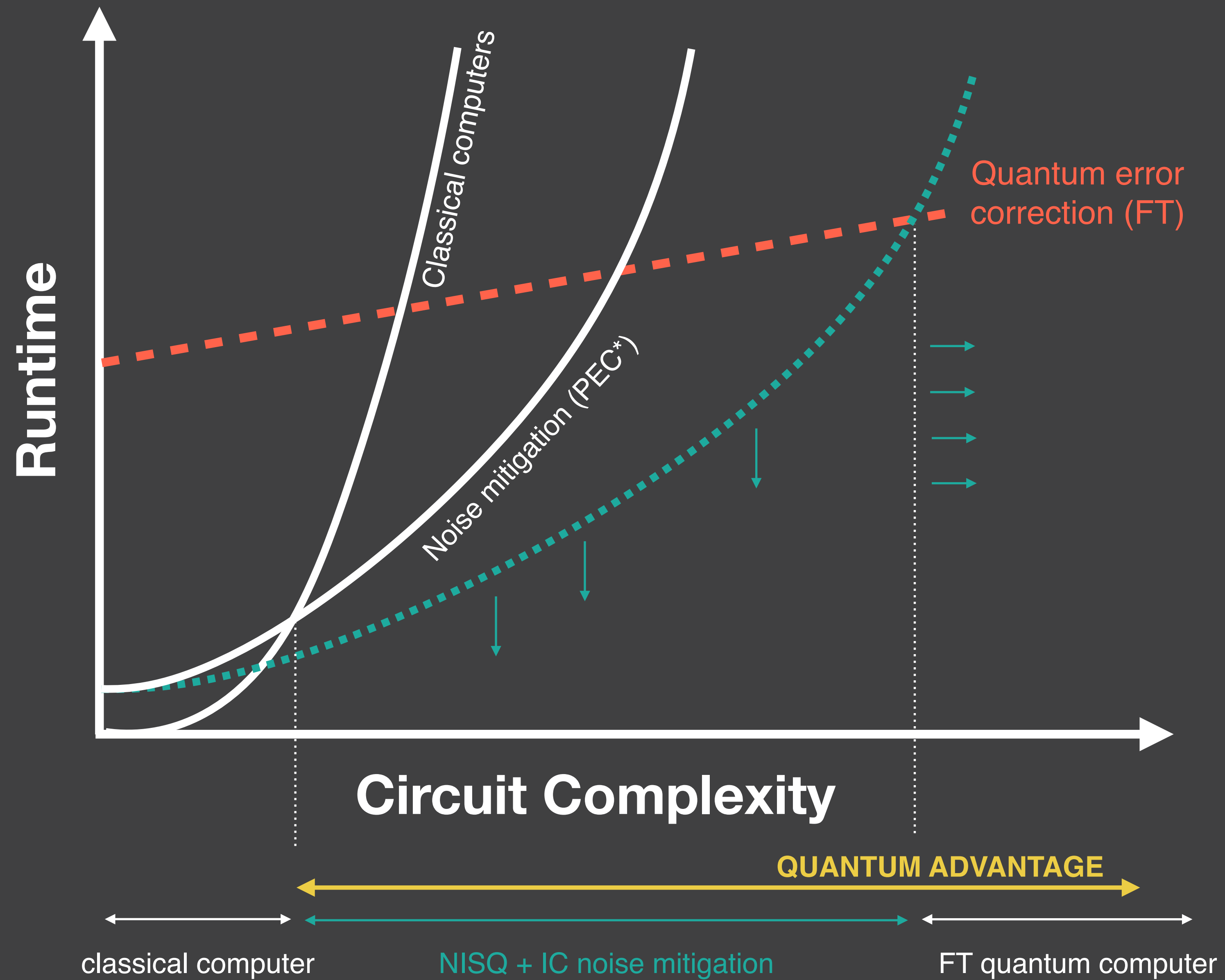
Adapt-VQE-SCF at work

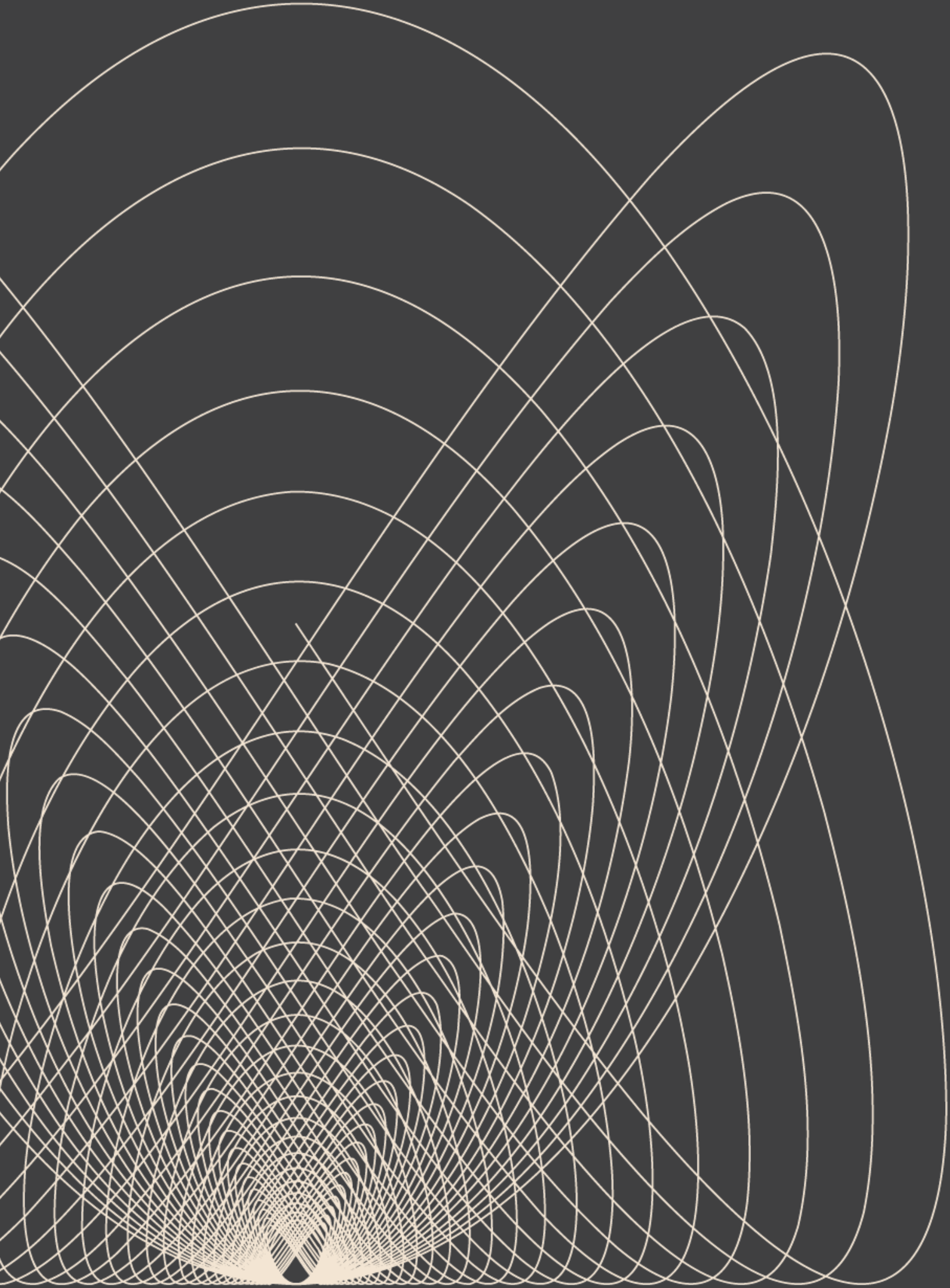
LiH / CAS(4,4)/cc-pVDZ



H₄ / CAS(4,4) / cc-pVDZ







Quantum
computers without
good algorithms
are useless
machines

How many sceptics in
the audience?



AGC

RAM: 4KB
hard disk:
32KB

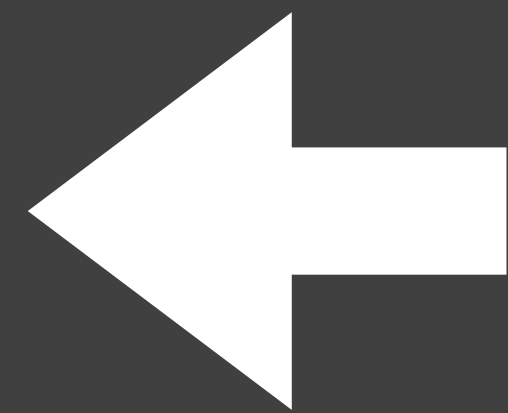
RAM: 4KB
not sufficient to store even a 5 qubit
density matrix with double precision

DSKY



Margaret Hamilton

The software of
the AGC





"Software eventually and necessarily gained the same respect as any other discipline"



"Looking back, we were the luckiest people in the world. There was no choice but to be pioneers; no time to be beginners"

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

