

S1 1 *Answer.* The Hartree-Fock (HF) method and the Full Configuration Interaction (FCI) method are both variational, while the Coupled Cluster (CC) method is non-variational.

The variational methods ensure that the estimated energies are greater than or equal to the ground state energy - i.e. the estimated energies always provide upper bounds, and do not give energies lower than the ground state energy. In the case of the FCI, we are additionally guaranteed convergence to the exact ground state energy. However, the FCI method has an exponential complexity dependence on the size of the chemical system of interest - making it only computationally tractable for the smallest chemical systems. HF is an efficient and decent approximation for very large molecules; however, it becomes qualitatively incorrect when electronic correlations become sufficiently strong.

The non-variational CC method violate the variational principle and can give energies lower than the ground state. However, this method often gives accurate energies and can be applied to modestly sized chemical systems, with a polynomial computational scaling in the number of orbitals of the chemical system of interest.

In practice approximate variational methods (such as HF) and non-variational methods (such as CC), can be used as ansatz for more accurate treatments, including quantum algorithms such as VQE.

We have generated PES using HF, CC and FCI for LiH in the associated S1 notebook. ■

S2 1 *Answer.* The fermionic operators satisfy the following algebra (CAR or, more generally, C^* algebra) - i.e. the fermionic commutation relations.

$$\begin{aligned}\{a_p^\dagger, a_q\} &= \delta_{p,q} \\ \{a_p^\dagger, a_q^\dagger\} &= \{a_p, a_q\} = 0\end{aligned}$$

This algebra is distinct from the usual $SU(2)$ algebra (i.e. of Pauli matrices) which gates on a quantum computer obey. To encode the Hamiltonian properly is to find a map (e.g. Jordan-Wigner transformation, Bravyi-Kitaev transformation, Parity transformation) between the two algebras. ■

2 *Answer.* After Jordan-Wigner transforming a real electronic Hamiltonian, the terms in the resulting qubit Hamiltonian are also real.

We have demonstrated the Jordan-Wigner and Bravyi-Kitaev transformations on the LiH molecule in the associated S2 notebook. ■

S3 1a *Answer.* UCC conserves each of the listed symmetries. ■

1b *Answer.* QCC does not conserve any of the listed symmetries. ■

2 *Answer.* ■

Imposing symmetry narrows the portion of the exponential Hilbert space that needs to be searched. Furthermore, the final and initial states will be in the same symmetry sector.

3 *Answer.* If a unitary transformation breaks the symmetries, they can be restored by including symmetry constraints and/or projection operations. For example, spin constraints ($\langle S^2 \rangle = 0$) can be imposed to restore the correct singlet spin symmetry on QMF solutions [I.G. Ryabinkin et al. J. Chem. Theory Comput. (2018)]. ■

S4 1 Answer. We can find the optimal splitting, given that one knows fragment variances ($\sigma_{H_n}^2$), by minimizing the total error $\sum_n \frac{\sigma_{H_n}^2}{N_n}$ under the constraint that $N_T = \sum_n N_n$. To do so, we first turn this constrained optimization problem into an unconstrained optimization (minimization) problem using Lagrange multipliers:

$$c(N) = \sum_n \frac{\sigma_{H_n}^2}{N_n} + \lambda(N_T - \sum_n N_n)$$

where $N = (N_1, N_2, \dots)$ and $\{\sigma_{H_n}\}$ is known.

Then, we can use the derivatives of $c(N)$ to find the optimal N .

$$\begin{aligned} \frac{\partial c(N)}{\partial N_n} &= -\frac{\sigma_{H_n}^2}{N_n^2} - \lambda = 0 \\ \Rightarrow \frac{\sigma_{H_n}^2}{N_n^2} &= \lambda \\ \Rightarrow N_n &= \frac{\sqrt{\sigma_{H_n}^2}}{\sqrt{\lambda}} \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{\partial c(N)}{\partial \lambda} &= N_T - \sum_n N_n = 0 \\ \Rightarrow N_T &= \sum_n N_n \text{ (as expected)} \end{aligned} \quad (2)$$

Then, from Equation 2 and Equation 2, we find that

$$\begin{aligned} N_T &= \sum_n \frac{\sqrt{\sigma_{H_n}^2}}{\sqrt{\lambda}} \\ \Rightarrow \sqrt{\lambda} &= \frac{\sum_n \sqrt{\sigma_{H_n}^2}}{N_T} \\ \Rightarrow N_n &= \frac{\sqrt{\sigma_{H_n}^2}}{\sum_m \sqrt{\sigma_{H_m}^2}} N_T \end{aligned}$$

This tells us how many measurements (i.e. N_n) we should perform per fragment.

We can also recover the optimal error using the above optimal splitting.

$$\begin{aligned} \text{Error}^2 &\leq \sum_n \frac{\sigma_{H_n}^2}{N_n} = \frac{\sum_m \sqrt{\sigma_{H_m}^2}}{N_T} \sum_n \frac{\sigma_{H_n}^2}{\sqrt{\sigma_{H_n}^2}} = \frac{\sum_m \sqrt{\sigma_{H_m}^2}}{N_T} \sum_n \sqrt{\sigma_{H_n}^2} = \frac{(\sum_m \sqrt{\sigma_{H_m}^2})^2}{N_T} \\ \text{Error} &\leq \frac{\sum_m \sqrt{\sigma_{H_m}^2}}{\sqrt{N_T}} \quad \checkmark \end{aligned} \quad (3)$$

■

2 Answer. Here, we may use a classically approximated $|\psi\rangle$ to help calculate $\sigma_{H_n}^2$ for the fragments of the QWC or FC partitions. Then, we can use Equation 3 to find when the error upper bound is equal to $\frac{1}{1000}$. ■

S5 1 *Answer.* Results shown in associated notebook.

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2 *Answer.* The same error-mitigation protocol can be used for more complicated symmetries \hat{S}^2 [[I.G. Ryabinkin et al. J. Chem. Theory Comput. (2019)].

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