Ground State Energy Determination of LiH Using the Variational Quantum Eigensolver (VQE) Algorithm

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Abstract. Exact solutions of the electronic structure problem scale exponentially with system size, limiting classical full configuration interaction (FCI) to small systems. We simulate the variational quantum eigensolver (VQE) to compute the ground-state potential energy curve of lithium hydride (LiH) in the STO-3G basis. The Hamiltonian was mapped to 12 qubits through the Jordan-Wigner transformation (631 Pauli terms), and a hardware-efficient ansatz of R_y rotations and CNOT ladders (8 layers, 96 parameters) was optimized with Adam in PennyLane for Li-H distances from 0.8 to 2.4 Å. The circuit was initialized to reproduce the Hartree-Fock (HF) state, and reference HF and FCI energies were obtained with PySCF. The energies satisfy $E_{HF} > E_{VQE} > E_{FCI}$ at every distance. Near equilibrium (1.6 Å), E_{VQE} = -7.8776 Ha lies 4.7 mHa above FCI, recovering 77% of the correlation energy (65-79% across the curve), with accuracy degrading at stretched bonds. Chemical accuracy was not reached, and ansätze with 2-4 layers barely improved on HF.

I. INTRODUCTION

Predicting molecular energies is a central task of quantum chemistry, yet exact FCI requires resources that grow exponentially with the number of orbitals, while mean-field HF neglects electron correlation and fails as bonds stretch. Feynman (1982) [1] argued that quantum systems are naturally simulated by quantum devices. The VQE puts this idea into practice in a hybrid scheme: a parameterized circuit prepares a trial state, and a classical optimizer minimizes the measured energy, which the variational principle bounds from below by the exact ground-state energy (Peruzzo et al., 2014) [2].

Hardware-efficient ansatz (HEA) circuits use shallow layers of native gates and have been demonstrated experimentally for H_2, LiH and BeH_2 (Kandala et al., 2017) [3]. Here, a noiseless VQE simulation is used to obtain the LiH potential energy curve and quantify the correlation energy recovered by a HEA.

II. METHODOLOGY

The LiH Hamiltonian was built in the STO-3G basis (12 spin orbitals) with PennyLane and mapped to 12 qubits by the Jordan-Wigner transformation, giving 631 Pauli terms. HF and FCI reference energies were computed with PySCF for Li-H distances from 0.8 to 2.4 Å in steps of 0.2 Å.

The ansatz (Fig. 1) has $L = 8$ layers, each with an R_y rotation on every qubit followed by a CNOT ladder, for 96 parameters. Because the ladder permutes basis states, the input state was chosen so that all-zero parameters reproduce the HF state exactly, which guarantees $E_{VQE} \leq E_{HF}$. The energy was minimized with Adam (step size 0.05, up to 400 iterations) on a state-vector simulator with adjoint differentiation. Each distance used a warm start from the previous one plus one random restart ($\sigma = 0.1$), keeping the lowest energy.

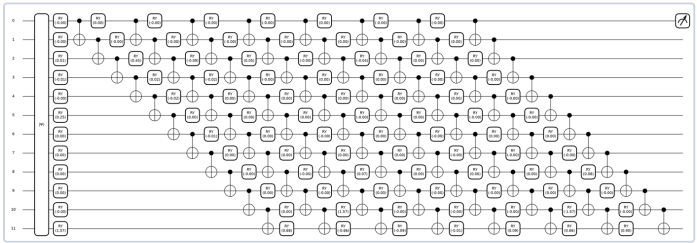


Fig. 1. Quantum circuit of the hardware-efficient ansatz: 12 qubits, 8 layers of R_y rotations followed by a CNOT ladder (96 parameters).

III. RESULTS AND DISCUSSION

Figure 2 shows the potential energy curves. The hierarchy $E_{HF} > E_{VQE} > E_{FCI}$ holds at all distances, so the VQE improves on HF everywhere without violating the variational principle. At 1.6 Å, E_{HF} = -7.8619 Ha, E_{VQE} = -7.8776 Ha and E_{FCI} = -7.8823 Ha: the VQE error relative to FCI is 4.7 mHa versus 20.5 mHa for HF, i.e. 77% of the correlation energy is captured.

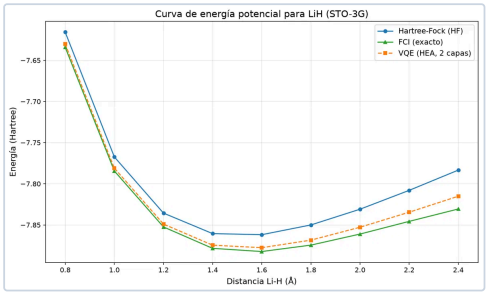


Fig. 2. LiH potential energy curve (STO-3G).

As shown in Fig. 3, 75-79% of the correlation energy is recovered for 0.8-1.8 Å, but the fraction falls to 65% and the error rises to 16.4 mHa at 2.4 Å, where static correlation grows and the shallow circuit lacks flexibility. Chemical accuracy (1.6 mHa) was not reached at any distance. Ansätze with 2-4 layers improved on HF by less than 1 mHa at 1.6 Å, so depth is essential for this HEA. All runs reached the 400-iteration limit, so the reported energies are variational upper bounds that may improve with longer optimization. These noiseless results are a baseline for deeper or chemistry-inspired ansätze and for hardware noise studies.

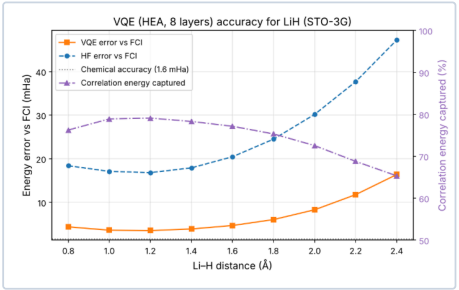


Fig. 3. VQE error relative to FCI and correlation energy captured vs. Li-H distance.

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