

A state-averaged quantum algorithm for an equal footing description of ground and excited states on a near term quantum computer

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In quantum computing, solving the electronic structure problem from quantum chemistry is considered as the “killer application” for near term quantum computers. Recently, many efforts have been devoted to the development of quantum algorithms capable of treating this problem on the current “Noisy Intermediate-Scale Quantum” computers. In this context, the hybrid quantum/classical “Variational-Quantum-Eigensolver” (VQE) algorithm is considered as one of the best methods due to its low requirement of quantum resources. While VQE has been proficiently applied to find electronic eigenstates/energies of various small molecules, using this approach on more complex systems is still a genuine challenge especially when peculiar spectral features such as degeneracies are present.

Motivated by this issue, our work focuses on the following question: how to use a VQE algorithm to accurately describe conical intersections (singular points of degeneracy between electronic states). In nature, conical intersections are crucial and play a key role in many prominent reactions. For instance, in the process of vision, the retinal molecule is known to undergo a photoisomerization mediated by a non-radiative relaxation through a conical intersection. In such a situation, characterizing the phenomenon requires to precisely describe the shape of the conical intersection, with both qualitative and quantitative high-level treatments. This makes it a difficult target to current quantum algorithms, such as VQE.

To solve this problem, we introduce a NISQ friendly method called “State-Averaged Orbital-Optimized VQE” (SA-OO-VQE) which combines two algorithms: a state-averaged orbital-optimizer, and a state-averaged VQE. The combination of these two algorithms makes it possible to treat on an equal footing every degenerate eigenstates, ensuring then a coherent representation of the degeneracy within an active space. We demonstrate the strength of this method on the formalimine molecule (a minimal model for retinal featuring a similar conical intersection). We show that the SA-OO-VQE method is able to qualitatively and quantitatively reproduce the molecule's conical intersection within a vastly reduced active space.