Supplementary Information for

Overlap-ADAPT-VQE: Practical Quantum Chemistry on Quantum Computers via Overlap-Guided Compact Ansätze

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Supplementary Note 1: Operator identification through overlap gradient computations

Let us assume that we are at the m^{th} iteration of the ADAPT-VQE algorithm, i.e., we have a current ansatz wave-function $|\Psi^{m-1}\rangle$ as well as a target wave-function $|\Psi_{\text{ref}}\rangle$. We now wish to identify the parameterized exponential qubit excitation evolution operator $\widehat{A}_m(\theta_m)$ whose action on the current ansatz $|\Psi^{m-1}\rangle$ will produce a new wave-function with the largest overlap with respect to the target wave-function using the overlap gradient expression give by

$$\frac{\partial}{\partial \theta_m} \langle \Psi_{\text{ref}}| \, \widehat{A}_m(\theta_m) \Psi^{m-1} \rangle \big|_{\theta_m=0}.$$

To do so, recall that any parameterized qubit excitation evolution operator $\widehat{A}_m(\theta_m)$ is of the form

$$\widehat{A}_m(\theta_m) = \exp\left(-i\theta \mathscr{B}_m\right),$$

where $\mathscr{B}_m$ is a sum of so-called Pauli strings involving X and Y single qubit Pauli gates.

Using the chain rule, we therefore deduce that

$$\frac{\partial}{\partial \theta_m} \langle \Psi_{\text{ref}}| \, \widehat{A}_m(\theta_m) \Psi^{m-1} \rangle = \frac{\partial}{\partial \theta_m} \langle \Psi_{\text{ref}}| \exp\left(-i\theta \mathscr{B}_m\right) \Psi^{m-1} \rangle = \langle \Psi_{\text{ref}}| \, i\mathscr{B}_m \exp\left(-i\theta \mathscr{B}_m\right) \Psi^{m-1} \rangle .$$

Consequently, we obtain that

$$\begin{aligned} \frac{\partial}{\partial \theta_m} \langle \Psi_{\text{ref}}| \, \widehat{A}_m(\theta_m) \Psi^{m-1} \rangle \big|_{\theta_m=0} &= \langle \Psi_{\text{ref}}| \, i\mathscr{B}_m \exp\left(-i\theta \mathscr{B}_m\right) \Psi^{m-1} \rangle \big|_{\theta_m=0} \\ &= \langle \Psi_{\text{ref}}| \, i\mathscr{B}_m \Psi^{m-1} \rangle . \end{aligned} \tag{1}$$

We have thus reduced the problem of computing the sought-after overlap gradients at the m^{th} Overlap-ADAPT iteration to one of measuring the overlap between the target wave-function $|\Psi_{\text{ref}}\rangle$ and an intermediate wave-function $|i\mathscr{B}_m \Psi^{m-1}\rangle$ where $\mathscr{B}_m$ is a sum of so-called Pauli strings involving X and Y single qubit Pauli gates. Let us emphasize here that our overlap operator identification process is based on finding qubit excitation evolution operator that maximizes the magnitude of the above computed gradient (and not the value of the gradient itself).

For classically represented target wave-functions (such as CIPSI wave-functions), such overlaps can be readily computed on classical architecture by making use of the usual determinant-based expansion of wave-functions. On the other hand, Equation (1) cannot be directly evaluated on a quantum computer.

In order to evaluate Equation (1) on quantum architecture, we proceed as follows. Using a direct calculation based on the Taylor series together with the commutation relations of Pauli matrices, we first deduce that

$$\exp(-i\theta\mathscr{B}_m) = I + (\cos(\theta)-1)\mathscr{B}_m^2 - i\sin(\theta)\mathscr{B}_m,$$

which immediately yields that

$$\begin{aligned}\langle\Psi_{\text{ref}}|\,\widehat{A}_m(\theta_m)\Psi^{m-1}\rangle &= \langle\Psi_{\text{ref}}|\,\exp(-i\theta\mathscr{B}_m)\,\Psi^{m-1}\rangle \\ &= \langle\Psi_{\text{ref}}|\Psi^{m-1}\rangle + (\cos(\theta)-1)\,\langle\Psi_{\text{ref}}|\mathscr{B}_m^2\Psi^{m-1}\rangle - \sin(\theta)\,\langle\Psi_{\text{ref}}|\,i\mathscr{B}_m\Psi^{m-1}\rangle\,.\end{aligned}$$

Plugging in the values $\theta_m = \pm\frac{\pi}{2}$ and $\theta_m = \pm\frac{\pi}{3}$, we can deduce from some tedious but straight-forward algebra that

$$\begin{aligned}&\frac{1}{2}\left|\langle\Psi_{\text{ref}}|\,\widehat{A}_m\left(-\frac{\pi}{2}\right)\Psi^{m-1}\rangle\right|^2 - \frac{1}{2}\left|\langle\Psi_{\text{ref}}|\,\widehat{A}_m\left(\frac{\pi}{2}\right)\Psi^{m-1}\rangle\right|^2 \\ &+\frac{2}{\sqrt{3}}\left|\langle\Psi_{\text{ref}}|\,\widehat{A}_m\left(\frac{\pi}{3}\right)\Psi^{m-1}\rangle\right|^2 - \frac{2}{\sqrt{3}}\left|\langle\Psi_{\text{ref}}|\,\widehat{A}_m\left(-\frac{\pi}{3}\right)\Psi^{m-1}\rangle\right|^2 \\ &= -2\,\langle\Psi_{\text{ref}}|\Psi^{m-1}\rangle\,\langle\Psi_{\text{ref}}|\,i\mathscr{B}_m\Psi^{m-1}\rangle\,,\end{aligned}$$

where we have used the fact that $\langle\Psi_{\text{ref}}|\,i\mathscr{B}_m\Psi^{m-1}\rangle \in \mathbb{R}$. As a consequence, we obtain that

$$\begin{aligned}\left|\frac{\partial}{\partial\theta_m}\langle\Psi_{\text{ref}}|\,\widehat{A}_m(\theta_m)\Psi^{m-1}\rangle\,\big|_{\theta_m=0}\right| = \left|\langle\Psi_{\text{ref}}|\,i\mathscr{B}_m\Psi^{m-1}\rangle\right| = \frac{1}{2}\frac{1}{|\,\langle\Psi_{\text{ref}}|\Psi^{m-1}\rangle\,|}\Bigg|&\frac{1}{2}\left|\langle\Psi_{\text{ref}}|\,\widehat{A}_m\left(-\frac{\pi}{2}\right)\Psi^{m-1}\rangle\right|^2 \\ &- \frac{1}{2}\left|\langle\Psi_{\text{ref}}|\,\widehat{A}_m\left(-\frac{\pi}{2}\right)\Psi^{m-1}\rangle\right|^2 + \frac{2}{\sqrt{3}}\left|\langle\Psi_{\text{ref}}|\,\widehat{A}_m\left(\frac{\pi}{3}\right)\Psi^{m-1}\rangle\right|^2 \\ &- \frac{2}{\sqrt{3}}\left|\langle\Psi_{\text{ref}}|\,\widehat{A}_m\left(-\frac{\pi}{3}\right)\Psi^{m-1}\rangle\right|^2\Bigg|.\end{aligned}$$

Each of the terms on the right-hand side of the above expression is now measurable on a quantum computer using the usual methods. Consequently, the sought-after overlap gradient can be computed at the cost of four measurements of the overlap $\langle\Psi_{\text{ref}}|\,\widehat{A}_m(\theta_m)\Psi^{m-1}\rangle$, i.e., one for each $\theta_m = \pm\frac{\pi}{2}$ and $\theta_m = \pm\frac{\pi}{3}$ as well as knowledge of the overlap from the previous iteration, i.e., $|\,\langle\Psi_{\text{ref}}|\Psi^{m-1}\rangle\,|$.

Let us remark here that since only four overlap evaluations are required to evaluate a single overlap gradient, the Overlap-ADAPT-VQE process is very sober in terms of quantum resources. Indeed, we recall that computing a single expectation value of the Hamiltonian (or one energy gradient) involves measuring nearly each Pauli string in the Jordan-Wigner encoding of the Hamiltonian, which represents $O(N^4)$ function evaluations. Note however that some innovative techniques allow subsequent savings in the number of measurements for the expectation value of the Hamiltonian[1–3].

Supplementary Note 2: Additional data on operator and gate counts

Supplementary Table 1. Single- and double-qubit evolution operator (resp. SQ, DQ) count for every simulation carried out in this study.

Molecule	Procedure	SQ operators	DQ operators	CNOTs
N_2 (12 qubits)	All	0	50	650
BeH_2 at 1.3264Å (14 qubits)	QEB-ADAPT	8	42	570
	Full-CI Overlap-ADAPT	8	42	570
	QEB-ADAPT + Overlap-ADAPT	8	42	570
BeH_2 at 3Å (14 qubits)	QEB-ADAPT	7	43	580
	Full-CI Overlap-ADAPT	8	42	570
	12 parameters CIPSI-Overlap-ADAPT	6	44	590
	25 parameters CIPSI-Overlap-ADAPT	8	42	570
	40 parameters QEB-ADAPT + Overlap-ADAPT	6	34	460
	45 parameters QEB-ADAPT + Overlap-ADAPT	6	39	525
	50 parameters QEB-ADAPT + Overlap-ADAPT	7	43	580
H_6 (12 qubits)	QEB-ADAPT	17	33	480
	Full-CI Overlap-ADAPT	0	50	650
	CIPSI-Overlap-ADAPT	2	48	630

Supplementary References

1. Yen, T.-C., Ganeshram, A. & Izmaylov, A. F. Deterministic improvements of quantum measurements with grouping of compatible operators, non-local transformations, and covariance estimates. *npj Quantum Inf.* **9**, 14 (2023).
2. Loaiza, I., Marefat Khah, A., Wiebe, N. & Izmaylov, A. F. Reducing molecular electronic hamiltonian simulation cost for linear combination of unitaries approaches. *Quantum Sci. Technol.* (2022).
3. Choi, S., Yen, T.-C. & Izmaylov, A. F. Improving quantum measurements by introducing "ghost" pauli products. *J. Chem. Theory Comput.* **18**, 7394–7402 (2022).