1. HAMILTONIAN OF HE–H\(^+\) WITH RESPECT TO THE INTERATOMIC DISTANCE

According to the second-order quantization representation, any Hamiltonian can be represented as

\[ H = \sum_{p,q} h_{p,q} a_p^\dagger a_q + \sum_{p,q,r,s} h_{p,q,r,s} a_p^\dagger a_q a_r^\dagger a_s + \cdots, \]  

(S1)

where \(a^\dagger\) and \(a\) represent the creation and annihilation operators, respectively. By Jordan-Wigner transformation, Eq. (S1) can be presented as a linear summation of Pauli operators as

\[ H = \sum_j w_j \cdot \sigma_j + \sum_{jk} w_{jk} \cdot \sigma_j \otimes \sigma_k + \cdots. \]  

(S2)

The coefficients \(w_j, w_{jk}, \cdots\) are calculated during the transformation.

Here, we have calculated the molecular Hamiltonians with respect to the interatomic distance for He–H\(^+\) using Psi4 module, and listed the coefficients in Table S1 [1]. \(X, Y, Z, I\) here stand for the Pauli matrices \(\sigma_x, \sigma_y, \sigma_z\) and the identity operators, respectively. Note that, while the Hamiltonian has nine Pauli string terms, it only requires four measurement settings (Group 1∼4) to obtain all the values.

| R [Å] | Group 1 | Group 2 | Group 3 | Group 4 |
|-------|---------|---------|---------|---------|
|       | II      | IZ      | ZI      | ZZ      | IX      | ZX      | XI      | XZ      | XX      |
| 0.05  | 33.9557 | -2.4784 | -2.4784 | 0.2746  | -0.1515 | 0.1515  | -0.1515 | 0.1515  | 0.1412  |
| 0.1   | 13.3605 | -2.4368 | -2.4368 | 0.2081  | -0.1626 | 0.1626  | -0.1626 | 0.1626  | 0.2097  |
| 0.2   | 3.633   | -2.2899 | -2.2899 | 0.1176  | -0.1405 | 0.1405  | -0.1405 | 0.1405  | 0.3027  |
| 0.5   | -2.3275 | -1.5236 | -1.5236 | 0.1115  | -0.157  | 0.157   | -0.157  | 0.157   | 0.3309  |
| 0.7   | -3.3893 | -1.2073 | -1.2073 | 0.1626  | -0.1968 | 0.1968  | -0.1968 | 0.1968  | 0.3052  |
| 0.9   | -3.8505 | -1.0466 | -1.0466 | 0.2356  | -0.2288 | 0.2288  | -0.2288 | 0.2288  | 0.2613  |
| 1.1   | -4.0539 | -0.982  | -0.982  | 0.3225  | -0.243  | 0.243   | -0.243  | 0.243   | 0.2053  |
| 1.5   | -4.1594 | -0.991  | -0.991  | 0.4945  | -0.2086 | 0.2086  | -0.2086 | 0.2086  | 0.0948  |
| 2     | -4.1347 | -1.0605 | -1.0605 | 0.6342  | -0.1119 | 0.1119  | -0.1119 | 0.1119  | 0.0212  |
| 2.5   | -4.0918 | -1.1128 | -1.1128 | 0.701   | -0.0454 | 0.0454  | -0.0454 | 0.0454  | 0.0032  |

Table S1. The table of Pauli operators and weights constituting Hamiltonian in respect to interatomic distance [2]. Four measurement settings (Group 1∼4) are required for obtain all the nine Pauli strings.
2. THE TEST RESULTS OF CLASSICAL OPTIMIZERS

A. Gradient-free optimizers

We have evaluated three classical optimizers with 1,000 trials of classical computer emulation. The initial parameters have set randomly for each emulation and experiments. Figure S1 shows the histogram of each classical optimizer in terms of (a) the estimated energy, and (b) the number of iterations. In Fig. S1 (a), the red line indicate the theory value with the emulation condition of interatomic distance \( R = 0.9\text{Å} \). The gray region represents the area of success criteria corresponding to tolerance of optimizer, \( \text{ftol} = 0.01 \). The mean values of the estimated energy \( \langle H \rangle \) with Nelder-Mead, Powell and COBYLA methods are \(-2.861 \pm 0.004\), \(-2.863 \pm 0.004\) and \(-2.860 \pm 0.003\). The differences from the theoretical value are negligible. From Fig. S1 (b), we can notice that the mean iteration numbers of VQE with Nelder-Mead, Powell and COBYLA method are 130, 112, and 51, respectively. In the iteration number histogram of Nelder-Mead method, inner histogram has some cases over 3,000 iterations due to trap in local minimums. We note that each iteration requires one QPU call, which takes up most time in our VQE loop, so that we select COBYLA method as our classical optimizer.

Figure S2 shows the experimental results of each classical optimizers. Figure S2(a) shows the change of input parameters (WP’s angles) during a single VQE run. Figure S2(b) shows that the estimated bound energy at \( R = 0.9\text{Å} \) with respect to the number of iterations in five independent VQE runs. For five independent trials, Nelder-Mead, Powell, and COBYLA have successfully found the ground state energy 1, 4, and 4 times, respectively.

**Fig. S1.** The classical computer emulation test results of the classical optimizers with 1,000 trials. (a) the estimated energy and (b) the number of iterations. In (a) the red solid line represents theoretical value of our simulated Hamiltonian, \( R = 0.9\text{Å} \). The gray region shows the range of the objective value tolerance condition, \( \text{ftol} = 0.01 \), which is corresponding to success criteria.
Fig. S2. The experimental results of real VQE runs with different classical optimizers. (a) the waveplate (WP) angles change during the single VQE run. (b) the estimated energy changes during the iteration in five independent VQE runnings.

B. Gradient-based optimizers

We have evaluated four gradient-based classical optimizers with 1,000 trials of classical computer emulation. Unlike gradient-free classical optimizers, gradient-based optimizers require hyper-parameters such as step-size and gain. In our emulation, we have numerically found the optimized hyper-parameters. Figure S3 shows the histogram of each gradient-based classical optimizer, CG, L-BFGS-B, and SLSQP in terms of (a) the estimated energy, and (b) the number of iterations. In Fig. S3 (a), the red line indicate the theory value with the emulation condition of interatomic distance $R = 0.9\text{Å}$. The gray region represents the area of success criteria corresponding to tolerance of optimizer, $ftol = 0.01$. The success probability of each optimizer is 0.84, 0.89, and 0.60, respectively. The mean values of the estimated energy $\langle H \rangle$ with CG, L-BFGS-B, and SLSQP methods are $-2.859 \pm 0.003$, $-2.859 \pm 0.003$ and $-2.857 \pm 0.003$. The differences from the theoretical value are negligible. From Fig. S3 (b), we can notice that the mean iteration numbers of VQE with CG, L-BFGS-B, and SLSQP method are 153, 125, and 38, respectively.

The SPSA optimizer, one of the most promising optimizers for VQE experiment, can have a stopping criterion in the form of the number of iterations \[3\]. We have tested the SPSA optimizer

Fig. S3. The classical computer emulation test results of the gradient-based classical optimizers with 1,000 trials. (a) the estimated energy and (b) the number of iterations. In (a) the red solid line represents theoretical value of our simulated Hamiltonian, $R=0.9\text{Å}$.
Fig. S4. The estimated energy histograms of classical computer emulation with SPSA optimizer. Each row has the different stopping criterion that the total number of iterations is 30, 60, and 90. The red solid line represents theoretical value of our simulated Hamiltonian, \( R=0.9\,\text{Å} \).

Fig. S5. The experimental results with SPSA optimizer. (a) the waveplate (WP) angles change during the single VQE run. (b) the estimated energy changes during the iteration in five independent VQE runnings.

performance with the number of 30, 60 and 90 iterations. Figure S4 shows the histogram of the estimated energy in each number of total iterations. The gray region represents the area of success criteria corresponding to tolerance of optimizer, \( \text{ftol} = 0.01 \). The success probability of each case is 0.76, 0.91, and 0.95, respectively. The mean values of the estimated energy \( \langle H \rangle \) with the number of total iteration of SPSA method as 30, 60, and 90 are \(-2.856 \pm 0.002\), \(-2.857 \pm 0.003\) and \(-2.858 \pm 0.003\). The differences from the theoretical value are also negligible.

We have also experimentally verified the performance of the SPSA optimizer with 60 iterations, see Fig. S5. SPSA optimizers have successfully found the ground state energy one time out of five VQE runs.

In summary, COBYLA shows the best performance among all gradient-free and gradient-based optimizers in our system.
3. PHOTONIC FOUR DIMENSIONAL QUANTUM STATE GENERATION AND MEASUREMENT

We have tested our QPU by generating and measuring various four-dimensional quantum states. Here, we have generated the ququart states in mutually unbiased bases and checked the state purity through quantum state tomography (QST) \[4\]. Figure S6 and S7 show the QST results with the values of state purity. For clear description, we present $|aH\rangle$, $|aV\rangle$, $|bH\rangle$ and $|bV\rangle$ to $|0\rangle$, $|1\rangle$, $|2\rangle$ and $|3\rangle$, respectively.

**Fig. S6.** The QST and its state purity results of given ququart states (part 1).
In order to compensate the phase drift between path modes $|a\rangle$ and $|b\rangle$, we prepare the state as
\[
|\psi\rangle_{\text{pol}} \otimes |\psi\rangle_{\text{path}} = |H\rangle \otimes \frac{1}{\sqrt{2}} (|a\rangle + |b\rangle) = |H\rangle \otimes |+\rangle,
\]
where the first and second qubits represent the polarization and path qubits, respectively. By projecting the polarization qubit onto $|H\rangle$ using Q4, H4, Q5 and H5 in Fig. 2(b), we can solely consider the path qubit. If the interferometer has the phase drift $\delta$ between path modes $|a\rangle$ and $|b\rangle$, the input state becomes,
\[
|\psi\rangle_{\text{path}} = \frac{1}{\sqrt{2}} (|a\rangle + |b\rangle) \rightarrow \frac{1}{\sqrt{2}} (|a\rangle + e^{i\delta}|b\rangle).
\]
After the PBD2, the paths $|a\rangle$ and $|b\rangle$ are translated into the polarization states $|V\rangle$ and $|H\rangle$, respectively. Therefore, the phase drift $\delta$ between path modes can now be compensated in the polarization modes. In particular, a HWP at $H_p$ between two QWP at 45° provides the phase, $\Delta\phi = 4H_p$, between the polarization states $|H\rangle$ and $|V\rangle$ [5], and thus, we can compensate the path phase drift $\delta$ using the HWP. The phase compensation is ensured by maximizing and minimizing the path qubit outcomes of $|+\rangle$ and $|-\rangle = \frac{1}{\sqrt{2}} (|a\rangle - |b\rangle)$, respectively.
REFERENCES

1. J. M. Turney, A. C. Simmonett, R. M. Parrish, E. G. Hohenstein, F. A. Evangelista, J. T. Fermann, B. J. Mintz, L. A. Burns, J. J. Wilke, M. L. Abrams et al., “Psi4: an open-source ab initio electronic structure program,” Wiley Interdiscip. Rev. Comput. Mol. Sci. 2, 556–565 (2012).

2. A. Peruzzo, J. McClean, P. Shadbolt, M.-H. Yung, X.-Q. Zhou, P. J. Love, A. Aspuru-Guzik, and J. L. O’Brien, “A variational eigenvalue solver on a photonic quantum processor,” Nat. Commun. 5, 1–7 (2014).

3. J. C. Spall, “Implementation of the simultaneous perturbation algorithm for stochastic optimization,” IEEE Transactions on aerospace electronic systems 34, 817–823 (1998).

4. J. Yoo, Y. Choi, Y.-W. Cho, S.-W. Han, S.-Y. Lee, S. Moon, K. Oh, and Y.-S. Kim, “Experimental preparation and characterization of four-dimensional quantum states using polarization and time-bin modes of a single photon,” Opt. Commun. 419, 30–35 (2018).

5. J. Yoon, T. Pramanik, B.-K. Park, Y.-W. Cho, S.-Y. Lee, S. Kim, S.-W. Han, S. Moon, and Y.-S. Kim, “Experimental comparison of various quantum key distribution protocols under reference frame rotation and fluctuation,” Opt. Commun. 441, 64–68 (2019).