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# Computing Free Energies with Fluctuation Relations on Quantum Computers

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One of the most promising applications for quantum computers is the dynamic simulation of quantum materials. Current hardware, however, sets stringent limitations on how long such simulations can run before decoherence begins to corrupt results. The Jarzynski equality, a fluctuation theorem that allows for the computation of equilibrium free energy differences from an ensemble of short, non-equilibrium dynamics simulations, can make use of such short-time simulations on quantum computers. Here, we present a quantum algorithm based on the Jarzynski equality for computing free energies of quantum materials. We demonstrate our algorithm using the transverse field Ising model on both a quantum simulator and real quantum hardware. As the free energy is a central thermodynamic property that allows one to compute virtually any equilibrium property of a physical system, the ability to perform this algorithm for larger quantum systems in the future has implications for a wide range of applications including the construction of phase diagrams, prediction of transport properties and reaction constants, and computer-aided drug design.

## I. INTRODUCTION

Thermodynamics is one of the most well-established and powerful physical theories, with impacts ranging from deep concepts, such as the arrow of time, to practical and technological applications, like the steam engine. Its principles can be used to make predictions about heat transport, complex chemical reactions, and biological processes without detailed knowledge of the microscopic constituents. Its ability to compute bulk properties of macroscopic systems stems from dealing with averages over very large numbers of particles where individual deviations from the mean become insignificant. However, as system sizes decrease down to microscopic scales, these deviations, or fluctuations, from the average become appreciable. In finite temperature systems, thermal motion is the main source of fluctuations, while in zero- and low-temperature systems quantum effects begin to play an important role. Regardless of their source, when fluctuations about the average become significant, classical thermodynamics begins to lose accuracy and it becomes necessary to apply stochastic thermodynamics.

Stochastic thermodynamics allows thermodynamic concepts such as work and heat to be defined in terms of the statistics of trajectories of the system [1–3]. This framework has led to the discovery of fluctuation relations [4, 5], which relate fluctuations in non-equilibrium processes to equilibrium properties like the free energy. As a result, fluctuation relations can be used to study the behavior of systems far from equilibrium. Arguably the most celebrated fluctuation relation is the Jarzynski equality [6, 7], in which the free energy difference between two equilibrium states of a system may be derived from an exponential average over an ensemble of measurements of the work required to drive the system from one state to the other in an arbitrarily short amount of time (i.e. via a non-equilibrium process). While the Jarzynski equality was initially proven and experimentally verified for classical systems [8–13], it has since been extended to the quantum regime, for both closed [4, 14–

17] and open systems [18–26]. Experimental verification of the quantum Jarzynski equality was proposed [27] and later demonstrated with a liquid-state nuclear magnetic resonance platform [28] and with cold trapped-ions [29].

While the Jarzynski equality has proven important theoretically, providing one of the few strong statements that can be made about non-equilibrium systems, its utility for computing free energies of relevant quantum systems has thus far been limited. This is because simulating the exact trajectories of quantum systems on classical computers requires resources that scale exponentially with system size. Therefore, computing even a single trajectory of a quantum system with tens of particles can quickly become intractable on classical computers, let alone an ensemble of trajectories.

One potential path forward is to employ quantum computers to compute this ensemble of trajectories of the quantum system. Simulating quantum systems is a natural application for quantum computers, which can efficiently simulate their dynamics given an initial state and governing Hamiltonian [30–33]. Above and throughout the rest of the paper we use the term trajectory to evoke the correspondence with classical stochastic thermodynamics but we note that the classical notion of a trajectory is not directly applicable to quantum systems. We instead use the term trajectory as a mathematical tool to define physical quantities that are given by averages over single realizations of physical processes [34].

Current and near-term quantum computers, known as noisy intermediate-scale quantum (NISQ) computers [35], suffer from short qubit decoherence times and high gate error-rates. Furthermore, they do not yet have high enough numbers of qubits to implement error-correcting schemes that will alleviate these constraints in the future. As a result, NISQ computers are limited in the depth of quantum circuits that they can execute with high-fidelity. Long-time simulations of general quantum systems, therefore, are currently not feasible on NISQ computers, as circuit depths tend to grow with increasing numbers of simulation time-steps [36, 37]. Short-time

simulations, however, are more feasible.

The Jarzynski equality, which can utilize an ensemble of short-time, non-equilibrium dynamic simulations to compute the free energy of a quantum system is thus a perfect match for NISQ computers. Here, we present a quantum algorithm to compute free energy differences of quantum systems based on the Jarzynski equality. By capitalizing on the ability of quantum computers to efficiently perform short-time dynamic simulations, our algorithm enables the computation of thermodynamic properties of quantum systems, allowing for deeper exploration into the evolving field of quantum thermodynamics.

## II. THEORETICAL BACKGROUND AND FRAMEWORK

To use the Jarzynski equality in practice, we define a parameter-dependent Hamiltonian for the system of interest,

$$H(\lambda) = T + U(\lambda), \quad (1)$$

where  $\lambda$  is an externally controlled parameter of the system that can be adjusted according to a fixed protocol,  $T$  is the kinetic energy of the system and  $U$  is the potential energy. Without loss of generality, we assume the initial equilibrium state of the system is represented by the Hamiltonian  $H(\lambda = 0)$ , and the final state is represented by  $H(\lambda = 1)$ . An ensemble of measurements of the work performed on the system as the parameter  $\lambda$  is varied from 0 to 1 is then collected. A single evolution of the system through time as  $\lambda$  is varied is generally referred to as a trajectory of the system. The Jarzynski equality uses work measurements from an ensemble of trajectories to compute the free energy difference between the initial and final equilibrium states. The equality is given by

$$e^{-\beta\Delta F} = \langle e^{-\beta W} \rangle, \quad (2)$$

where  $\beta = \frac{1}{k_B T}$  is the inverse temperature  $T$  of the system ( $k_B$  is Boltzmann's constant) in its initial equilibrium state,  $\Delta F$  is the free energy difference between the initial and final equilibrium states,  $W$  is the work measured for a single trajectory, and  $\langle \dots \rangle$  represents taking an average over the ensemble of trajectories.

In the lab, this can be accomplished by performing a large number of experiments measuring the work performed during the evolution of the system from a fixed initial equilibrium state as some external knob varies  $\lambda$  according to a fixed protocol  $\lambda(t)$ . Since engineering precise initial conditions and parameter-varying protocols that are identical across all experimental trajectories can be difficult to achieve, computer simulation provides a promising alternative for collecting an ensemble of work measurements, as it is trivial to set the initial conditions and the  $\lambda(t)$  protocol for each simulation. In this computational setting, a large number of non-equilibrium dynamic simulations of the system are performed as the

parameter  $\lambda$  is varied from 0 to 1. The initial state of the system for each trajectory is sampled from the initial equilibrium (Boltzmann) distribution at inverse temperature  $\beta$ , and the work performed during each simulation is measured.

In the simulation of classical systems, where particles are represented by well-defined positions and momenta, it is straightforward to compute work incrementally by monitoring the instantaneous values of these variables throughout the simulation. For a quantum system, however, the position and momentum of a particle are defined as distributions, which cannot be measured simultaneously, nor without destroying the quantum state of the system. This makes the work performed in a single simulation a non-trivial value to compute. In fact, work is not an observable for quantum systems [38]. One way to understand this is that the range of possible values for work is generally larger than the Hilbert space of the system [39, 40] and thus a Hermitian operator representing work cannot exist. Another way to understand this is that work characterizes a process rather than an instantaneous state of system [41].

While there is still active debate over how best to define work for open quantum systems [3, 4, 41–51], a general consensus seems to have been formed for defining work in closed quantum systems, namely the two-measurement protocol (TMP) [4, 15, 16, 52]. In the TMP, the energy of the isolated quantum system is measured at the beginning and at the end of the trajectory, and the work over that trajectory is defined as the difference between the initial and final energy measurements. Thus, the TMP can be used to generate a work distribution from an ensemble of trajectories, where each trajectory is initialized in a thermal state of the system in equilibrium at some inverse temperature  $\beta$ .

Preparing thermal states on a quantum computer is a non-trivial problem for which only a handful of algorithms have been proposed, most of which are either not NISQ-friendly (in terms of circuit complexity) or struggle to scale to large or complex systems. Algorithms for thermal state preparation fall into two main paradigms. The first are algorithms that initialize the qubits into the full thermal (i.e., mixed) state. The thermal average of an observable can be computed directly by measuring the observable in this state. Examples include algorithms that prepare the Gibbs state using phase estimation [53, 54], which require quantum circuits that are too large for NISQ computers. Other examples include the variational quantum thermalizer (VQT) [55] as well as methods that prepare thermofield double states [56, 57], which rely on variational techniques; the variational nature of these algorithms necessitates the classical calculation of a cost function. These cost functions involve computation of the system entropy or knowledge of the eigenstates of the system Hamiltonian, both of which are generally hard to compute for relevant systems, rendering these methods difficult to scale to large or complex systems.

In the second paradigm, the qubits are initialized into one pure state at a time, where each pure state has been sampled according to the correct statistics from the mixed thermal equilibrium state. To calculate thermal averages, the desired observable is measured in each of the different pure states and the results are averaged over the ensemble. As pure states are much easier to prepare on a quantum computer than mixed states, this model for thermal state preparation is more promising for NISQ computers.

One sampling method that is particularly promising for quantum computers produces a Markov chain of sampled pure states, known as minimally entangled typical thermal states (METTS) [58, 59], whose statistics identically mimic those of the desired thermal system. The quantum version of the METTS algorithm, known as QMETTS, gives a procedure to generate METTS on quantum computers using quantum imaginary time evolution (QITE) [60]. While initially presented as an algorithm to obtain thermal averages of static observables, QMETTS was recently shown to enable calculation of time-dependent observables by time-evolving the METTS on quantum computers [61]. Thus, QMETTS can be used to generate the initial sampled states for the non-equilibrium trajectories to generate initial and final thermal energies to compute the work distributions for use in the Jarzynski equality.

### III. ALGORITHM

We now describe our algorithm, which provides a procedure for obtaining a work distribution from non-equilibrium dynamic simulations of a closed quantum system on a quantum computer which can be used to compute free energies using the Jarzynski equality in Eq. (2). The non-equilibrium dynamic simulations require three main steps: (i) prepare the initial thermal states of each trajectory, (ii) evolve the quantum system under the time-dependent Hamiltonian  $H(\lambda)$  as  $\lambda$  is varied from  $\lambda = 0$  to  $\lambda = 1$  according to  $\lambda(t)$ , and (iii) measure the work for the given trajectory. Our algorithm utilizes QMETTS to address task (i), Trotterized time-evolution to address task (ii) and TMP to address task (iii).

Pseudocode for the algorithm is shown in Algorithm 1. The algorithm takes as input the parameter-dependent Hamiltonian  $H(\lambda)$ , the inverse temperature  $\beta$  of the initial system at equilibrium, the protocol  $\lambda(t)$  to evolve the parameter from  $\lambda = 0$  to  $\lambda = 1$ , and the total number of trajectories  $T$ . The algorithm builds up a work distribution by looping over the  $T$  trajectories. For each trajectory, a circuit is generated which prepares the sampled initial state at inverse temperature  $\beta$ , denoted as `circ_TS` in Algorithm 1. According to the QMETTS protocol, this is accomplished by initializing the qubits into an initial product state (i.e., a computational basis state), denoted by the variable `QMETTS_state` in Algorithm 1, and then evolving the system under the initial

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#### Algorithm 1: Pseudocode for computation of free energies using Jarzynski equality on quantum computers

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```

Input:  $H(\lambda)$ ,  $\beta$ ,  $\lambda(t)$ ,  $T$ 
Output: Free energy difference
1 work_distribution = []
2 QMETTS_state = random_product_state()
  /* Loop over T trajectories */
3 for  $n=[0, T]$  do
  /* make thermal state preparation circuit */
4   circ_TS = TS_circ( $\frac{\beta}{2}$ ,  $H(\lambda = 0)$ , QMETTS_state)
  /* get initial state for next trajectory */
5   QMETTS_state = collapse(circ_TS, n)
  /* measure initial energy */
6    $E_i$  = measure(circ_TS,  $H(\lambda = 0)$ )
  /* make Hamiltonian evolution circuit */
7   circ_hamEvol = hamEvol_circuit( $\lambda(t)$ ,  $H(\lambda)$ )
  /* measure final energy */
8   total_circ = circ_TS + circ_hamEvol
9    $E_f$  = measure(total_circ,  $H(\lambda = 1)$ )
10  work =  $E_f - E_i$ 
11  work_distribution.append(work)
12 return compute_free_energy(work_distribution,  $\beta$ )

```

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Hamiltonian  $H(\lambda = 0)$  for an imaginary time  $\beta/2$  using QITE. For the first trajectory, `QMETTS_state` is a random product state, while for all subsequent trajectories `QMETTS_state` is determined by a projective measurement of `circ_TS` from the previous trajectory. This projective measurement happens next, by collapsing `circ_TS` into a basis which depends on the parity of the trajectory. In order to ensure ergodicity and reduce autocorrelation times, it is helpful to switch between measurement bases throughout sampling [59]. Following the method of Ref. [59] proposed for spin- $\frac{1}{2}$  systems, for even trajectories we measure (i.e., collapse) along the  $z$ -axis, while for odd trajectories we measure along the  $x$ -axis.

The thermal state circuit is then used twice more to measure the initial and final energies of the system which can be used to compute the work value for the trajectory using the TMP. Therefore, the next step measures the initial energy  $E_i$  by measuring the initial Hamiltonian  $H(\lambda = 0)$  in the thermal state. Next, a circuit is created that evolves the system through real-time under the time-dependent Hamiltonian  $H(\lambda)$  as it is varied according to the protocol  $\lambda(t)$ . The real-time evolution by a time-dependent Hamiltonian is carried out with Trotterization according to the method outlined in Ref [62]. This circuit, denoted as `circ_hamEvol` in Algorithm 1, is concatenated with `circ_TS`, and this total circuit, denoted as `total_circ` in Algorithm 1, is used to measure the final energy by measuring  $H(\lambda = 1)$ . With the initial and final energies computed, the value of work for the given trajectory is appended to the work distribution array, and the loop continues to the next trajectory. After the work distribution has been generated from the  $T$  trajectories, it is a straightforward matter to compute the free energy

difference using the Jarzynski equality in Eq. (2).

A workflow diagram for the circuits that must be generated and executed is shown in Figure 1. The thermal state (TS) preparation circuit is depicted in Figure 1a. The circuit is embedded into three separate circuits shown in Figure 1b: one to generate the next sampled thermal state according to the QMETTS procedure (MM), and two more for computing a value for work with the TMP, one circuit each to measure the initial and final energies. The initial energy measurement circuit ( $E_i$ ) simply composes the TS circuit with a set of gates that measures the value of the initial Hamiltonian,  $H(\lambda = 0)$ . The final energy measurement circuit ( $E_f$ ) composes the TS circuit with real-time evolution of the system as  $H(\lambda)$  is varied according to the protocol  $\lambda(t)$ , as well as a set of gates that measures the value of the final Hamiltonian,  $H(\lambda = 1)$ . Figure 1c shows how a work value is derived from these circuits for each trajectory and how measurement of the MM circuit from the previous trajectory provides input to the TS circuit for the next trajectory. We note that the first few work values should be discarded as “warm-up” values to remove the effect of choosing a random initial product state for the first trajectory [58].

#### IV. RESULTS

We demonstrate our algorithm on both a quantum simulator and real quantum hardware with a parameter-dependent transverse field Ising model (TFIM), where the strength of the transverse magnetic field will be controlled by the parameter  $\lambda$ . The Hamiltonian is defined as

$$H(\lambda) = -J_z \sum_{i=1}^{N-1} \sigma_i^z \sigma_{i+1}^z - [1 - \lambda(t)] \mu_x \sum_{i=1}^N \sigma_i^x, \quad (3)$$

where  $N$  is the number of spins in the system,  $J_z$  is the strength of the exchange interaction between pairs of nearest neighbor spins,  $\mu_x$  is the strength of the transverse magnetic field, and  $\sigma_i^\alpha$  is the  $\alpha$ -Pauli operator acting on spin  $i$ . The system starts in thermal equilibrium at an inverse temperature  $\beta$  with an initial Hamiltonian  $H_i = H(\lambda = 0)$ . Thus, the system begins with the transverse field fully turned on with a strength of  $\mu_x$ . The parameter  $\lambda$  is then increased to  $\lambda = 1$  according to a linear protocol  $\lambda(t)$ , resulting in a system with a final Hamiltonian  $H_f = H(\lambda = 1)$ , where the transverse field is completely turned off. By measuring the work performed as  $\lambda$  is varied from 0 to 1 over many trajectories, we can construct a work distribution which can be used in the Jarzynski equality to compute the free energy difference. We perform this procedure for a range of initial values of  $\mu_x$ .

Generating the thermal state preparation circuits for general systems can be computationally expensive due to their dependence on the QITE algorithm, which re-

quires multiple steps of classical optimization and generates long quantum circuits. Therefore, we limit our demonstrations to toy models with either two or three qubits. Previous work, however, has shown that these costs can be drastically reduced for systems with certain symmetries [61]. Therefore, our algorithm can in principle be extended to larger systems with special symmetry properties.

Figure 2 shows the free energy differences for a 3-qubit TFIM computed with our algorithm for various initial values of the transverse magnetic field  $\mu_x$ , calculated on a quantum simulator (i.e. a classical computer that simulates a quantum computer). The system was initialized to an equilibrium inverse temperature of  $\beta = 9.0$ . The blue circles give the analytically computed free energy differences, which are possible to compute due to the small system size and serve as reference points for the ground truth. The red circles are the free energy differences computed with our algorithm using the Jarzynski equality with an ensemble of one thousand simulated trajectories. We observe that the results from the quantum simulator agree well with the analytically computed results.

Without applying the mathematical tricks outlined in [61] to reduce the depths of the circuits generated by the QITE algorithm, the thermal state preparation circuits are too deep for high-fidelity results on current hardware for system sizes larger than 2-qubits. All 2-qubit circuits, however, can be reduced to a short constant depth [63, 64], and thus can be executed on a real quantum processor. We therefore provide a proof-of-concept demonstration of our algorithm on a real quantum processor for a 2-qubit system. In principle, however, using circuit optimization techniques such as those that reduce the depths of QITE circuits [61] or those that reduce the depths of time-evolution circuits [65], can extend our algorithm to larger systems on quantum processors.

Figure 3 shows the free energy differences for a 2-qubit TFIM computed with our algorithm for various initial values of the transverse magnetic field  $\mu_x$ , calculated on the IBM quantum processor *ibmq\_bogota*. The system was initialized to an equilibrium inverse temperature of  $\beta = 5.0$ . The blue circles give the analytically computed free energy differences, while the red circles are the free energy differences computed via the Jarzynski equality from an ensemble of one hundred simulated trajectories. The results from the quantum computer give the raw data with no error mitigation of any kind performed. We observe remarkable agreement between the results computed on the quantum computer with our algorithm and the analytically computed results.

The work distributions for the different initial values of  $\mu_x$  are shown in Figure 4. This shows the distributions over which we compute the exponential average to measure free energies (Figure 3). For reference, the free energy difference for each system is denoted by the dashed black line. As expected, the ensemble of measured

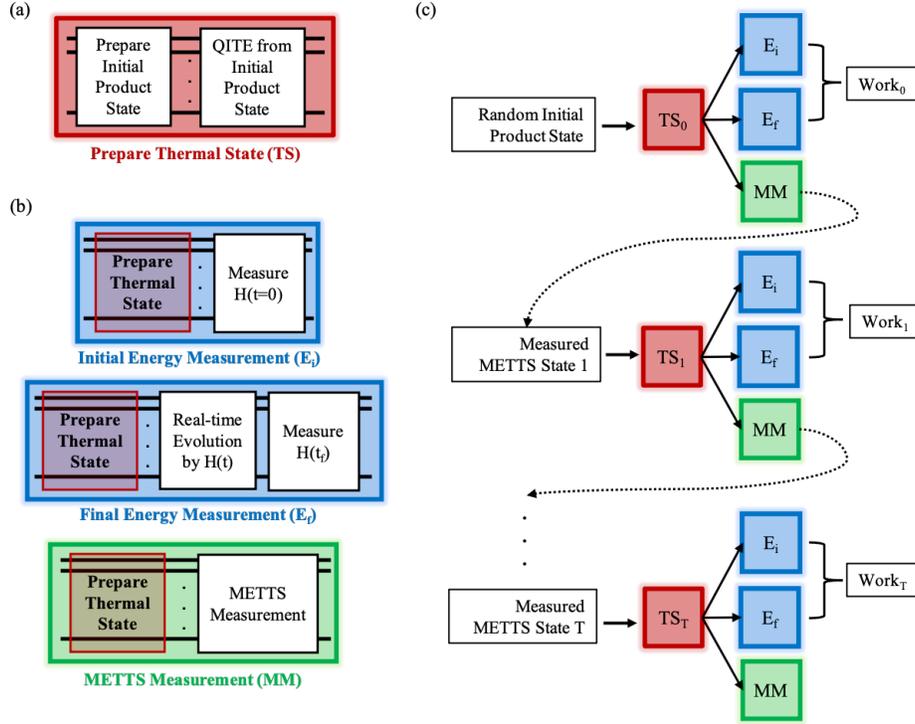


FIG. 1. Circuits generated and workflow diagram of the algorithm. (a) Quantum circuit diagram for the thermal state preparation circuit, which relies on QITE. (b) Quantum circuit diagrams for the three circuits that must be generated using the thermal state preparation circuit including two circuits for measuring the initial and final energies as well as a circuit to measure the initial product state for the subsequent trajectory. (c) Workflow diagram depicting the necessary circuits to generate and their order for execution to produce a work distribution for use in the Jarzynski equality.

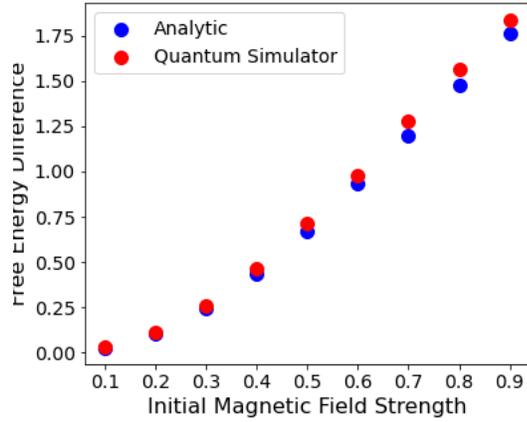


FIG. 2. Free energy differences for a 3-qubit system for varying initial strengths of the transverse magnetic field. The blue circles give the analytically computed values, while the red circles give the free energy differences computed on a quantum simulator.

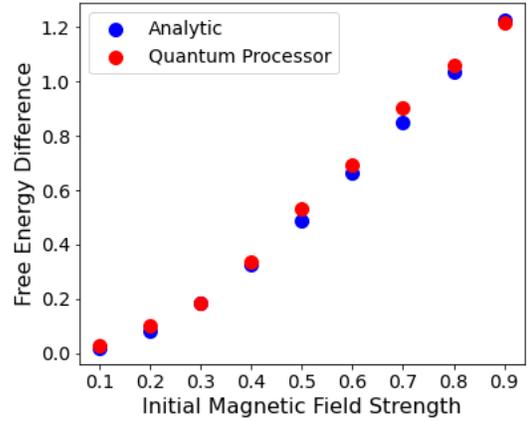


FIG. 3. Free energy differences for a 2-qubit system for varying initial strengths of the transverse magnetic field. The blue circles give the analytically computed values, while the red circles give the free energy differences computed on a real quantum processor.

work values from the different trajectories are distributed around the free energy difference.

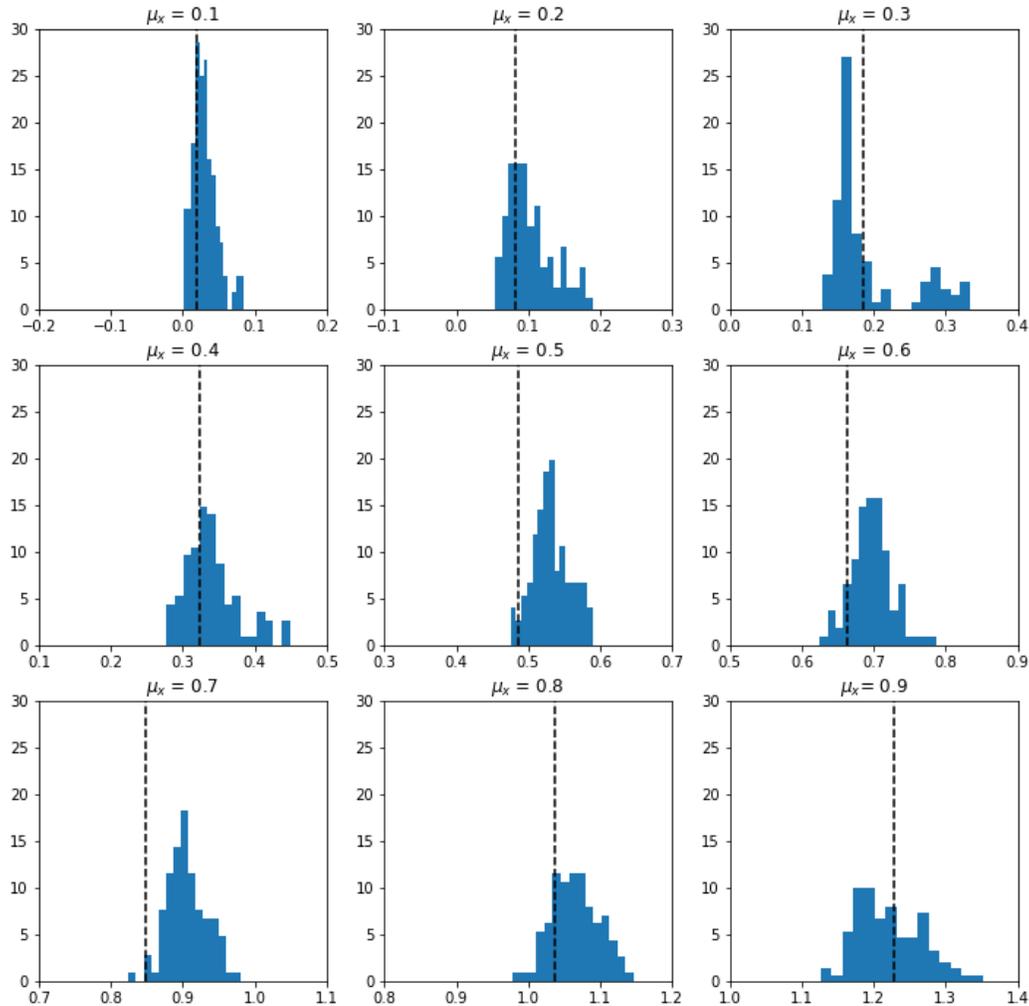


FIG. 4. Work distributions for various initial strengths of the transverse magnetic field for the 2-qubit TFIM computed on a real quantum processor. The black dotted line denotes the analytically computed free energy difference for each system.

## V. CONCLUSION

Here we have introduced an algorithm for measuring free energy differences of quantum systems on quantum computers. We demonstrated our algorithm on IBM’s quantum simulator and a real quantum processor for the transverse field Ising model, showing accurate measurement of free energy differences. The most resource intensive component of our algorithm is the generation of the initial thermal states, due to its dependence on the QITE algorithm. We emphasize that other thermal state preparation algorithms [57] could potentially be substi-

tuted here in the future without changing the nature of our algorithm. We anticipate this and related [66] algorithms to become increasingly important as a means to explore the thermodynamics of quantum systems as quantum hardware becomes more powerful.

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