Electronic Supplementary Information

A Feasible Approach for Automatically Differentiable Unitary Coupled-Cluster on Quantum Computers

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EIGENSTATES OF FERMIONIC GENERATORS

Take, without loss of generality, Eq. (28) of the main text. Following the definitions of the main text, the eigenstates of this operator can directly be constructed to be

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left(\left|o_{\mathbf{q}}^{\mathbf{p}}\right\rangle \pm i\left|o_{\mathbf{p}}^{\mathbf{q}}\right\rangle\right) \tag{1}$$

with corresponding eigenvalues ± 1. On all configuration outside that manifold the generator will act as zero making them also eigenstates with eigenvalue 0. Consider a two electron system within two spatial orbitals (four spin orbitals) as example. In particular that could be H_2/STO-3G or He/6-31G. Within the Jordan-Wigner encoding ($0_\uparrow \to 0, 0_\downarrow \to 1, 1_\uparrow \to 2, 1_\downarrow \to 3$), this system is directly mapped to four qubits which are then representing the Fock space of four spin-orbitals (*i.e.* also one, three and four electron states are included). Lets consider a single excitation that excites a spin-up electron from the first spatial orbital (*i.e.* qubit 0) to a spin-up electron on the second spatial orbital (*i.e.* qubit 2), so the generator is $G_{02} = i\left(a_2^\dagger a_0 - h.c.\right)$. The manifold of states that have qubit 0 and 1 both occupied $|1\cdot 1\cdot\rangle$ or unoccupied $|0\cdot 0\cdot\rangle$ span the nullspace of this generator. All states that have qubit 0 occupied and qubit 1 unoccupied and vice versa span the eigenstates with eigenvalues ± 1 according to the formula above which can be seen from how the generator acts on the corresponding states

$$G_{02}\,|1\cdot 0\cdot\rangle = i\,|0\cdot 1\cdot\rangle\,, \tag{2}$$
$$G_{02}\,|0\cdot 1\cdot\rangle = -i\,|1\cdot 0\cdot\rangle \tag{3}$$

which can be described as a high dimensional σ_y operation. Note, that this is also the reason, why the corresponding unitaries create real superpositions, in similar ways as single qubit R_y rotations do.

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DERIVATION OF EQ. (14)

$$
\begin{aligned}
U(\theta) &= e^{-i\frac{\theta}{2}G} = e^{-i\frac{\theta}{4}(G_+ + G_-)} && (4)\\
&= e^{-i\frac{\theta}{4}G_+} e^{-i\frac{\theta}{4}G_-} && (5)\\
&= \left(\cos\left(\frac{\theta}{4}\right) - i\sin\left(\frac{\theta}{4}\right)G+\right)\left(\cos\left(\frac{\theta}{4}\right) - i\sin\left(\frac{\theta}{4}\right)G-\right) && (6)\\
&= \cos^2\left(\frac{\theta}{4}\right) - i\cos\left(\frac{\theta}{4}\right)\sin\left(\frac{\theta}{4}\right)(G_+ + G_-) - \sin^2\left(\frac{\theta}{4}\right)G_+G_- && (7)\\
&= \left(\cos^2\left(\frac{\theta}{4}\right) - \sin^2\left(\frac{\theta}{4}\right)\right) - 2i\cos\left(\frac{\theta}{4}\right)\sin\left(\frac{\theta}{4}\right)G + 2\sin^2\left(\frac{\theta}{4}\right)P_0 && (8)\\
&= \cos\left(\frac{\theta}{2}\right) - i\sin\left(\frac{\theta}{2}\right)G + \left(1 - \cos\left(\frac{\theta}{2}\right)\right)P_0 && (9)
\end{aligned}
$$

For the derivation we used the following properties and identities

$$
\begin{aligned}
&G = P_1 - P_{-1} && (10)\\
&P_1 + P_{-1} + P_0 = 1 && (11)\\
&G^2 = P_1 + P_{-1} && (12)\\
&P_iP_j = \delta_{ij}, \quad i,j \in \{-1,1,0\} && (13)\\
&GP_0 = P_0G = 0 && (14)\\
&G_+G_- = G_-G_+ = G^2 - P_0 = 1 - 2P_0 && (15)\\
&[G_+, G_-] = 0 && (16)\\
&G_+^2 = G_-^2 = 1 && (17)\\
&\left(\cos^2\left(\frac{\theta}{4}\right) - \sin^2\left(\frac{\theta}{4}\right)\right) = \cos\left(\frac{\theta}{2}\right) && (18)\\
&\cos\left(\frac{\theta}{4}\right)\sin\left(\frac{\theta}{4}\right) = \frac{1}{2}\sin\left(\frac{\theta}{2}\right) && (19)\\
&\sin^2\left(\frac{\theta}{4}\right) = \frac{1 - \cos\left(\frac{\theta}{2}\right)}{2} && (20)
\end{aligned}
$$

as well as properties from the main text.

OVERLAP EXPECTATION VALUES

For completeness we show here to reformulate absolute squares of overlaps as expectation values (see also [1]):

$$
\begin{aligned}
S_{ij}^2 &= |\langle i|j\rangle|^2\\
&= \langle i|j\rangle\langle j|i\rangle\\
&= \langle i|U_j|0\rangle\langle 0|U_j^\dagger|i\rangle\\
&= \langle \mathbf{Q}_+\rangle_{U_j^\dagger U_i}. && (21)
\end{aligned}
$$

Excited states can be found by applying the variational principle to a projected Hamiltonian QH where the $Q = (1 - |\Psi_i\rangle\langle\Psi_i|$ projects out already converged states $|\Psi_i\rangle$ prepared by the unitary U_i (note that the unitary includes the reference preparation). Using the idempotency of the projector and the assumption, that the states Ψ_i are real eigenstates of the Hamiltonian we arrive at

$$
QH = H - \sum_i E_i |\Psi_i\rangle\langle\Psi_i| . \tag{22}
$$

Using the above expression for the overlap objective, expectation values of the projected Hamiltonian can then be written as sum of expectation values of the original Hamiltonian and squares of overlaps of the current circuit U

$$\begin{aligned}\langle QH\rangle_U &= \langle H\rangle_U - \sum_i E_i S^2_{\Psi_U\Psi_i} \\ &= \langle H\rangle_U - E_i\langle \boldsymbol{Q}_+\rangle_{U_i^\dagger U}. \end{aligned} \tag{23}$$

Note, that within the VQE framework, Ψ_i is not necessarily a real eigenstate and potential errors accumulate and effect higher lying excited states (see Ref. [1] for more details).

INITIALIZATION CIRCUITS FOR CIS STATES

The circuits used for the initialization, for the excited states calculation are shown below. For completeness we also show the initialization of a triplet excitation. The circuits are explicit for the Jordan-Wigner representation and would look different for other encodings.

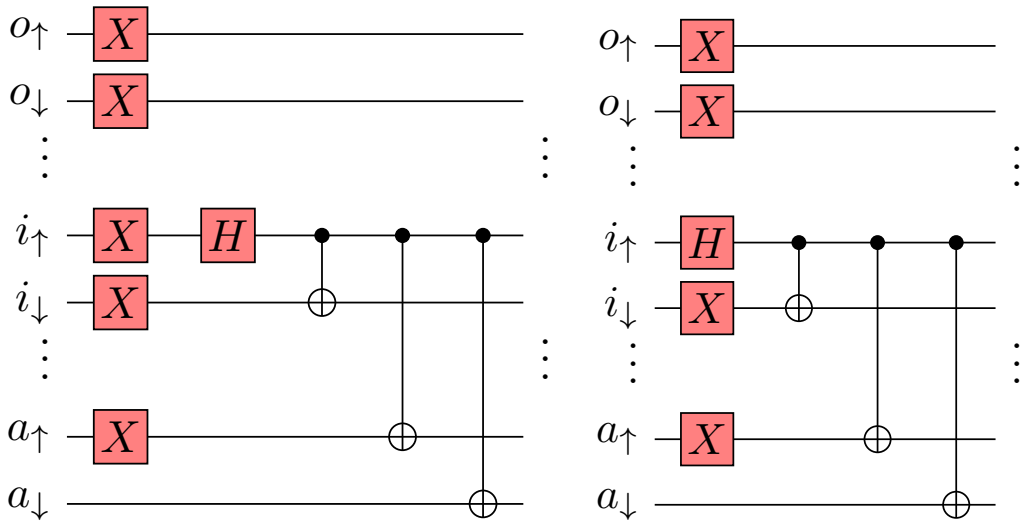

Figure 1. Circuits used for the initialization in the excited states calculation. The qubit indices, $o_\uparrow$ and $o_\downarrow$, represent the occupied orbitals, and the excitation from $i_\uparrow$ and $i_\downarrow$ to $a_\uparrow$ and $a_\downarrow$ represent the two main contributions in the CIS state. Left Panel: The circuit for the Singlet configuration. Right Panel: The circuit for the Triplet configuration.

[1] J. Lee, W. J. Huggins, M. Head-Gordon, and K. B. Whaley, Generalized unitary coupled cluster wave functions for quantum computation, Journal of chemical theory and computation **15**, 311 (2018).