Electronic Structure Methods for NISQ-era Quantum Computing

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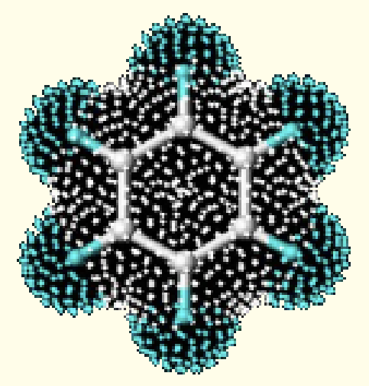
1. The Quantum Chemistry Problem



$\longleftrightarrow \quad \mathcal{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$

- In quantum chemistry, one of the main focuses is in obtaining the ground state energy of molecular systems.
- This information is useful in fields such as chemistry, condensed-matter physics and materials science, where determining the chemical properties of molecules is necessary - e.g. in the design of novel pharmaceuticals and catalysts.
- For classical computers, this can be a computationally expensive task since the memory requirement to handle such a system scales **exponentially** with the size of the molecule.

2. Quantum Computing and NISQ algorithms

- Quantum computers promise to overcome this bottleneck through using **qubits** instead of classical bits that harness quantum superposition and entanglement. Quantum algorithms can reduce the exponential scaling of electronic structure problems to **polynomial order** [1].
- Due to current physical limitations in technology, quantum computing is still in a "Noisy Intermediate Scale Quantum (NISQ)" era:
  - Lots of circuit noise
  - Qubits don't live for long (decoherence)
  - Not many qubits available
- The best solution given the current architecture is the **Variational Quantum Eigensolver** (VQE), which reformulates the eigenvalue problem into a minimisation of the expectation value of H.
- This takes advantage of the quantum strength in preparing and measuring states, whilst utilising optimisation methods that classical computers are currently better at.

$$\langle\psi|\,\mathcal{H}\,|\psi\rangle \equiv \langle\mathcal{H}\rangle = h^{i}_{\alpha}\langle\sigma^{i}_{\alpha}\rangle + h^{ij}_{\alpha\beta}\langle\sigma^{i}_{\alpha}\sigma^{j}_{\beta}\rangle + h^{ijk}_{\alpha\beta\gamma}\langle\sigma^{i}_{\alpha}\sigma^{j}_{\beta}\sigma^{k}_{\gamma}\rangle + \ldots$$

Easy for a Quantum Computer: Easy for a Classical Computer:

$\boxed{\langle\sigma^{i}_{\alpha}\sigma^{j}_{\beta}\sigma^{k}_{\gamma}\ldots\rangle} \longrightarrow \boxed{+,\times\to\langle H\rangle}$

3. Project Aims

⇒ Explore a method for reducing the qubit requirement of the VQE, known as a **basis-set-free** approach.

⇒ Implement a **quantum subspace expansion** method within the basis-set-free representation to further improve the performance of the VQE.

4. Basis-set-free Representation

- Electronic wavefunctions are discretized for implementation on computers through **basis sets** → independent, mutually orthogonal functions.

STO-3G, 6-31G, cc-pVDZ, aug-cc-pCVTZ, 6-31G*, ZaPa, def-SVP, d-aug-cc-pVQZ, 2-ZaPa, cc-pwCVTZ, 3-ZaPa-NR-CV, aug-cc-pV5Z, def2-SVP, def-QZVP, def2-QZVP, cc-pV(D+d)Z, aug-cc-pCV(T+d)Z, aug-cc-pVTZ, STO-6G, 6-31G, cc-pV(5+d)Z, ANO-R3, aug-admm-2, def2-SV(P), HGBS-9, pc-0, pc-3, pc-4, pc-emd-2, Sapporo-DZB, pV6Z, pV7Z, cc-pV6Z, aug-cc-pCV5Z, ANO-R4, 6-21G, 6-31+G, 6-31++G, 6-31+G*, STO-5G, cc-pVQZ, ...**

Lots of basis sets to choose from

- A recently presented basis-set-free approach uses **multiresolution analysis** (MRA) to optimize the orbitals directly without a rigid, defined basis set [2], resulting in a compact molecular Hamiltonian.
- We take advantage of this representation to explore its application in the context of the VQE and investigate its performance on several systems.

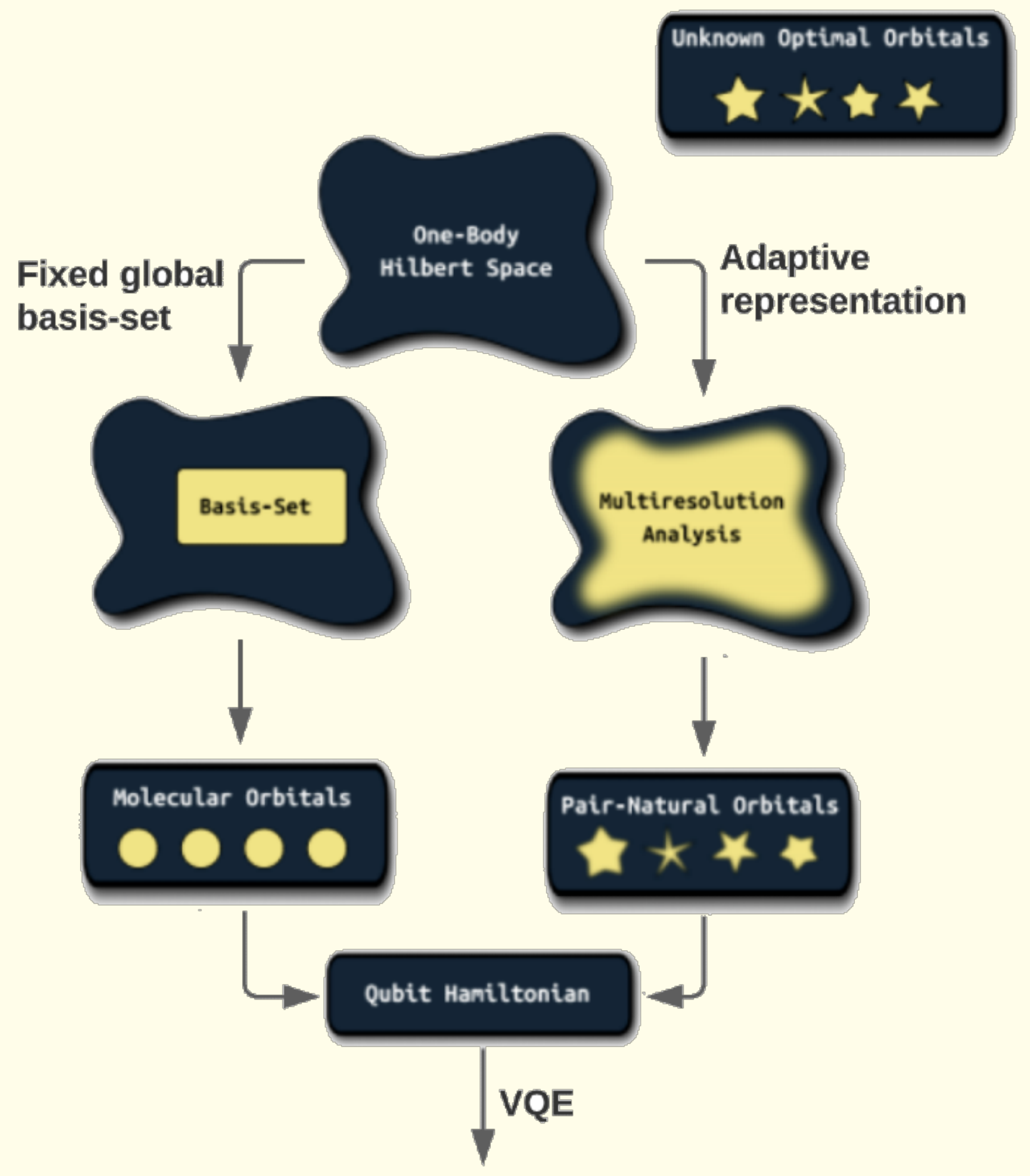


Figure 1: Constructing molecular qubit Hamiltonians[2]

5. Quantum Subspace Expansion

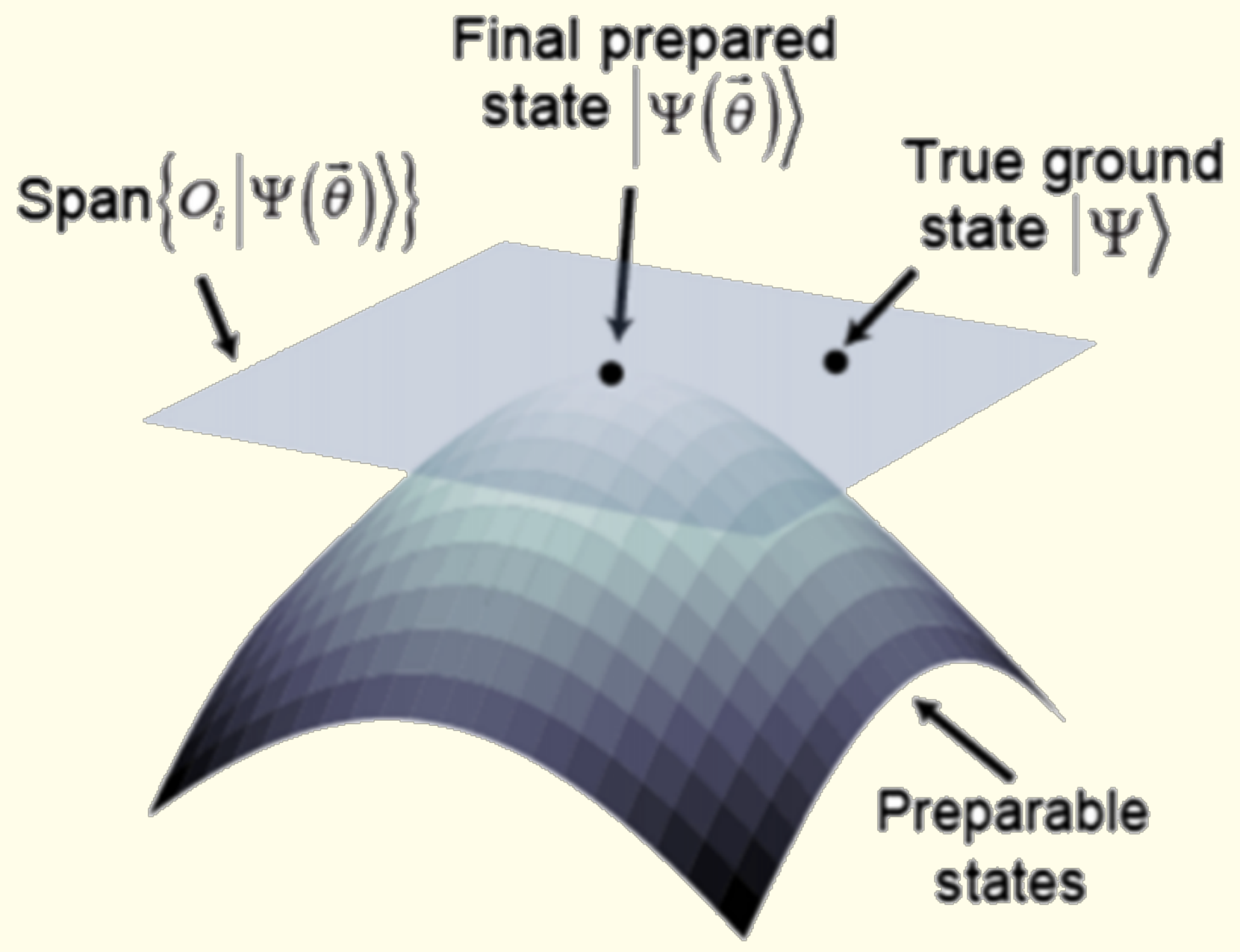


Figure 2: Cartoon of QSE protocol [3]

- The **Quantum Subspace Expanstion** (QSE) method expands about a prepared reference state by applying a set of fermionic excitation/annihilation operators.
- In the expanded space, the optimal solution for the ground and excited states can be found by solving the generalized eigenvalue problem

$$H'C = S'CE$$

- Originally used to approximate excited state energies, QSE has been shown to act as error suppression for ground state energies.
- In our work, we have implemented a cumulant-expansion approximation to this which can be calculated through only a few additional measurements and some classical post-processing, without requiring any additional qubits.

References

1. Aspuru-Guzik, A., Dutoi, A. D., Love, P. J. & Head-Gordon, M. Simulated Quantum Computation of Molecular Energies. *Science* **309,** 1704–1707 (Sept. 2005).
2. Kottmann, J. S., Schleich, P., Tamayo-Mendoza, T. & Aspuru-Guzik, A. Reducing Qubit Requirements while Maintaining Numerical Precision for the Variational Quantum Eigensolver: A Basis-Set-Free Approach. *J. Phys. Chem. Lett.* **12,** 663–673 (Jan. 2021).
3. Colless, J. I. *et al.* Computation of Molecular Spectra on a Quantum Processor with an Error-Resilient Algorithm. *Phys. Rev. X* **8,** 011021 (1 Feb. 2018).

6. Results

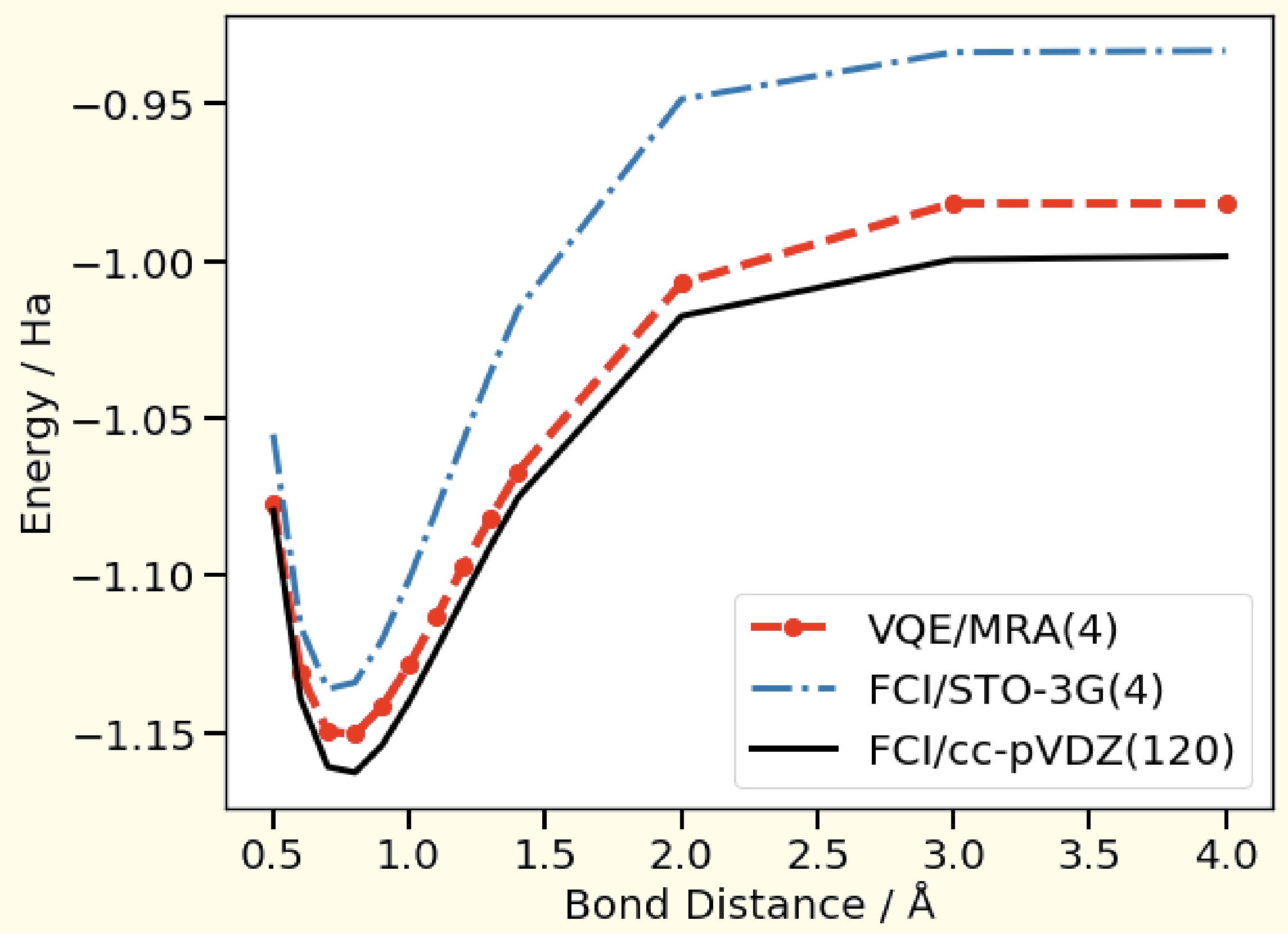


Fig. 3: Dissociation curve of Hydrogen molecule. VQE/MRA method compared to the best affordable variational methods using standard Gaussian basis sets. Number of qubits required shown in parentheses.

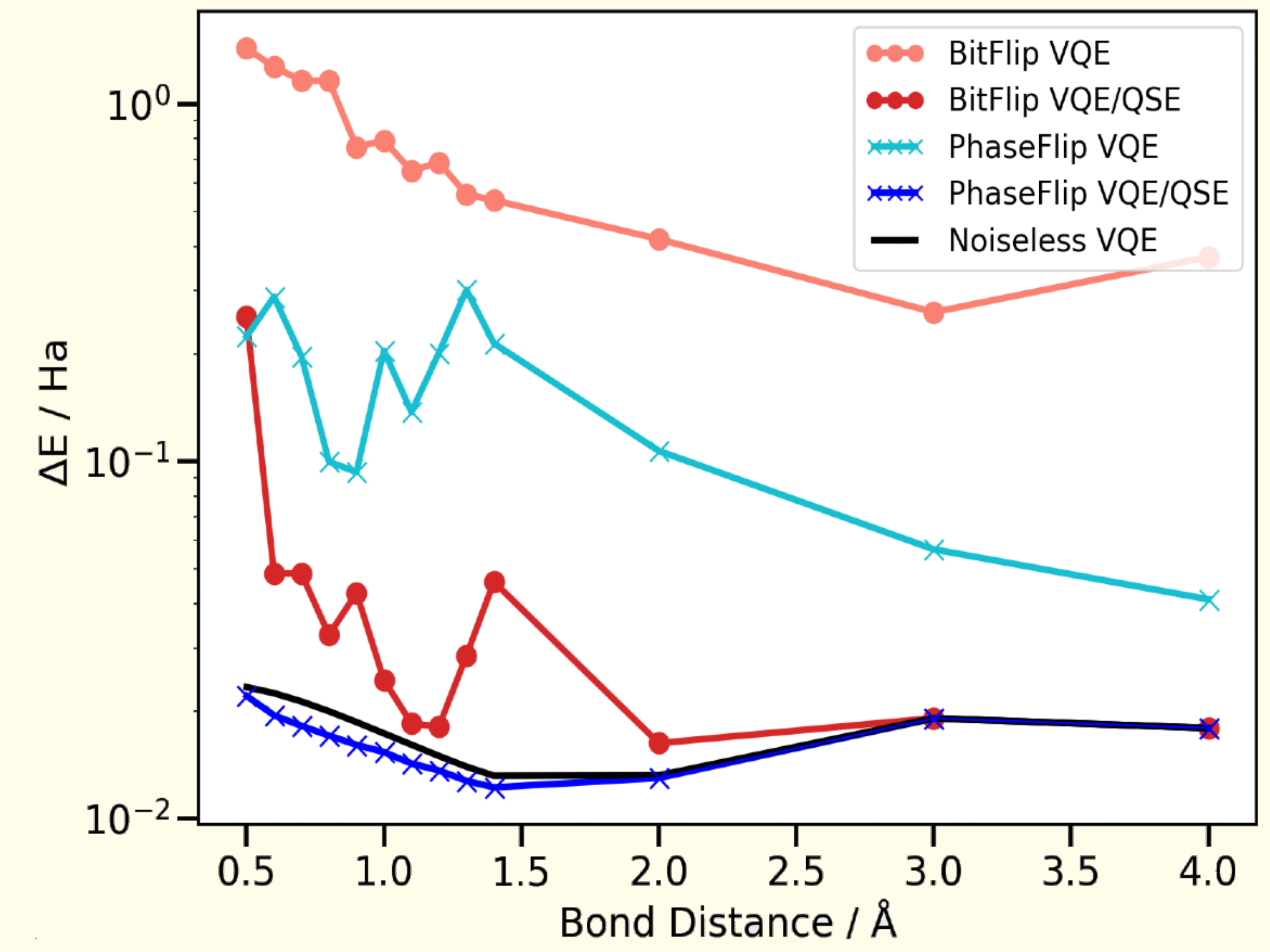


Fig. 4: Absolute energy error for VQE and VQE/QSE energies when Bit/PhaseFlip errors applied with probability $p = 0.01$, in comparison to H_2 FCI calculation in cc-pVDZ basis set.

7. Conclusion & Future Work

- Basis-set-free approach has shown a clear advantage over standard basis sets, achieving **high numerical precision** with a **significantly reduced number of qubits**.
- Quantum subspace expansion has demonstrated ability to **consistently correct** various types of circuit errors, **without additional qubit requirements**.
- Current work involves combining the basis-set-free approach to the QSE method, which should benefit from its compact representation.
- Further work will be done to reintroduce extra correlation effects from virtual orbital excitations.