Calculating transition amplitudes by variational quantum eigensolvers

C71.00241 : Implementation of excited state energy and its analytical derivatives for photochemical reaction simulations on NISQ devices

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arXiv:2002.11724

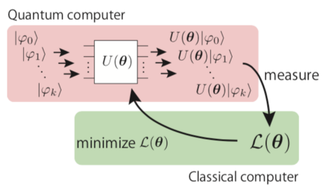
Summary

- ✓ Simulating excited states of molecules is of great concern in photophysics & photochemistry, and there are several methods based on a quantum algorithm, Variational Quantum Eigensolver (VQE)
- ✓ Among them, VQD method is remarkably accurate; however, there are no methods to calculate transition amplitudes (i.e., off-diagonal matrix elements) between eigenstates obtained by the VQD
- ✓ We propose such a method feasible on NISQ devices and demonstrate on a sampling simulator

Method for excited statesk	Accuracy	Easy to calculate transition amplitudes?
SSVQE	Fair	Yes
MCVQE	Intermediate	Yes
VQD	Excellent	~~No~~ Yes (This work)

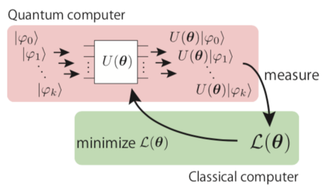
1. Methods for excited states based on VQE

SSVQE
Subspace-Search VQE
K. Nakanishi *et al,* Phys. Rev. Research **1**, 033062 (2019)



$$\mathcal{L}(\boldsymbol{\theta}) = \sum_{i=1}^{k} w_i \langle\varphi_i|U^\dagger(\boldsymbol{\theta})HU(\boldsymbol{\theta})|\varphi_i\rangle$$
$$(w_1 > w_2 > \cdots > 0)$$

MCVQE
Multistate-Contracted VQE
R. Parrish *et al,* Phys. Rev. Lett. **122**, 230401 (2019)



$$\mathcal{L}(\boldsymbol{\theta}) = \sum_{i=1}^{k} \langle\varphi_i|U^\dagger(\boldsymbol{\theta})HU(\boldsymbol{\theta})|\varphi_i\rangle$$

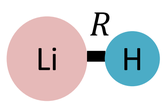
finally diagonalize on classical computer

VQD
Variational Quantum Deflation
O. Higgott *et al,* Quantum **3**, 159 (2019)

1. Obtain ground state $|\mathrm{E}_0\rangle$ with VQE
2. Execute VQE routine to minimize
$$\mathcal{L}_1(\theta) = \langle\psi(\theta)|H|\psi(\theta)\rangle + w_1|\langle \mathrm{E}_0|\psi(\theta)\rangle|^2$$
→ Obtain first excited state $|\mathrm{E}_1\rangle = |\psi(\theta_1^*)\rangle$
3. Repeat for higher excited states

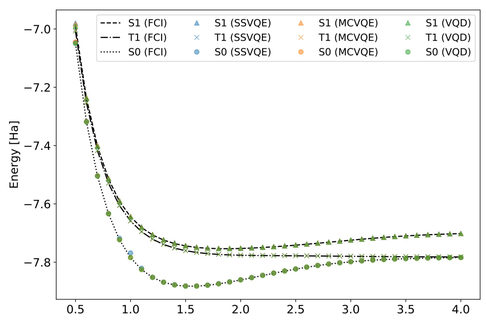
2. Comparison of methods by noiseless simulation

LiH

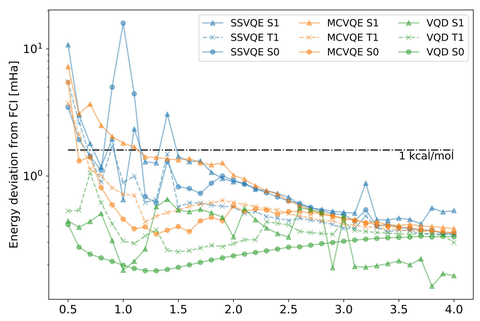


STO-3G
(4e, 6o)
(12 qubits)

Potential energy curve

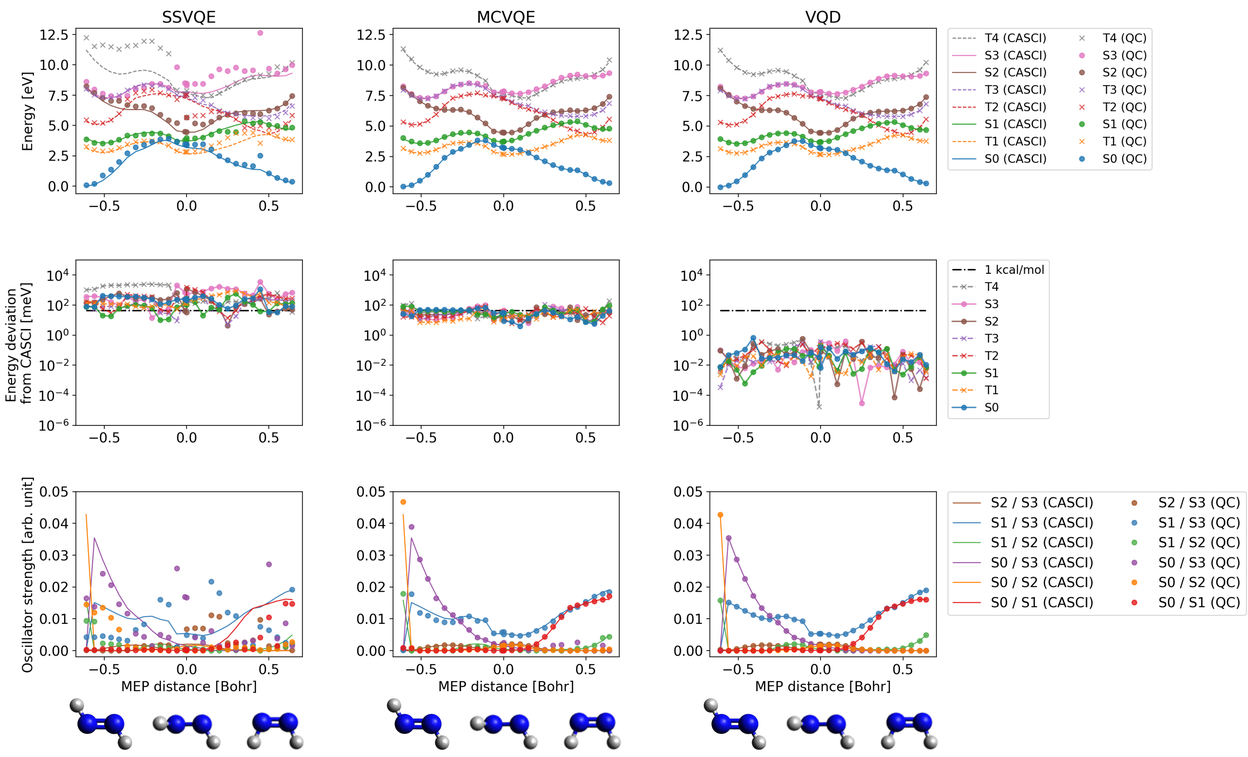


Error from exact calc.



Using RSP ansatz (D=10, see Appendix)

Diazene (N_2H_2)



Calculation setups
- Molecular structures: several points along minimum energy path between S2 Franck-Condon (cis/trans) & S2 minimum
- Calculation level: 6-31G*/CASCI(6e, 4o), 8 qubits
- Ansatz: RSP ansatz (D=20, see Appendix)
- High-speed simulator Qulacs [http://qulacs.org/] is used

Definition of oscillator strength f_{ij}

$$f_{ij} = \frac{2}{3}(E(\psi_j) - E(\psi_i)) \sum_{\alpha=x,y,z} |\langle\psi_j|R_\alpha|\psi_i\rangle|^2$$

where

$R_\alpha = \sum_{l=1}^{N} r_{l,\alpha}$: electric dipole moment operator in atomic units

$r_{l,\alpha}$: α-coordinate of the l-th electron

For results on azobenzene, see our paper on arXiv!

- ✓ VQD can generate excited states the most accurately
- ✓ SSVQE and MCVQE can readily calculate transition amplitudes
- ✓ However, VQD has no known methods to calculate transition amplitudes on real NISQ devices
- ✓ Transition amplitudes are required for calculating various physical quantities (e.g., oscillator strengths)

$|\langle\psi_i|A|\psi_j\rangle|^2$ (A: Hermitian op.)

3. Calculating transition amplitudes

$A = \sum_i a_i P_i$: physical quantity (Hermitian op.), where $P_i \in \{I, X, Y, Z\}^{\otimes n}, a_i \in \mathbb{R}$.

Following equality holds for transition amplitude $|\langle\psi_1|A|\psi_2\rangle|^2$:

Assuming $\langle\psi_1|\psi_2\rangle = 0$
Unitary operators
$U_{ij,\pm} = \frac{1}{\sqrt{2}}(I \pm iP_i)\frac{1}{\sqrt{2}}(I \pm iP_j)$

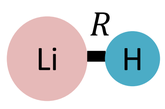
$$\underbrace{|\langle\psi_1|A|\psi_2\rangle|^2}_{\text{Unable to measure as it is } (A \text{ is not unitary})} = \sum_i a_i^2 |\langle\psi_1|P_i|\psi_2\rangle|^2 + \sum_{i<j} a_i a_j \Big[2|\langle\psi_1|U_{ij,+}|\psi_2\rangle|^2 + 2|\langle\psi_1|U_{ij,-}|\psi_2\rangle|^2 - |\langle\psi_1|P_i|\psi_2\rangle|^2 - |\langle\psi_1|P_j|\psi_2\rangle|^2 - |\langle\psi_1|P_iP_j|\psi_2\rangle|^2\Big]$$

Each term can be measured on real devices

→ Enables calculation of transition amplitudes with VQD

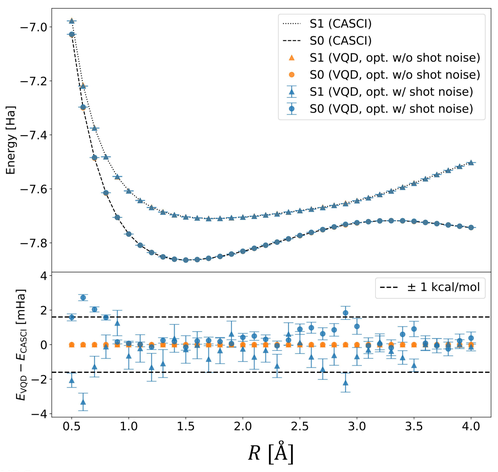
4. Sampling simulation with shot noise

LiH

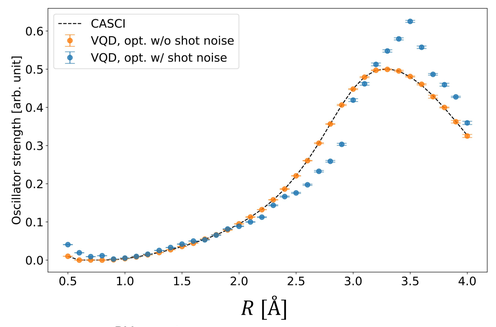


STO-3G
CASCI(2e, 2o)
(2 qubits)

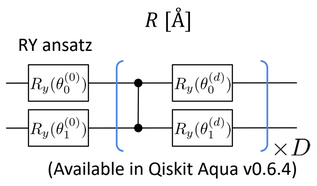
Potential energy curve & error



Oscillator strength



RY ansatz



(Available in Qiskit Aqua v0.6.4)

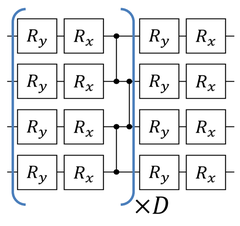
Calculation setups
- Calculation level: 6-31G*/CASCI(2e, 2o), 2 qubits (parity mapping is used to reduce the number of qubits)
- Ansatz: RY ansatz (D=2) J. T. Seeley *et al.*, J. Chem. Phys. **137**, 224109 (2012)
- Two options for optimization routine for this experiment
  Blue dots : use sampling simulator in the whole process (including optimization routine)
  Orange dots: use sampling simulator only for calculating oscillator strengths (parameters are optimized with noiseless simulator), still using our proposed method

5. Conclusion

- ✓ VQD is an accurate way to simulate excited states on a quantum computer
- ✓ We proposed a method to calculate transition amplitudes between two orthogonal states in a hardware-friendly manner, which is applicable (not only) for the VQD
- ✓ This work enlarges the possibility of the VQD and advances the field of excited states calculations on a quantum device

Appendix: Comparison of ansatz

Hardware-efficient ansatz



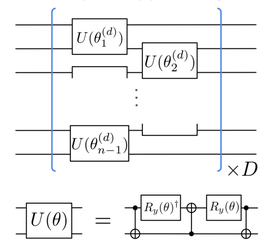
A. Kandala *et al.*, Nature **549,** 242 (2017)

UCC-SD ansatz

$$U_{UCCSD}(\boldsymbol{\theta}) = \exp\big(T_{SD}(\boldsymbol{\theta}) - T_{SD}^\dagger(\boldsymbol{\theta})\big)$$
$$T_{SD}(\boldsymbol{\theta}) = \sum_{\substack{i:\text{occupied} \\ a:\text{virtual}}} \theta_i^a c_a^\dagger c_i + \sum_{\substack{ij:\text{occupied} \\ ab:\text{virtual}}} \theta_{ij}^{ab} c_a^\dagger c_b^\dagger c_i c_j$$

A. Peruzzo *et al.*, Nat. Comm., **5**,4213 (2014)

RSP ansatz
(Real-valued symmetry preserving ansatz)



For symmetry-preserving ansatz, see
P. Barkoutsos *et al.*, Phys. Rev. A **98**, 022322 (2018)