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State-Averaged Orbital-Optimized VQE: A quantum algorithm for the democratic description of ground and excited electronic states

Martin Beseda [1,3,5¶], **Silvie Illésová** [1,2,3], **Saad Yalouz** [4], **and Bruno Senjean** [1]

1 ICGM, Université de Montpellier, CNRS, ENSCM, Montpellier, France **2** VSB - Technical University of Ostrava, 708 00 Ostrava, Czech Republic **3** IT4Innovations, VSB – Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic **4** Laboratoire de Chimie Quantique, Institut de Chimie, CNRS/Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France **5** Dipartimento di Ingegneria e Scienze dell'Informazione e Matematica, Università dell'Aquila, via Vetoio, I-67010 Coppito-L'Aquila, Italy ¶ Corresponding author

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Summary

The electronic structure problem is one of the main problems in modern theoretical chemistry. While there are many already-established methods both for the problem itself and its applications like semi-classical or quantum dynamics, it remains a computationally demanding task, effectively limiting the size of solved problems. Fortunately, it seems, that offloading some parts of the computation to *Quantum Processing Units (QPUs)* may offer significant speed-up, often referred to as *quantum supremacy* or *quantum advantage*. Together with the potential advantage, this approach simultaneously presents several problems, most notably naturally occurring quantum decoherence, hereafter denoted as *quantum noise* and lack of large-scale quantum computers, making it necessary to focus on Noisy-Intermediate Scale Quantum computers when developing algorithms aspiring to near-term applications. SA-OO-VQE package aims to answer both these problems with its hybrid quantum-classical conception based on a typical Variational Quantum Eigensolver approach, as only a part of the algorithm utilizes offload to QPUs and the rest is performed on a classical computer, thus partially avoiding both quantum noise and the lack of *quantum bits (qubits)*. The SA-OO-VQE has the ability to treat degenerate (or quasi-degenerate) states on the same footing, thus avoiding known numerical optimization problems arising in state-specific approaches around avoided crossings or conical intersections.

Statement of need

Recently, quantum chemistry is one of the main areas-of-interest in *Quantum Computing (QC)*(Bauer et al., 2020; McArdle et al., 2020; Reiher et al., 2017). That said, in many real-life applications, it is necessary to treat both the ground and excited states accurately and on an equal footing. The problem is magnified when the Born-Oppenheimer approximation breaks down due to a strong coupling among degenerate or quasi-degenerate states, most notably the ground and the first excited state, for which the accurate description requires (computationally demanding) multi-configurational approaches. A good example of such a case is a photoisomerization mechanism of the rhodopsin chromophore, which progresses from the initial photoexcitation of the *cis* isomer over the relaxation in the first excited state towards a conical intersection, where the population is transferred back to the ground state of the *trans* isomer. To describe such a process thoroughly, one must compute not only relevant

potential energy surfaces (PESs), but also their gradients w.r.t. nuclear displacements, utilized further in molecular dynamics simulations. Finally, a description of the conical intersection can be done by obtaining *non-adiabatic couplings (NACs)*.

Formally, the approaches describing PES topology, topography, and non-adiabatic couplings require Hamiltonian diagonalization, which represents the most significant bottleneck. Considering classical methods like State-Averaged Multi-Configurational Self-Consistent Field(Helgaker et al., 2013), only small complete active spaces have to be used for the large computational overhead inherently present. However, such an approximation brings missing dynamical correlation treatment, inducing the need to recover it ex-post, usually via some of the quasi-degenerate perturbation techniques(Granovsky, 2011; Park, 2019). On the other hand, QC brings the possibility of large complete active spaces back, thus retaining a substantial part of the dynamical correlation. Moreover, the dynamical correlation can be also retrieved a posteriori utilizing QPUs only at the expense of more measurements, with no additional demands on hardware infrastructure(Takeshita et al., 2020).

State-Averaged Orbital-Optimization Variational Quantum Eigensolver (SA-OO-VQE) method addresses the above-mentioned problems and provides a way to compute both PES gradients and NACs analytically(Omiya et al., 2022; Yalouz et al., 2021, 2022). Authored by Yalouz *et al.*, there is an exemplary implementation focusing on the pedagogical aspect and relying on matrix-vector multiplications rather than actual measurements, avoiding the utilization of real QC infrastructure. Our implementation differs in a way that it aims to be a production-ready solver utilizing both QCs and classical computing infrastructure efficiently, being able to run with different backgrounds, utilizing the Qiskit toolbox interface. The whole code is written in Python3, with YAML scripts enabling its fast installation and usage.

The results are illustrated on the molecule of formaldimine, which can be seen in Figure 1. Their comparison with the ones obtained via Molcas(Li Manni et al., 2023) implementation of Complete Active-Space Self-Consistent Field(Malmqvist & Roos, 1989) are shown in Figure 2,Figure 3 and Figure 4. All the computations were computed with 3 active orbitals containing 4 electrons and with *STO-3G* basis set.

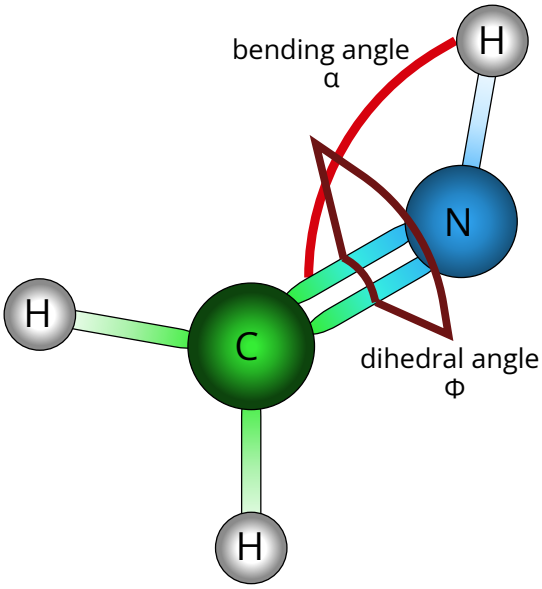

Figure 1: Molecule of formaldimine being described with bending and dihedral angles denoted α and ϕ, respectively.

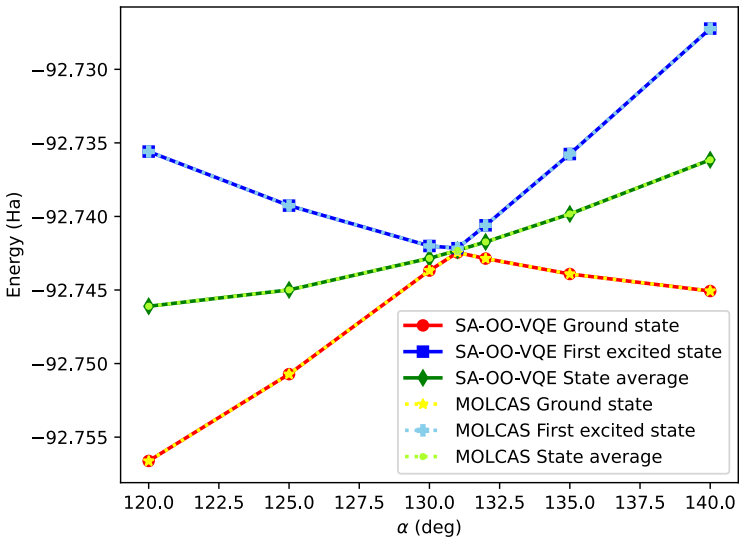

Figure 2: Comparison of potential energy depending on bending angle α in formaldimine molecule with dihedral angle $\phi = 90°$.

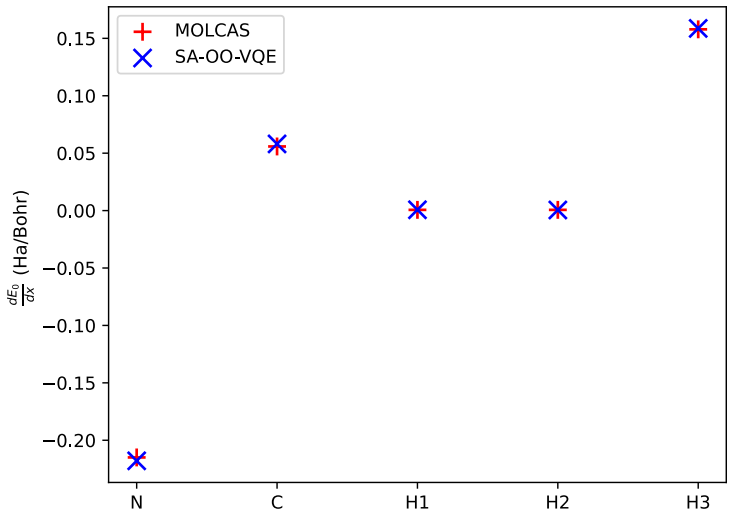

Figure 3: Comparison of ground-state gradients with bending angle $\alpha = 130^{\circ}$ and dihedral angle $\phi = 90^{\circ}$ in formaldimine molecule.

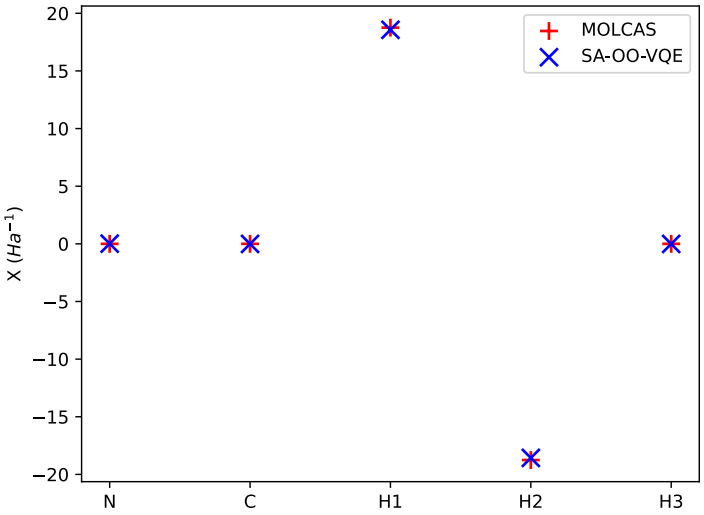

Figure 4: Comparison of total non-adiabatic couplings on bending angle $\alpha = 130^{\circ}$ and dihedral angle $\phi = 90^{\circ}$ in formaldimine molecule.

Features

With SA-OO-VQE you can obtain the following quantities:

- Potential energy surfaces
- Circuit (or Ansatz) gradients
- Orbital gradients

- Gradients of potential energy surfaces
- Non-adiabatic couplings

Also, for numerical optimization, you can use any of the optimizers supported by Qiskit[1] and our own implementation of

- Particle Swarm Optimization

Getting Started

The package is prepared with a priority of being very simple to use and the concise documentation can be found at sa-oo-vqe-qiskit.rtfd.io. To simplify the installation part, we recommend utilizing the Conda management system[2] together with the prepared `environment.yml` file.

At first, users should clone the repository.

```
git clone git@gitlab.com:MartinBeseda/sa-oo-vqe-qiskit.git
```

And install all the dependencies.

```
$ cd sa-oo-vqe-qiskit
$ conda env create -f environment.yml
$ conda activate saoovqe-env
$ python3 -m pip install .
```

These commands run in a terminal that will download and install all the necessary packages. The package availability can be tested afterward simply by importing the package and looking at its version.

```
$ python3

>>> import saoovqe
>>> saoovqe.__version__
```

Finally, usage examples are located both in the *examples* folder and in the documentation.

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[1] https://qiskit.org/documentation/stubs/qiskit.algorithms.optimizers.html
[2] https://docs.conda.io/en/latest/

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