

Subspace-Search Quantum Imaginary Time Evolution for Excited State Computations

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Abstract

Quantum systems in excited states are attracting significant interest with the advent of noisy intermediate scale quantum (NISQ) devices. While ground states of small molecular systems are typically explored using hybrid variational algorithms like the variational quantum eigensolver (VQE), the study of excited states has received much less attention, partly due to the absence of efficient algorithms. In this work, we introduce the *subspace search quantum imaginary time evolution* (SSQITE) method, which calculates excited states using quantum devices by integrating key elements of the subspace search variational quantum eigensolver (SSVQE) and the quantum imaginary time evolution (QITE) method. The effectiveness of SSQITE is demonstrated through calculations of low-lying excited states of benchmark model systems, including H₂ and LiH molecules. With its robustness in avoiding local minima, SSQITE shows promise for advancing quantum computations of excited states across a wide range of applications.

1 Introduction

Computational and theoretical studies of excited states are essential for understanding the photophysics of molecules, particularly in UV-vis and X-ray absorption spectroscopy of photochemical reactions.^{1,2} With the advent of quantum computing, new methodologies promise to significantly enhance these studies, potentially offering a quantum advantage in chemistry.^{3,4} Traditional computational methods, despite their powerful capabilities, face limitations in modeling complex excited-state phenomena due to the exponential scaling of resources required. Quantum computing, however, opens new frontiers for exploring a wide range of problems,^{5,6} including the crucial excited states in the photochemistry of organic molecules.⁷

In the near-term intermediate scale quantum (NISQ) era, quantum advantage of some specialized applications have already been put forward,^{8,9} such as the calculation of ground-state energy in quantum chemistry.¹⁰⁻¹² Popular approaches for calculating ground-state energies in quantum computers include the hybrid variational quantum eigensolver (VQE) algorithm^{10,12,13} and the quantum imaginary time evolution (QITE) method.^{13,14} Beyond ground-state energies, excited states are equally important for numerous applications,¹⁵⁻¹⁷ such as charge and energy transfer in photovoltaic materials, photodissociation,¹⁸ luminescence,⁷ intermediate states in chemical reactions,¹⁹ and mechanistic studies of catalytic systems.²⁰ This has driven significant interest in generalizing VQE and QITE to excited states of quantum systems. Notable algorithms designed for this purpose include the subspace-search variational quantum eigensolver (SSVQE)²¹ and the variational quantum deflation (VQD)¹⁸ algorithm. The VQD approach¹⁸ has been applied to calculations at Frank-Condon and the conical intersection geometries,²² and has been adapted to QITE^{23,24} for determining excited states.

In this paper, we introduce a novel algorithm called subspace search quantum imaginary time evolution (SSQITE). The SSQITE algorithm augments QITE with subspace search to computing excited states to enable the simultaneous calculation of ground and multiple

excited states. Its efficiency is successfully demonstrated with the calculation of the low-lying states of H_2 and LiH molecules. The paper is organized as follows. First, we introduce the SSVQE and QITE methods in Secs. 2 and 3, respectively. Then, we describe the SSQITE algorithm in Sec. 4 and illustrate its application to calculations of excited states of H_2 and LiH in Sec. 5. Conclusions are presented in Sec. 6.

2 Subspace-Search Variational Quantum Eigensolver

The subspace-search variational quantum eigensolver (SSVQE) algorithm extends the variational quantum eigensolver (VQE) hybrid method.^{10,12} The VQE is a hybrid quantum-classical algorithm designed to find the ground state of a quantum system described by the $2^n \times 2^n$ Hamiltonian, H , expressed as a sum of tensor products of Pauli matrices $\sigma_k^{(j)} = \{X, Y, Z, I\}$,

$$H = \sum_j c_j \bigotimes_{k=1}^n \sigma_k^{(j)}, \quad (1)$$

where $c_j = 2^{-n} \text{Tr}[H \times \bigotimes_{k=1}^n \sigma_k^{(j)}]$. VQE generates a trial state $|\psi(\vec{\theta})\rangle = U(\vec{\theta})|\psi_0\rangle$ by applying a quantum circuit $U(\vec{\theta})$ with variational parameters $\vec{\theta}$ to an initial vacuum state $|\psi_0\rangle$. These parameters are adjusted by a classical computer to minimize the expectation value of the Hamiltonian, $E(\vec{\theta}) = \langle\psi(\vec{\theta})|\hat{H}|\psi(\vec{\theta})\rangle$. This expectation value is computed by summing the expectation values of the tensor products of Pauli matrices, $\langle\psi(\vec{\theta})|\bigotimes_{k=1}^n \sigma_k^{(j)}|\psi(\vec{\theta})\rangle$, measured on the quantum computer. The process iteratively refines $\vec{\theta}$ to minimize $E(\vec{\theta})$, thereby approximating the lowest eigenvalue of H .

SSVQE extends the VQE algorithm to simultaneously find the k lower eigenstates of H .²¹ First, k orthogonal states $|\phi_j\rangle$ are initialized with $\langle\phi_k|\phi_j\rangle = \delta_{kj}$ and then they are evolved using the same circuit $U(\vec{\theta})$ with variational parameters $\vec{\theta}$. Orthogonality is thus preserved among the evolved states since $U(\vec{\theta})^\dagger U(\vec{\theta}) = I$, so $\langle\phi_k|U(\vec{\theta})^\dagger U(\vec{\theta})|\phi_j\rangle = \delta_{kj}$. The parameters $\vec{\theta}$ are optimized by minimizing the sum of the expectation values using the following loss

function:

$$\mathcal{L}_\omega(\vec{\theta}) = \sum_{j=0}^k \omega_j \langle \phi_j | U^\dagger(\vec{\theta}) H U(\vec{\theta}) | \phi_j \rangle. \quad (2)$$

Therefore, SSVQE finds the k orthogonal minimum energy states simultaneously. The coefficients ω_i , introduced by Eq. (2), with $\omega_i > \omega_j$ for $i < j$, are used to weight each energy level, effectively arranging the energy expectation values of all orthogonal states in ascending order.

In this paper, we introduce the subspace search quantum imaginary time evolution (SSQITE) algorithm by integrating this SSVQE methodology of orthogonal states with the QITE algorithm.^{13,14} The resulting SSQITE method thus enables the simultaneous calculation of multiple excited states by applying the same imaginary time evolution to an initial set of orthogonal states.

3 Quantum Imaginary Time Evolution

The quantum imaginary time evolution (QITE) algorithm is a hybrid quantum-classical method used to determine the ground-state energy of a quantum system by propagating an initial state $|\psi(0)\rangle$ in imaginary time toward $|\psi(\tau)\rangle$, where $\tau = it/\hbar$ is the imaginary time.^{13,14} This technique effectively implements the Wick-rotated Schrödinger equation,

$$\frac{d}{d\tau} |\psi(\tau)\rangle = -(\mathcal{H} - E_\tau) |\psi(\tau)\rangle, \quad (3)$$

with $E_\tau = \langle \psi(\tau) | \mathcal{H} | \psi(\tau) \rangle$. Propagating that initial state for a sufficiently long imaginary time, we obtain the ground-state $|E_0\rangle$, provided that $\langle E_0 | \psi(0) \rangle \neq 0$. This is expressed, as follows:

$$\lim_{\tau \rightarrow \infty} A(\tau) e^{-H\tau} |\psi(0)\rangle = |E_0\rangle, \quad (4)$$

where $A(\tau) = \langle \psi(0) | e^{-2H\tau} | \psi(0) \rangle^{-1/2}$ is the normalization factor obtained after imaginary-time propagation. To apply this procedure to a given parameterized ansatz $|\psi(\tau)\rangle =$

$U(\theta(\tau))|0\rangle$, McLachlan's variational principle can be leveraged, which states:

$$\delta \left\| \left(\frac{d}{d\tau} + \mathcal{H} - E_\tau \right) |\psi(\tau)\rangle \right\| = 0. \quad (5)$$

Applying this principle to the optimization of the variational parameters $\vec{\theta}$ that define $U(\vec{\theta}(\tau))$ results in the following linear system of ordinary differential equations:^{13,14}

$$\sum_j A_{ij} \dot{\theta}_j = C_i, \quad (6)$$

where

$$A_{ij} = \Re \left(\frac{\partial \langle \phi(\vec{\theta}(\tau)) | \partial \phi(\vec{\theta}(\tau)) \rangle}{\partial \theta_i} \frac{\partial \phi(\vec{\theta}(\tau))}{\partial \theta_j} \right), \quad (7)$$

and

$$C_i = -\Re \left(\left\langle \frac{\partial \phi(\vec{\theta}(\tau))}{\partial \theta_i} \middle| \mathcal{H} \middle| \phi(\vec{\theta}(\tau)) \right\rangle \right). \quad (8)$$

The values of A_{ij} and C_i are obtained using the Hadamard test on a quantum circuit by simply averaging the measurements on the ancilla qubit.¹³

Having obtained A_{ij} and C_i by measurements of the ancilla in the quantum circuit, the values of $\vec{\theta}$ are updated in a classical computer by integrating the Euler equation introduced by Eq. (6) using the 4th-order Runge-Kutta method.²⁵ The process is iterated until the values of $\vec{\theta}$ converge to optimum values, as determined by the McLachlan's variational principle introduced by Eq. 5.

4 Subspace-Search Quantum Imaginary Time Evolution

The subspace-search quantum imaginary time evolution (SSQITE) method, proposed in this paper, combines subspace search optimization with quantum imaginary time evolution to maintain orthogonality among states evolving in imaginary time. This approach allows for

the simultaneous variational computation of both ground and excited energy states using quantum imaginary time evolution.

The main difficulty in combining the subspace search optimization with quantum imaginary time evolution is that the imaginary time propagation only implicitly optimizes the loss function defined by the McLachlan’s variational principle in Eq. (5). Instead of defining a joint loss function, as in SSVQE, the SSQITE algorithm tunes the step size $d\tau_j$ of each level j individually, such that lower energy states have larger integration time steps (pseudo-code, Algorithm 1). Intuitively, this allows for lower energy states to overpower the higher energy states, ordering the output energy spectrum. The tuning of time-steps plays a similar role as the tuning of the weights ω_i in the SSVQE algorithm. In this way, after a sufficient number of iterations, the SSQITE algorithm returns the k -lowest-energy eigenstates.

Algorithm 1 Pseudo-code for the SSQITE Algorithm

Require: $\psi = \psi_i$, with $0 \leq i < k$.

Ensure: $\langle \psi_i | \psi_j \rangle = \delta_{ij}$

while not all_converged($\dot{\theta}$) **do**

$d\tau_i \leftarrow \{\frac{1}{2^i} | 0 \leq i < k\}$

▷ Initialize Step Sizes

$A_{ijl} \leftarrow \text{Measure_A}(U(\vec{\theta})\psi_l)$

$C_{il} \leftarrow \text{Measure_C}(U(\vec{\theta})\psi_l)$

$\dot{\theta}_{jl} \leftarrow A_{ijl}^{-1} C_{il}$

▷ Calculate $\dot{\theta}$

for $l = 0, l < k, l++$ **do**

if converged($\dot{\theta}_l$) **then**

for $i = l, i < k, i++$ **do**

$d\tau_i \leftarrow 2 * d\tau_i$

▷ Avoid Exponential Scaling with k

end for

end if

end for

for $j = 0, j < \text{num_params}, j++$ **do**

for $l = 0, l < k, l++$ **do**

$\theta_{jl} \leftarrow \theta_{jl} + d\tau_l * \dot{\theta}_{jl}$

▷ Update Theta

end for

end for

end while

The integration time steps are defined as follows:

$$d\tau_i = \frac{b}{2^i}. \quad (9)$$

with b a tunable parameter. This choice of integration time steps prevents higher energy levels from overpowering lower energy eigenstates, since

$$\frac{1}{2^i} \geq \sum_{j=i+1}^k \frac{1}{2^j}. \quad (10)$$

However, this approach requires a number of steps that scales exponentially as $\mathcal{O}(2^k)$, where k is the size of the subspace. This exponential scaling can be overcome by leveraging the convergence of lower energy levels. The integration time steps used for obtaining higher energy levels can be increased upon convergence of lower energy states since all remaining states must be orthogonal to the manifold of lower energy states $\langle E_j | \psi_i \rangle \approx \delta_{ji}$ for $i > j$. Therefore, the imaginary time evolution of higher excited states is restricted to an orthogonal subspace.

Due to the time evolution of excited states being restricted, the integration time step of these states can be doubled, mitigating the exponential scaling without significantly affecting the lower energy states. However, the imaginary time evolution of the ground state makes the overlap with excited states exponentially small, although not exactly zero $\langle E_0 | \psi_i \rangle \approx e^{-\tau}$. Therefore, in practice, some excited states can still evolve into the ground state if they are not fully orthogonalized. So, it is always necessary to confirm orthogonality with lower energy states during each round of SSQITE.

5 Results: Ground and Excited states of H_2 and LiH

Figure 1 illustrates the energy expectation values for the three lowest energy states of H_2 during joint SSQITE optimization (with a fixed H-H bond-length of 0.95\AA). The imaginary

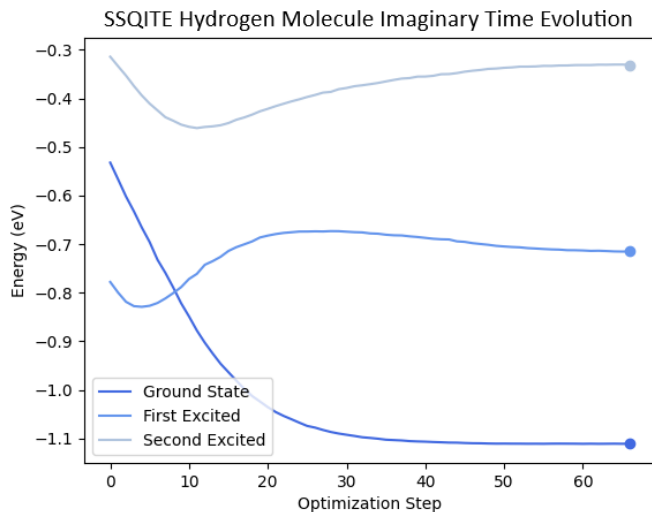


Figure 1: Simultaneous evolution of the energy expectation values for the three lower energy states of H_2 (with fixed bond-length $R = 0.95 \text{ \AA}$) during the first 70 integration steps of SSQITE optimization. Final energy values are highlighted on the right, and corresponding statistical errors are of the order 10^{-4} eV.

time propagation causes these states to interfere through their contributions to $\vec{\theta}$. As shown in Fig. 1, the evolution of the ground state for $\tau \in [0, 20]$ leads to an increase in the energy of the first excited state, as it is forced into a subspace orthogonal to the ground state. This effect is also reciprocal, since the evolution of the first excited state likely slows the evolution of the ground state, as evidenced by the linear slope of the ground state from $\tau = 0$ to $\tau = 15$.

Figures 2(a),(c) show the three lowest energy eigenvalues of H_2 determined through SSQITE optimization. These calculations use a general two-qubit ansatz depicted in Figure 3, as a function of the interatomic H-H distance.²⁶ These results demonstrate excellent agreement with exact results on both noiseless (Figure 2(a)) and noisy (Figure 2(c)) quantum simulators. In fact, the comparison to numerically exact calculations shown in Figures 2(a),(c) demonstrates the accuracy and capabilities of the SSQITE algorithm over the entire range of bond-lengths.

Figure 2(b) [Figure 2(d)] shows the errors of the noiseless [noisy] SSQITE calculations

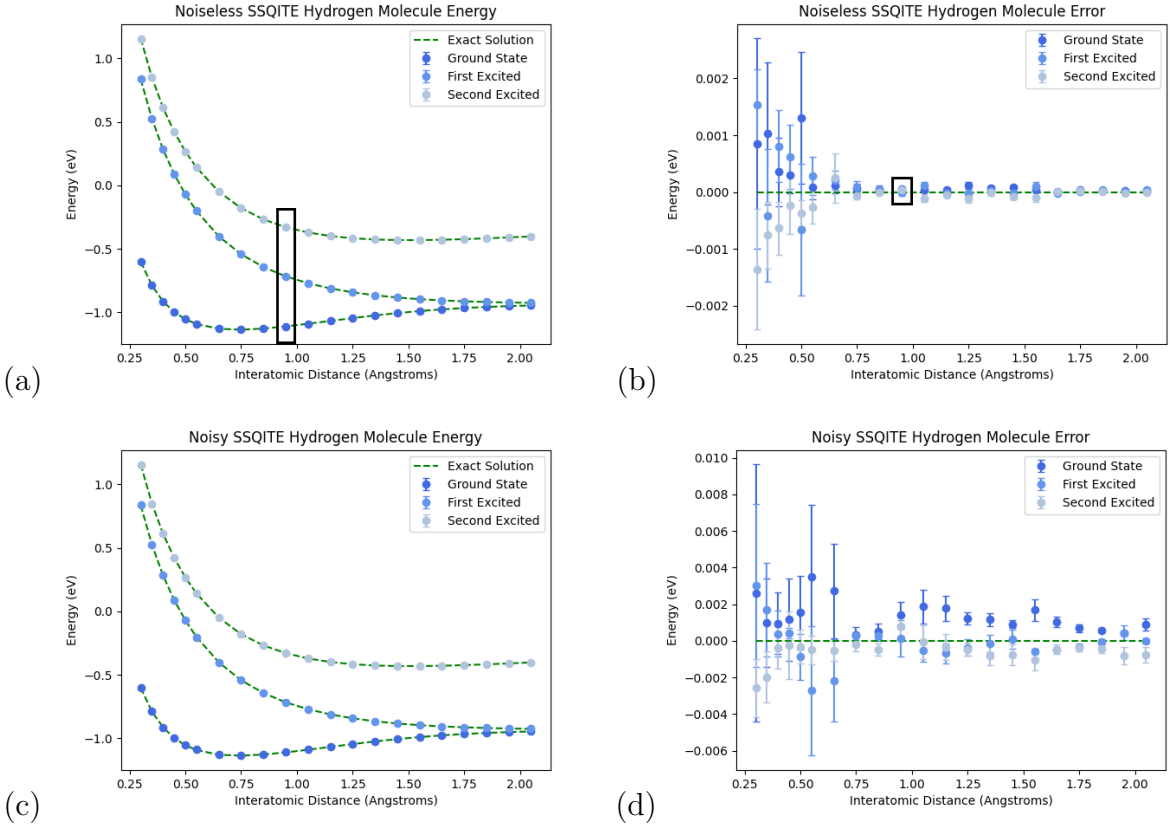


Figure 2: Comparison of the three lowest energy eigenvalues of H_2 determined through (a)-(b) noiseless and (c)-(d) noisy SSQITE optimization to numerically exact calculations (dashed lines) as a function of the interatomic HH distance. Boxed values correspond to the final values shown highlighted in Fig. 1. Deviations of (b) noiseless and (d) noisy SSQITE calculations from the ground truth energy levels of the H_2 molecule. All noisy simulations are performed using the qiskit FakeSherbrooke backend.

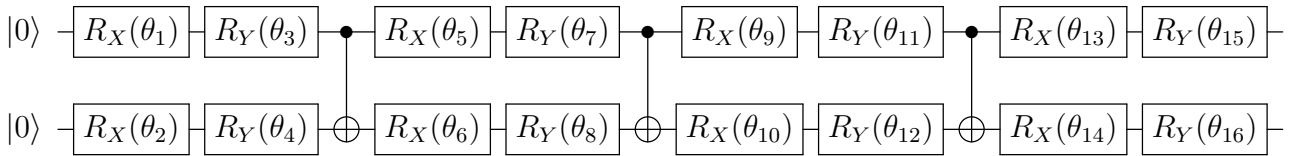


Figure 3: Variational quantum circuit ansatz with two qubits used for the SSQITE H_2 calculations shown in Fig. 2. The TwoLocal ansatz involves one layer of parameterized RX and RY gates, followed by a CNOT gate. This ansatz is general, in the sense that it can realize any two-qubit operation.

for the H_2 molecule, which remain within 5.5×10^{-5} Ha (1.3×10^{-4} Ha), i.e., within chemical accuracy of 1.6×10^{-3} Ha.¹⁸

For comparison, we also apply the SSQITE algorithm to the LiH molecule,²⁷ using a

custom excitation preserving ansatz with 16 adjustable parameters shown in Figure 4.

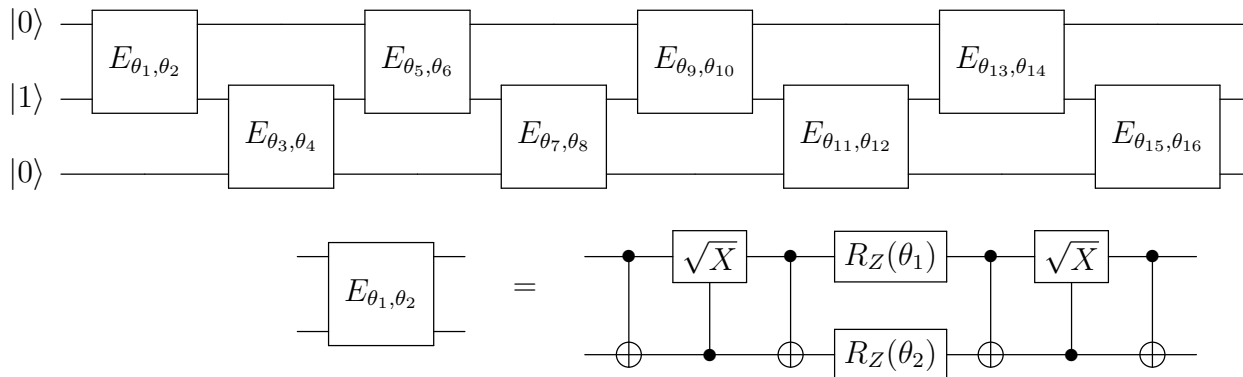


Figure 4: Top: Variational quantum circuit ansatz with three qubits used for the SSQITE LiH calculations shown in Fig. 5 based on a custom excitation preserving ansatz. Bottom: Excitation preserving subcircuit with two tunable parameters.

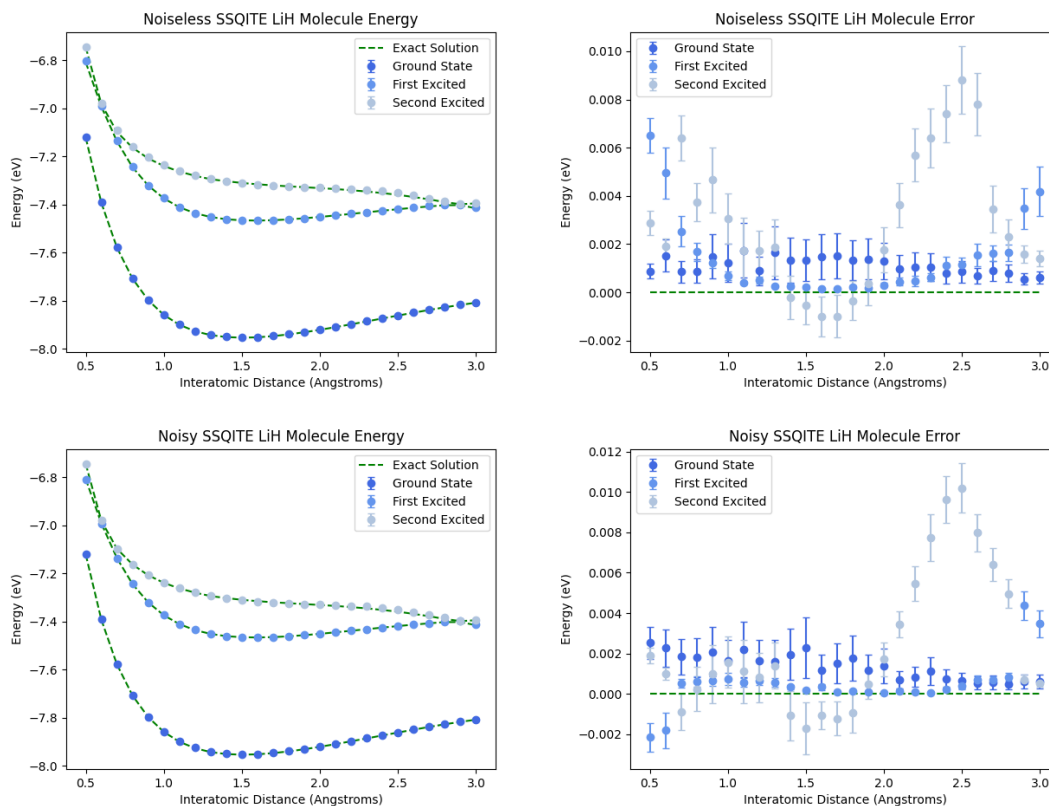


Figure 5: Comparison of the three lowest energy eigenvalues of LiH determined through (a)-(b) noiseless and (c)-(d) noisy simulation of SSQITE optimization to numerically exact calculations (dashed lines). Deviations of the (b) noiseless and (d) noisy SSQITE calculations from the ground truth energy levels of the LiH molecule. All noisy simulations are performed using the qiskit FakeSherbrooke backend.

Figures 5(a),(c) show the three lowest energy eigenvalues of LiH as a function of the interatomic Li-H distance for the noiseless [Figure 5(a)] and noisy [Figure 5(c)] SSQITE optimization. The results show excellent agreement with benchmark calculations of the entire range of interatomic distances.

Figures 5(b),(d) shows the errors of SSQITE calculations for the LiH molecule, which remain within chemical accuracy. Similarly to the performance for the H₂ molecule, SSQITE performs well in calculations of ground and excited state energies of LiH. In fact, as shown in Fig. 5, the noiseless (noisy) algorithm exhibits a maximum deviation of 3.3×10^{-4} Ha (3.7×10^{-4} Ha), below the benchmark of 1.6×10^{-3} Ha.

6 Conclusions

We have introduced the SSQITE method for computations of excited states using quantum devices. This method combines key aspects of the SSVQE and QITE methodologies. We demonstrated the capabilities of SSQITE by calculating the low-lying excited states of H₂ and LiH molecules. The results showed robustness in avoiding local minima and excellent agreement with numerically exact calculations. Additionally, SSQITE is not sensitive to degenerate states, unlike folded-spectrum VQE or folded-spectrum QITE, which calculate excited states by altering the Hamiltonian to $(\mathcal{H} - E)^2$,^{24,28} where E is the energy of interest.

We have shown that using QITE as a foundation for excited state algorithms offers potential benefits relative to VQE, since some local minima typically found during VQE gradient descent are absent in QITE.¹³ Additionally, we anticipate that the subspace-search methodology implemented in SSQITE could also be applied to exploit the advantages of the QIPA algorithm, which was shown to require fewer iterations than QITE for quantum optimization of ground states.¹⁴ This suggests that the combination of subspace-search and imaginary time quantum evolution methodologies could outperform other currently available algorithms for computations of excited states.

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8 Code availability

The Python code for the SSQITE simulations is available at [this link](#).

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