



Enabling Accurate Quantum Chemistry Calculations on Near-Term Quantum Devices

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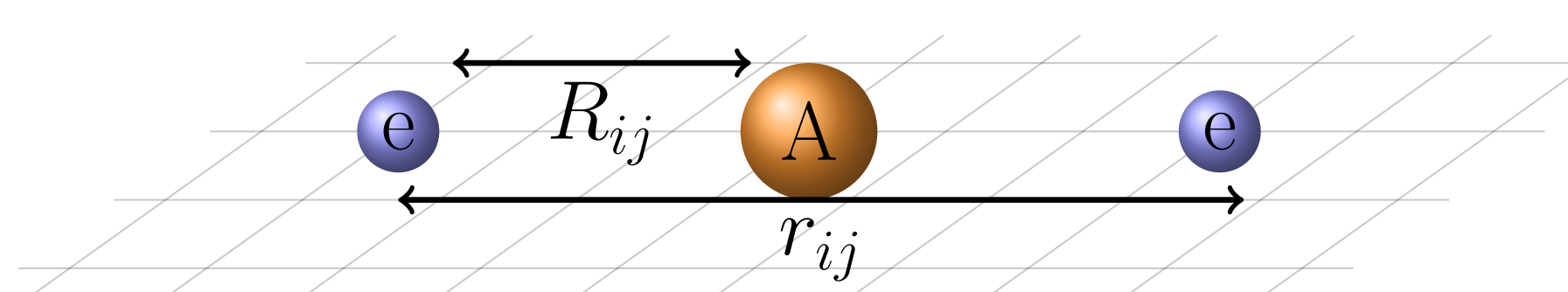
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Quantum Chemistry

All necessary information of a quantum system contained in electronic molecular Hamiltonian

$$\hat{H} = \underbrace{-\sum_i \nabla_{\mathbf{r}_i}^2}_{\text{kinetic energy of } e^-} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{e^- - e^- \text{ repulsion}} - \underbrace{\sum_{I,J} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_j|}}_{\text{Potential}}$$



Electronic properties: Ground- and low-lying excited state properties, energy differences, polarization, response functions, ...

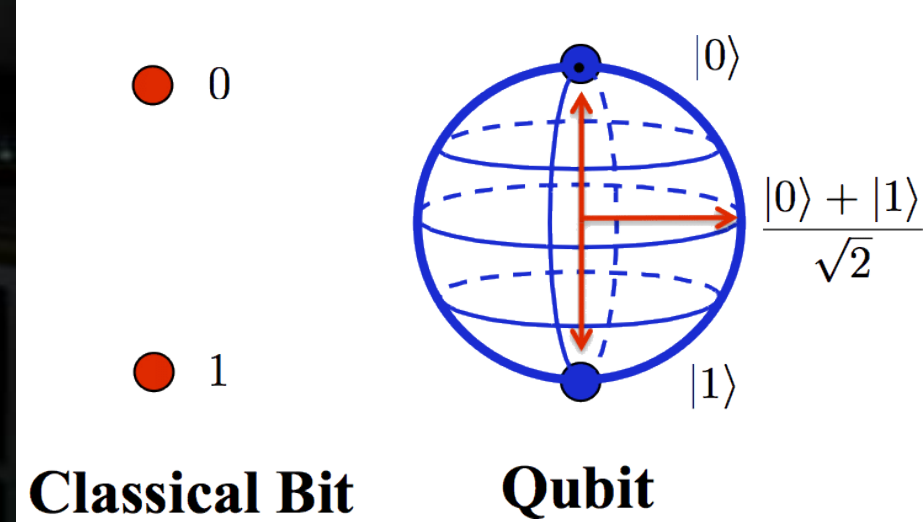
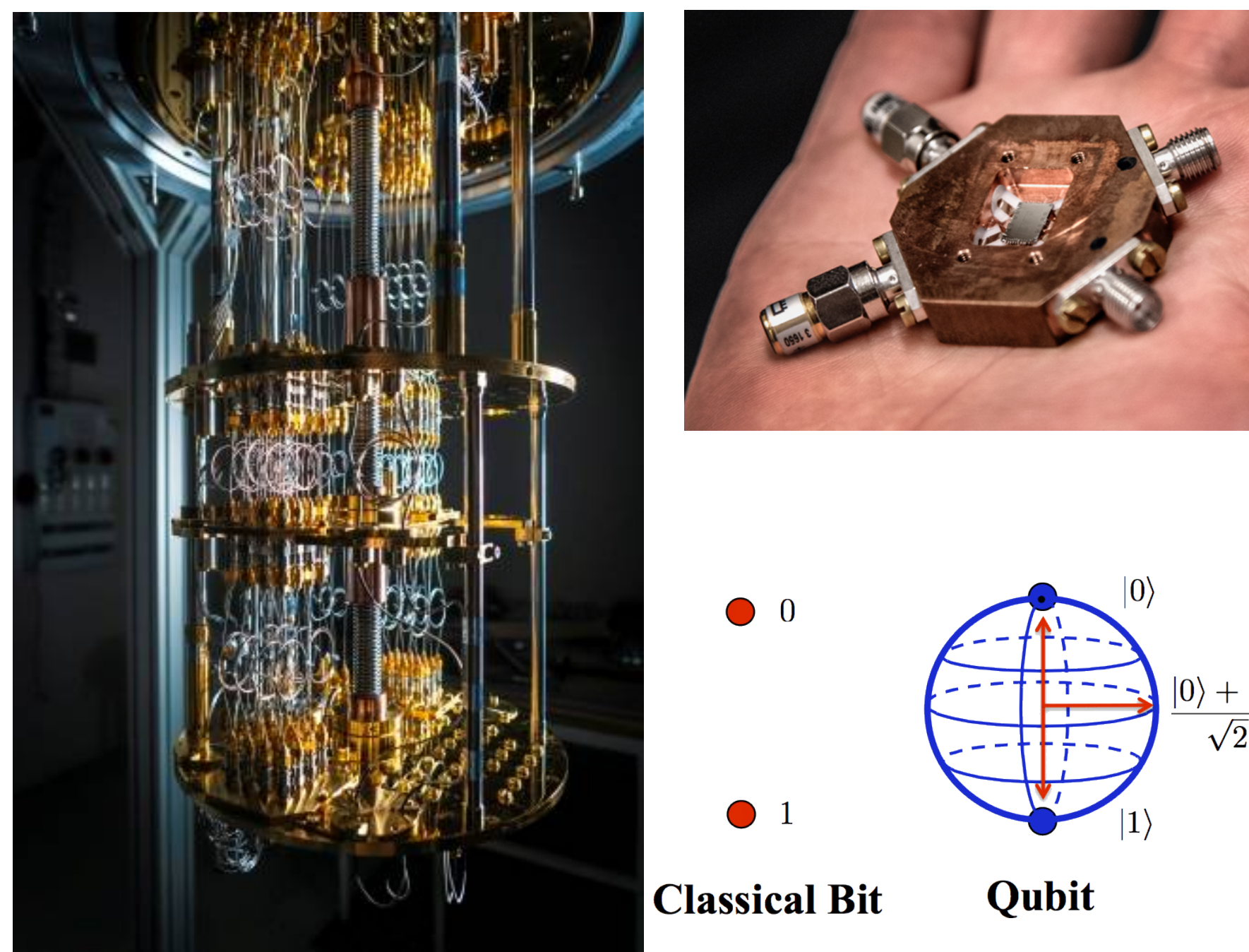
Target: High / chemical accuracy to ensure predictability, interpretability and comparison with experimental results

Problem: Exponentially growing problem size:

Mol.	#orbitals	#electrons	#states
H ₂	2	2	4
LiH	4	4	36
Be ₂	8	8	4900
H ₂ O	12	12	~ 8 · 10 ⁵
C ₂ H ₄	16	16	~ 16 · 10 ⁶
F ₂	18	18	~ 2 · 10 ⁹

Quantum Computing

“Nature isn’t classical, dammit, and if you want to make a simulation of nature, you’d better make it quantum mechanical” – R. Feynman 1981



Due to **entanglement** and **superposition**: n qubits can encode **exponentially many** states:

$$\underbrace{(|0\rangle_1 + |1\rangle_1)}_{\text{qubit1}} \otimes \underbrace{(|0\rangle_2 + |1\rangle_2)}_{\text{qubit2}} = |00\rangle + |01\rangle + |10\rangle + |11\rangle$$

$$|q_1\rangle \otimes |q_2\rangle \otimes |q_3\rangle = |000\rangle + |001\rangle + |010\rangle + |100\rangle + |011\rangle + |101\rangle + |110\rangle + |111\rangle$$

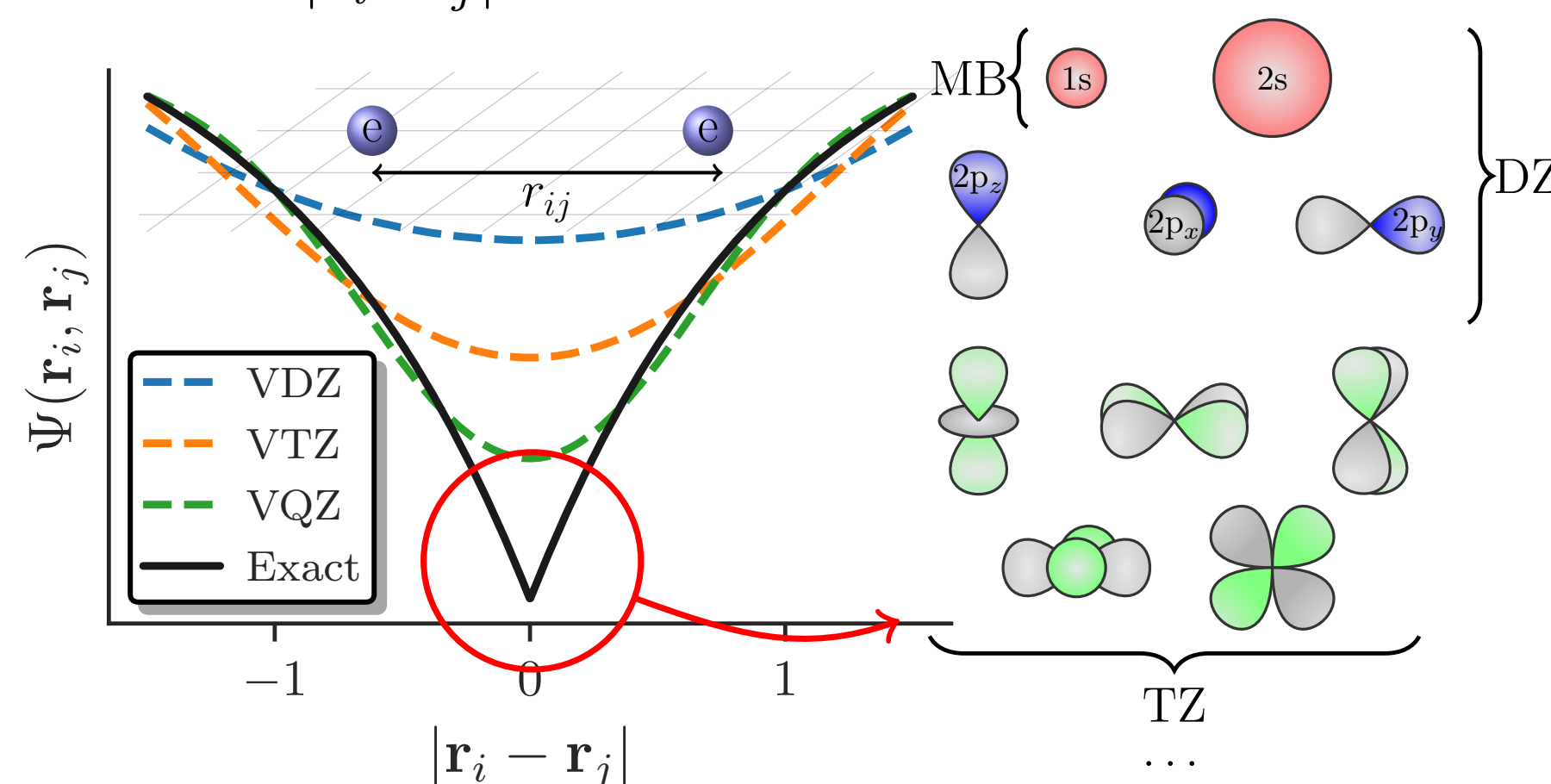
Quantum Algorithms harness this exponential state space **BUT**:

Every spin-orbital needs a qubit → Minimal basis far from CBS results!

Important to account for noise and errors in calculations through *noise-tolerant algorithms*.

Transcorrelated Method

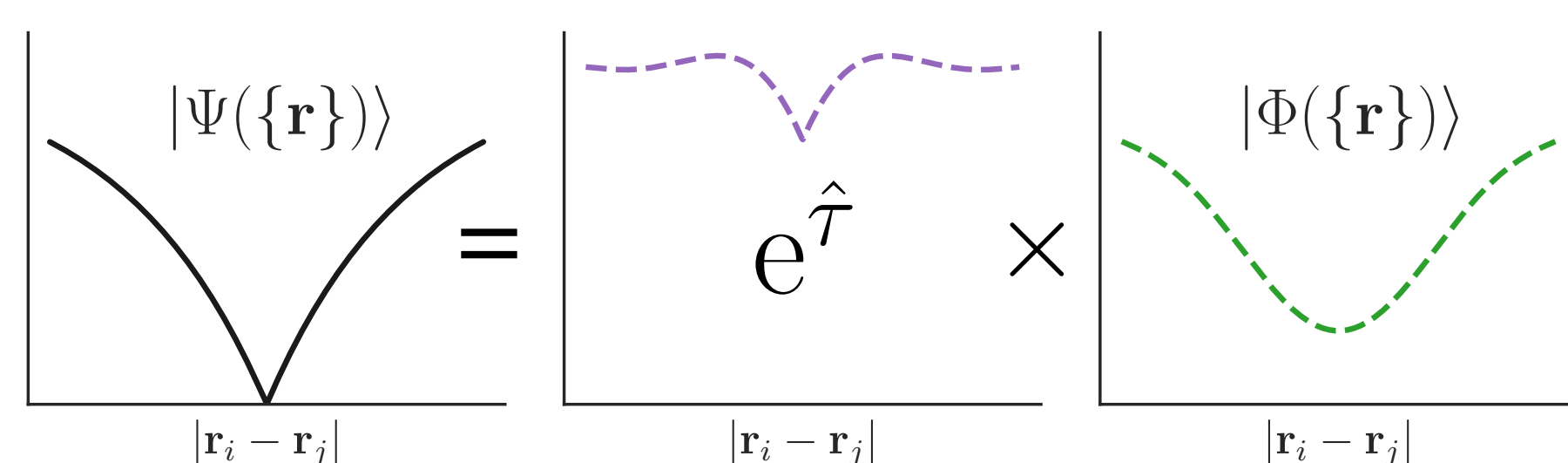
Correlated wavefunction Ansatz^{1,6} to reduce the computational footprint on quantum hardware: **Cusp condition**² due to singularity of Coulomb potential, $\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$, for $|\mathbf{r}_i - \mathbf{r}_j| = 0$



Cusp necessitates more orbitals for accurate results → higher cost, **more qubits**

Describe the cusp exactly and capture part of correlation with a **correlated wavefunction Ansatz**

$$|\Psi(\{\mathbf{r}\})\rangle = e^{\hat{\tau}} |\Phi(\{\mathbf{r}\})\rangle,$$



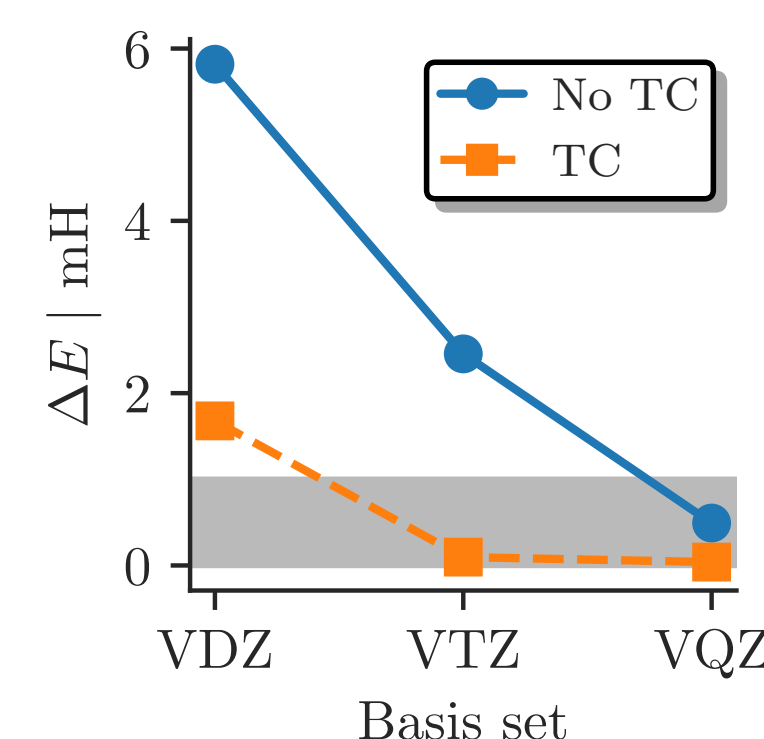
Similarity Transformation of Hamiltonian.

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \rightarrow (e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}}) |\Phi\rangle = E |\Phi\rangle$$

→ **non-Hermitian** Hamiltonian.

Requires less orbitals for higher accuracy!

Correlator $e^{\hat{\tau}}$ obtainable with polynomial cost



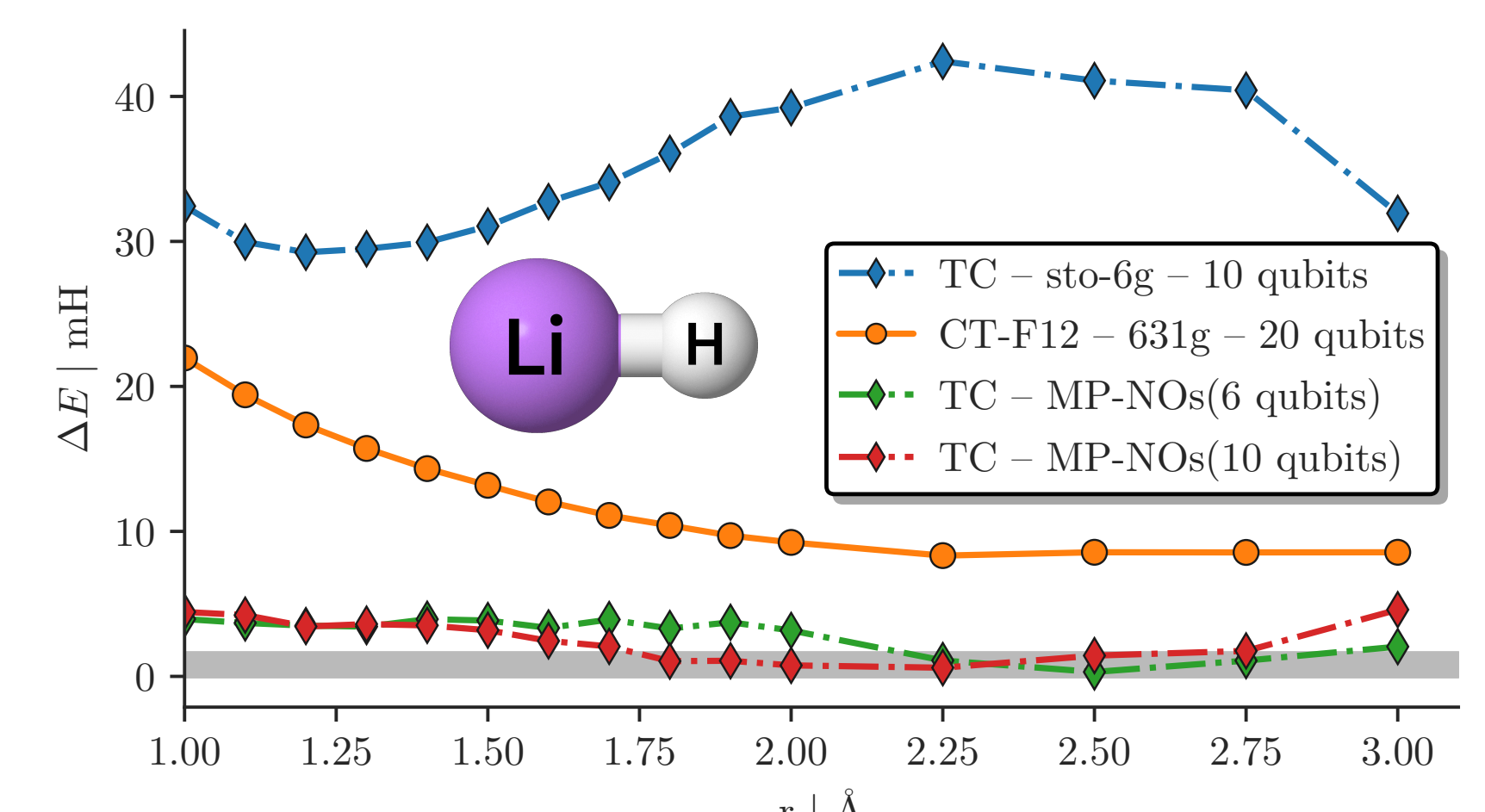
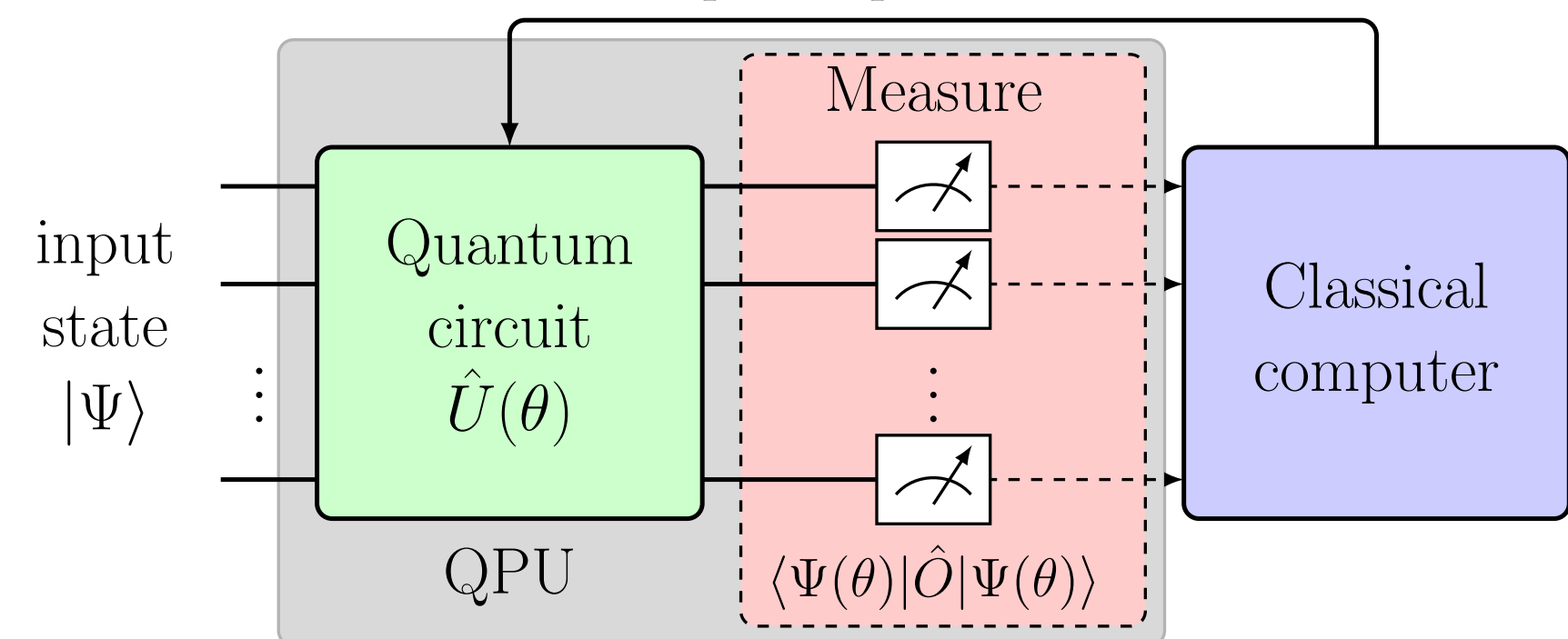
Imaginary Time Evolution

Variational methods like VQE³ not applicable. Use imaginary-time evolution⁴ to obtain GS

$$i \frac{\partial |\Psi\rangle}{\partial t} = \hat{H} |\Psi\rangle \xrightarrow{\tau \equiv it} \frac{\partial |\Psi\rangle}{\partial \tau} = -\hat{H} |\Psi\rangle$$

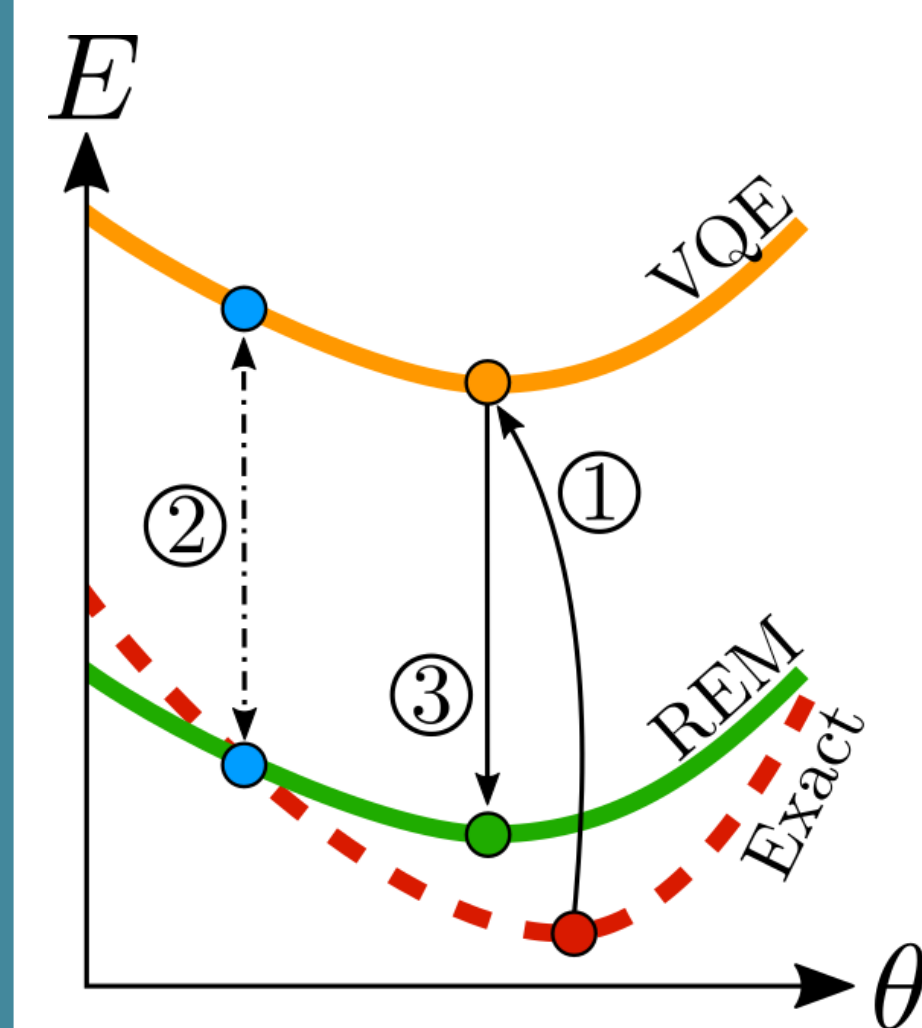
$$\rightarrow |\Psi_0\rangle = \lim_{\tau \rightarrow \infty} N(\tau) e^{-\hat{H}\tau} |\Psi(0)\rangle$$

Can be implemented on Quantum Hardware^{5,6}



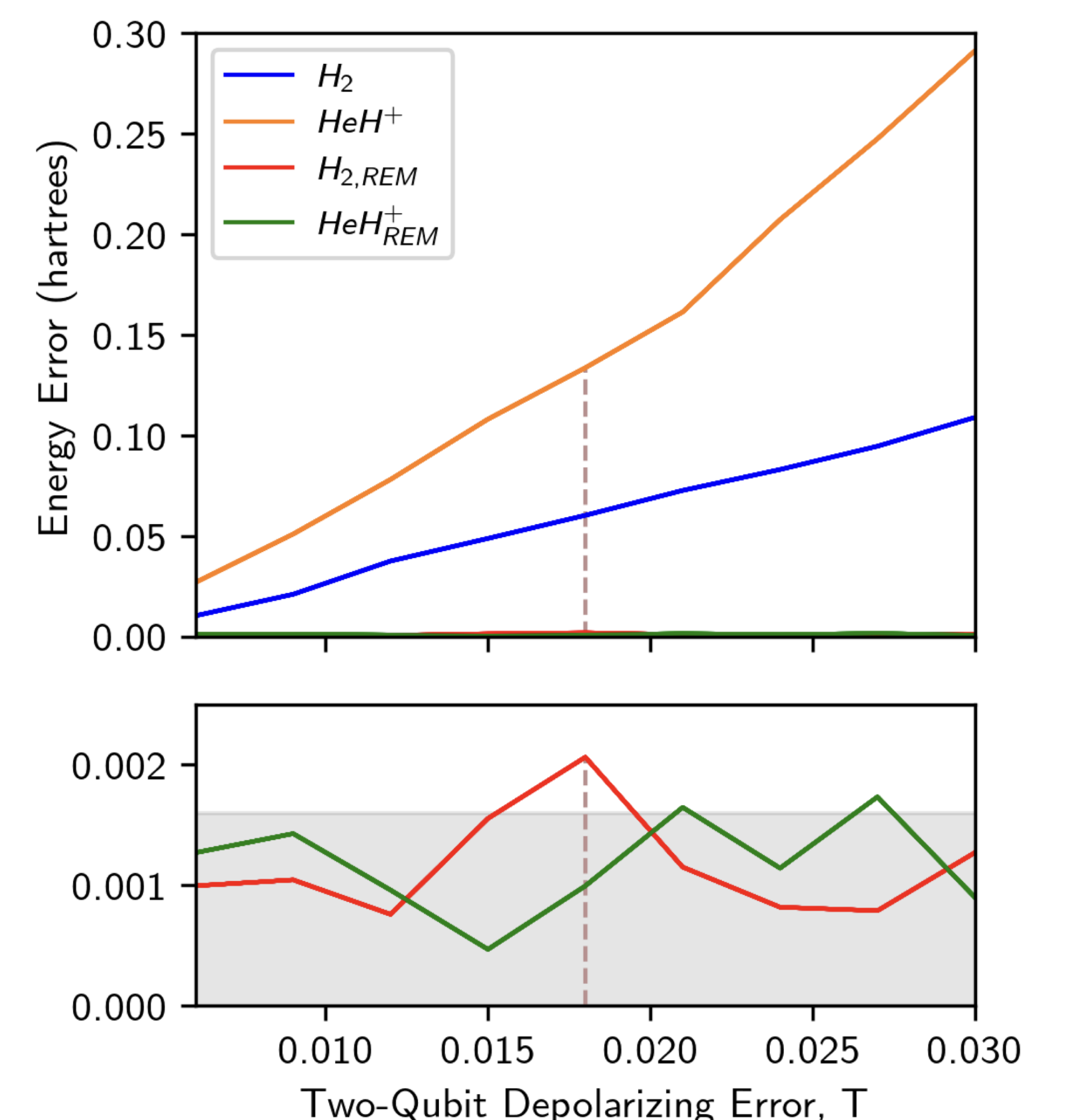
Reference Error Mitigation

Taking advantage of classically tractable points in the VQE parameter space, one can make an approximation for the errors in quantum calculations.⁸



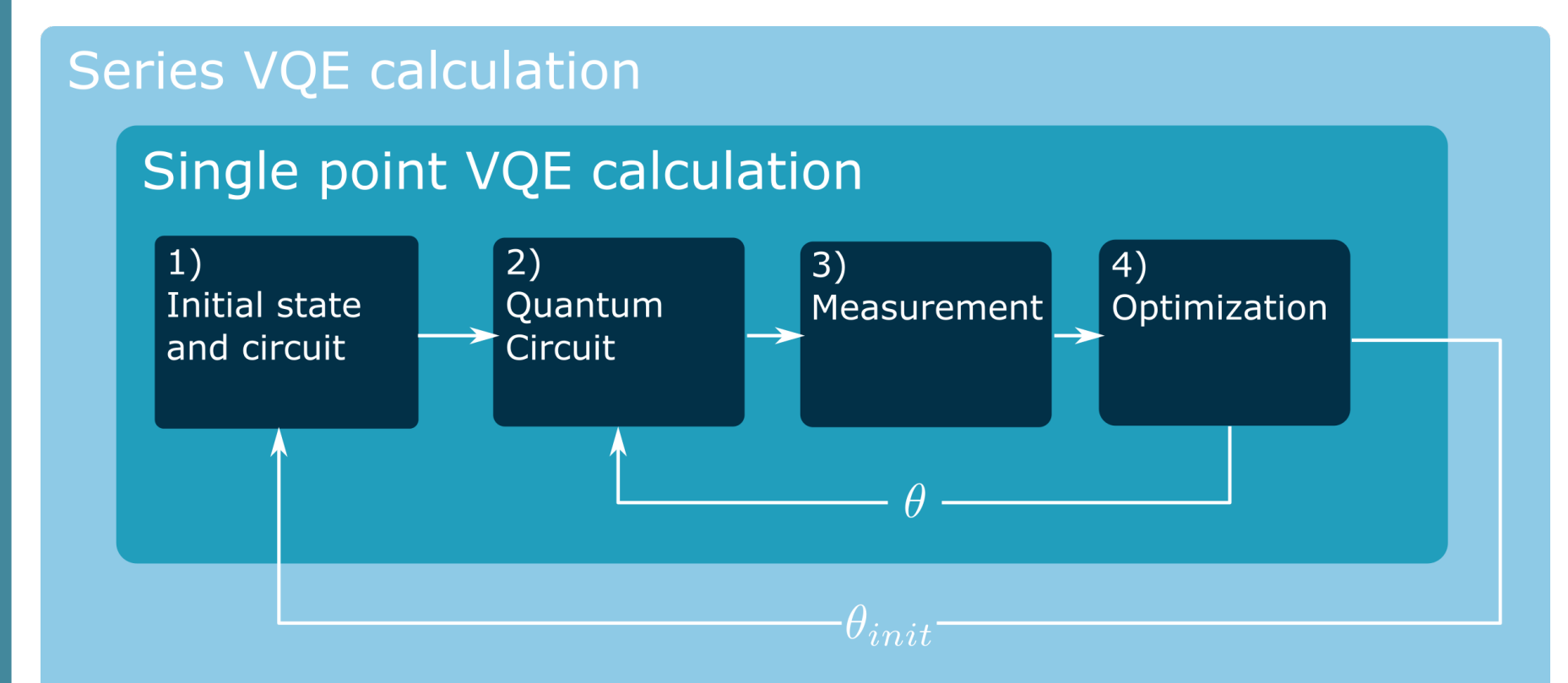
- Noise affects VQE.
- An *exact* reference calculation is made.
- Expectation value can be corrected.

REM is noise-resilient. Guaranteed to get equal or better result than classical.

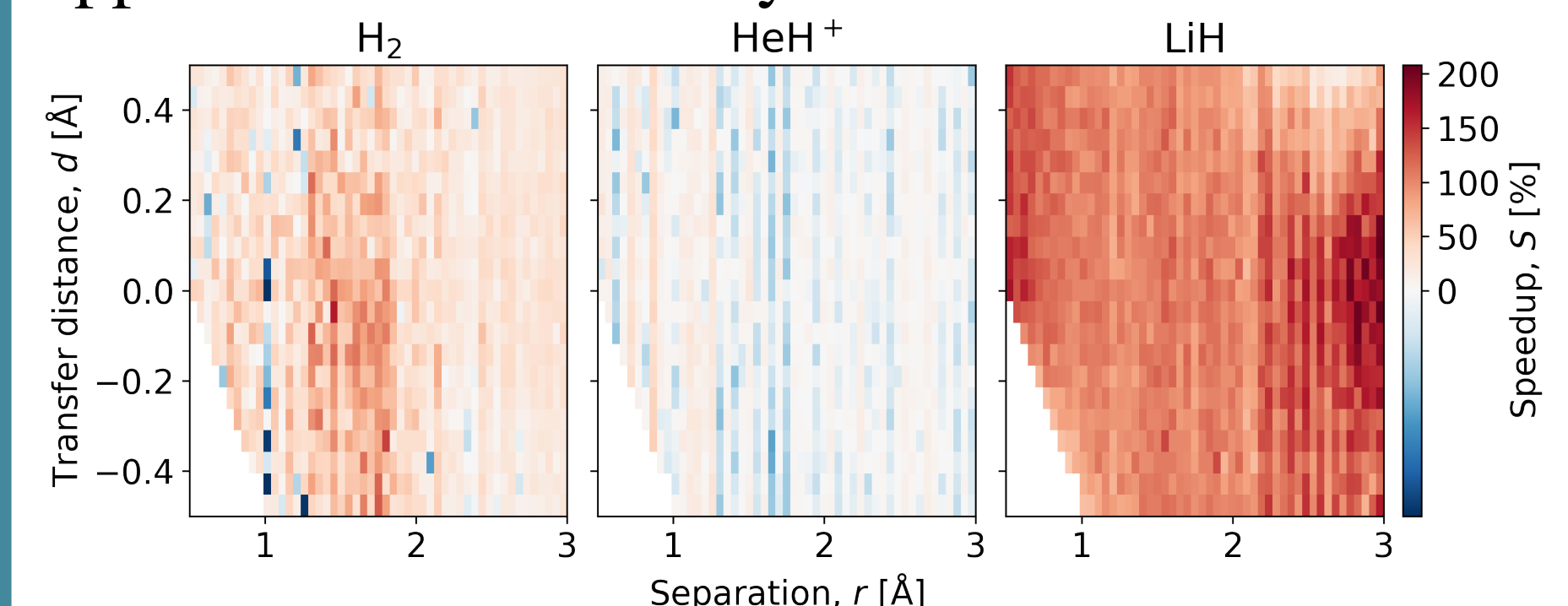


VQE Parameter Transfer

Using chemical insight, we can give a better initial guess for VQE calculations performed in series.



Effective for correlated systems, aligning with QC applications in chemistry.



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