

1 State-Averaged Orbital-Optimized VQE: A quantum 2 algorithm for the democratic description of ground 3 and excited electronic states

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9 Summary

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

27 Statement of need

28 Recently, quantum chemistry is one of the main areas-of-interest in *Quantum Computing*
29 (*QC*) ([Bauer et al., 2020](#); [McArdle et al., 2020](#); [Reiher et al., 2017](#)). That said, in many real-life
30 applications, there is the necessity of treating both the ground and excited states accurately
31 and in an equal footing. The problem is magnified when the Born-Oppenheimer approximation
32 breaks down due to a strong coupling among degenerate or quasi-degenerate states, most
33 notably the ground and the first excited state, for which the accurate description requires
34 (computationally demanding) multi-configurational approaches. A good example of such case
35 is a photoisomerization mechanism of the rhodopsin chromophore, which progresses from the
36 initial photoexcitation of the *cis* isomer over the relaxation in the first excited state towards a
37 conical intersection, where the population is transferred back to the ground state of the *trans*
38 isomer. In order to describe such a process thoroughly, one must compute not only relevant
39 *potential energy surfaces (PESs)*, but also their gradients w.r.t. nuclear displacements, utilized
40 further in molecular dynamics simulations. Finally, description of the conical intersection can
41 be done via obtaining *non-adiabatic couplings (NACs)*.

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

53 *State-Averaged Orbital-Optimization Variational Quantum Eigensolver (SA-OO-VQE)* method
54 addresses the above-mentioned problems and provides a way to compute both PES gradients
55 and NACs analytically (Yalouz et al., 2021; Yalouz, Koridon, Senjean, Lasorne, et al., 2022).
56 Authored by Yalouz et al., there is an exemplary implementation (Yalouz, Koridon, & Senjean,
57 2022) focusing on the pedagogical aspect and relying on matrix-vector multiplications rather
58 than actual measurements, avoiding the utilization of real QC infrastructure. Our implemen-
59 tation differs in a way that it aims to be a production-ready solver utilizing both QCs and
60 high-performance computing infrastructure in an efficient way, being able to run with different
61 backgrounds, utilizing Qiskit toolbox interface. The whole code is written in Python3, with
62 YAML scripts enabling its fast installation and usage.

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

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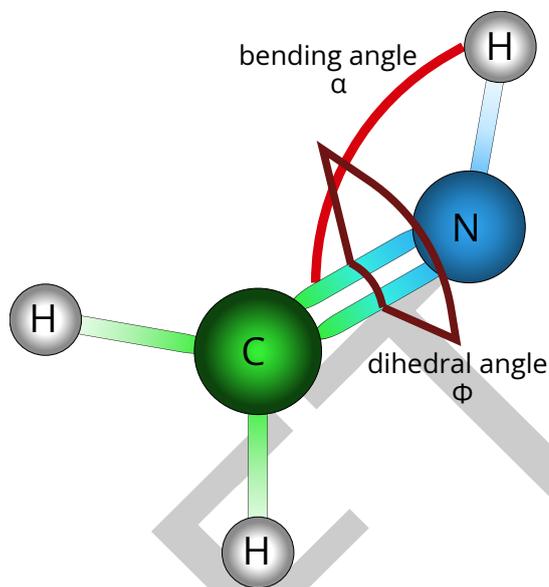


Figure 1: Molecule of formalimine being described with bending and dihedral angles denoted α and ϕ , respectively.

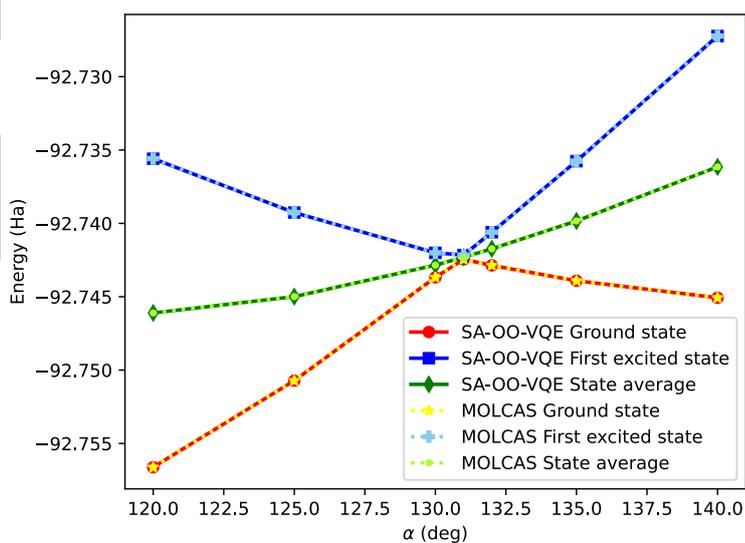


Figure 2: Comparison of potential energy depending on bending angle α in formalimine molecule with dihedral angle $\phi = 90^\circ$.

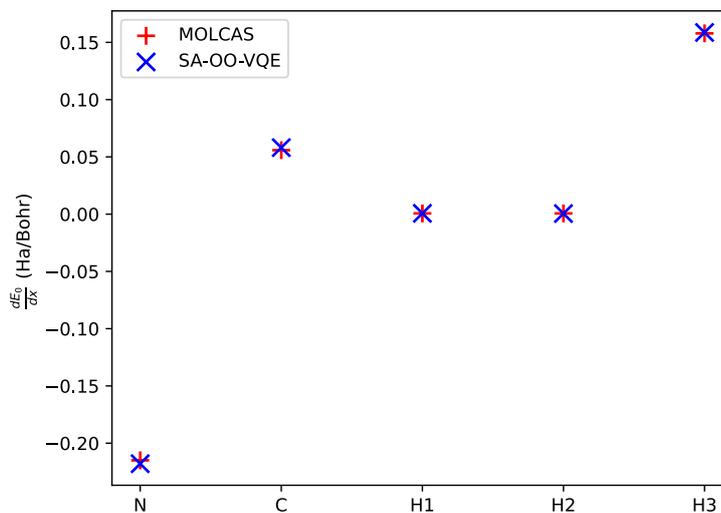


Figure 3: Comparison of ground-state gradients with bending angle $\alpha = 130^\circ$ and dihedral angle $\phi = 90^\circ$ in formalimine molecule.

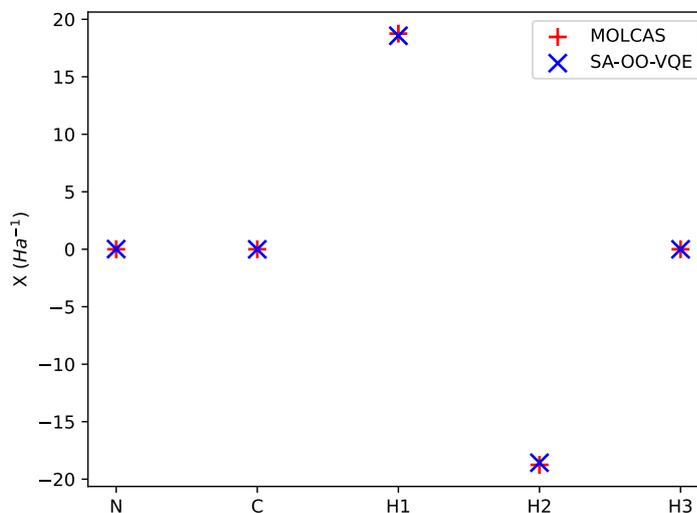


Figure 4: Comparison of total non-adiabatic couplings on bending angle $\alpha = 130^\circ$ and dihedral angle $\phi = 90^\circ$ in formalimine molecule.

68 Features

69 With SA-OO-VQE you can obtain following quantittes:

- 70 ■ Potential energy surfaces
- 71 ■ Circuit (or Ansatz) gradients
- 72 ■ Orbital gradients

- 73 ▪ Gradients of potential energy surfaces
- 74 ▪ Non-adiabatic couplings

75 Also, for numerical optimization you can use any of the optimizers supported by Qiskit¹ and
76 our own implementation of

- 77 ▪ Particle Swarm Optimization

78 Getting Started

79 The package is prepared with a priority of being very simple to use and the concise documenta-
80 tion can be found at sa-oo-vqe-qiskit.rtdfd.io. To simplify the installation part, we recommend
81 utilizing Conda management system² together with prepared `environment.yml` file.

82 At first, users should clone the repository.

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

84 And install all the dependencies.

```
85 $ conda env create -f environment.yml  
86 $ conda init bash  
87 $ source ~/.bashrc  
88 $ conda activate saooovqe-env  
89 $ pip install .
```

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

```
93 $ python3  
94  
95 >>> import saooovqe  
96 >>> saooovqe.__version__
```

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

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¹<https://qiskit.org/documentation/stubs/qiskit.algorithms.optimizers.html>

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