Computing Free Energies with Fluctuation Relations on Quantum Computers

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As a central thermodynamic property, free energy enables the calculation of virtually any equilibrium property of a physical system, allowing for the construction of phase diagrams and predictions about transport, chemical reactions, and biological processes. Thus, methods for efficiently computing free energies, which in general is a difficult problem, are of great interest to broad areas of physics and the natural sciences. The majority of techniques for computing free energies target classical systems, leaving the computation of free energies in quantum systems less explored. Recently developed *fluctuation relations* enable the computation of free energy differences in quantum systems from an ensemble of dynamic simulations. While performing such simulations is exponentially hard on classical computers, quantum computers can efficiently simulate the dynamics of quantum systems. Here, we present an algorithm utilizing a fluctuation relation known as the Jarzynski equality to approximate free energy differences of quantum systems on a quantum computer. We discuss under which conditions our approximation becomes exact, and under which conditions it serves as a strict upper bound. Furthermore, we successfully demonstrate a proof of concept of our algorithm using the transverse field Ising model on a real quantum processor. As quantum hardware continues to improve, we anticipate that our algorithm will enable computation of free energy differences for a wide range of quantum systems useful across the natural sciences.

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Introduction.—Free energy is a central thermodynamic property used to compute virtually all equilibrium properties of a physical system [1]. Broadly useful across the natural sciences, free energy differences are employed in the construction of phase diagrams [2–5], the prediction of transport properties and reaction constants [6], and the calculation of protein-ligand binding affinities required for computer-aided drug design [7–11]. In general, computing free energy differences is a difficult problem due to the challenges in adequately sampling the important configurations of a system [1]. As such, a great deal of research has focused on developing techniques for calculating free energy differences [1,12–16]. The majority of techniques have been developed for classical systems; less well studied are methods for computing free energy differences in quantum systems [6,17–19] (see Section I in the Supplemental Material [20], which includes Refs. [21–24]).

In general, extending thermodynamics to the quantum realm is nontrivial, as its theoretical constructs tend to focus on bulk properties of macroscopic-size systems derived from averages over a very large number of constituent particles. An implicit assumption here is that individual deviations from the average become practically insignificant, allowing thermodynamics to make predictions about systems without detailed knowledge of the microscopic constituents. However, as the size of the system begins to shrink, these deviations, originating from thermal motion (and possibly quantum effects), become more appreciable. Rather surprisingly, these deviations, or fluctuations, satisfy some profound equalities, generally referred to as fluctuation relations (FRs) [25,26]. FRs relate fluctuations in nonequilibrium processes to equilibrium properties like free energy differences.

Arguably the most celebrated FR is the Jarzynski equality [27,28], in which the free energy difference between two equilibrium states is derived from an exponential average over an ensemble of measurements of the work required to drive the system from one state to the other. While the Jarzynski equality has proven important theoretically, providing one of the few strong statements that can be made about nonequilibrium systems, its utility for computing free energies of 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 for computing this ensemble of trajectories is to employ quantum computers, which were proven capable of efficiently simulating the dynamics of quantum systems over two decades ago [29–32]. A plethora of recent work has successfully demonstrated dynamic simulations of the Hubbard model [33], the Schwinger model [34], and various spin models [35–40] on currently available quantum hardware, while further work has shown how such dynamic simulations can be used to compute various static properties such as cross sections in inelastic neutron scattering [41], magnon spectra [42], and transport properties [43].

Here, we present an algorithm to approximate free energy differences using the Jarzynski equality based on dynamic simulations performed on a quantum computer. We discuss under which conditions the approximation becomes exact and under which conditions the approximation gives a strict upper bound, which is tighter than the usual upper bound given by the reversible work theorem. We provide a proof-of-concept demonstration for our algorithm by computing free energy differences in a transverse field Ising model (TFIM) on a real quantum processor. Further improvements in quantum circuit generation [44–47], error mitigation techniques [48,49], and quantum hardware [50] will enable our algorithm to compute free energy differences for scientifically relevant systems on quantum computers in the near future (see Section II of the Supplemental Material [20], which includes Refs. [51–57]). Our algorithm demonstrates how quantum computers, with their ability to efficiently perform dynamic simulations of quantum systems, provide an unprecedented platform for computing free energy differences.

Theoretical background and framework.—Initially derived and experimentally verified for classical systems [58–63], the Jarzynski equality has since been extended to both closed [25,26,64–68] and open [69–77] quantum systems, theoretically. Experimental verification of the Jarzynski equality in closed quantum systems was proposed [78] and later demonstrated with a liquid-state nuclear magnetic resonance platform [79] and with cold trapped ions [80]. To use the Jarzynski equality in practice, we define a parameter-dependent Hamiltonian for the system of interest $H(\lambda)$, where λ is an externally controlled parameter that can be adjusted according to a fixed protocol. The Jarzynski equality uses work measurements from an ensemble of trajectories as λ is varied to compute the free energy difference between the initial and final equilibrium states. The equality is given by

$$e^{-\beta\Delta F} = \langle e^{-\beta W} \rangle, \tag{1}$$

where $\beta = (1/k_B T)$ is the inverse temperature T of the system (k_B is Boltzmann's constant) in its initial equilibrium state, ΔF is the free energy difference between the initial and final equilibrium states, W is the work measured for a single trajectory, and $\langle \ldots \rangle$ represents taking an average over the ensemble of trajectories. Without loss of generality, we assume the initial Hamiltonian of the system $H_i = H(\lambda = 0)$, and the final Hamiltonian $H_f = H(\lambda = 1)$. As shown in Fig. 1(a), the protocol for varying λ, denoted $\lambda(t)$, occurs over a time τ, which can be defined to be as fast or slow as desired. In general, the faster the protocol, the more trajectories will be required to compute a more accurate estimate of the free energy [81] (see Section III in the Supplemental Material [20]).

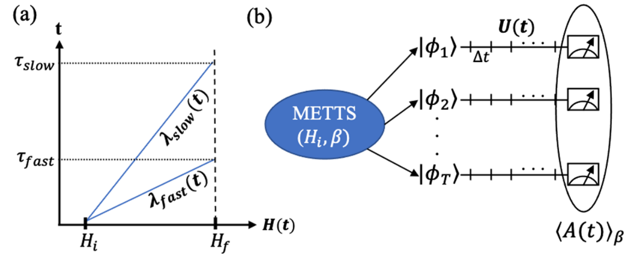

FIG. 1. (a) Schematic diagram depicting how the parameter-dependent Hamiltonian $H(\lambda)$ can be varied over different total times τ. (b) Schematic diagram for the METTS protocol. The protocol requires as input the Hamiltonian and the inverse temperature β of the equilibrium system. The protocol generates a Markov chain of pseudothermal states ϕ_i, which can be time evolved under a separate Hamiltonian, measured, and averaged over to produce the thermal average for some time-dependent observable $A(t)$ at inverse temperature β.

The main challenge in implementing such a procedure is preparing the initial thermal state on the quantum computer. This is a nontrivial problem for which only a handful of algorithms have been proposed, most of which generate circuits that are not feasible (i.e., too large) to run on near-term quantum devices or struggle to scale to large or complex systems [82–86]. A method that is particularly promising for near-term quantum computers produces a Markov chain of sampled pseudothermal states, known as minimally entangled typical thermal states (METTS) [87,88]. Averages of observables over the ensemble of METTS will converge to the true thermal average of the observable with increasing sample size. While initially presented as a method to obtain thermal averages of static observables, METTS can also be used to calculate thermal averages of time-dependent quantities by evolving the METTS in real time before measurement [89]. Recently, Motta *et al.* showed how to construct METTS on a quantum computer using the quantum imaginary time evolution (QITE) algorithm [90]. This approach was used to successfully measure thermal averages of both static [90] and dynamic observables [91] on current quantum hardware. Figure 1(b) shows schematically how measurements of a time-dependent observable $A(t)$ can be averaged over an ensemble of time-evolved METTS for a system with Hamiltonian H_i at inverse temperature β to give the thermal expectation value $\langle A(t) \rangle_\beta$. See Section IV in the Supplemental Material [20] for more details.

Algorithm 1. Pseudocode for approximation of free energy differences using METTS with the Jarzynski equality on quantum computers.

```
Input: H(λ), β, λ(t), M
Output: Free energy difference
work_distribution = [ ]
IPS = random_product_state()
/* Loop over M trajectories */
for m = (0, M) do
    /* make thermal state preparation circuit */
    circ_TS = make_TS_circ(β, H(λ = 0), IPS)
    /* get initial state for next trajectory */
    circ_M = make_M_circ(circ_TS, m)
    IPS = collapse(circ_M)
    /* measure initial energy */
    circ_E_i = make_E_i_circ(circ_TS, H(λ = 0))
    E_i = measure(circ_E_i)
    /* make Hamiltonian evolution circuit */
    circ_hamEvol = make_hamEvol_circ(λ(t), H(λ))
    /* measure final energy */
    circ_E_f = make_E_f_circ(H(λ = 1), circ_TS, circ_hamEvol)
    E_f = measure(circ_E_f)
    work = E_f − E_i
    work_distribution.append(work)
return compute_free_energy(work_distribution, β)
```

Given an ensemble of pseudothermal states generated with the METTS protocol, the initial thermal energy $\langle E_i \rangle$ of the system at inverse temperature β can be measured by averaging over energy measurements of the individual states in the ensemble. Similarly, the final thermal energy $\langle E_f \rangle$ of the system after the $\lambda(t)$ protocol has been implemented can be computed by time evolving each pseudothermal state in the ensemble under the $\lambda(t)$ protocol and averaging over energy measurements of the individual time-evolved states. Now, for closed quantum systems, the work performed in a process is given by the difference in energy of the system before and after the process; therefore, the average thermal energies computed with the METTS ensemble can be used to compute the average work performed over the $\lambda(t)$ protocol, as $\langle W \rangle = \langle E_f \rangle - \langle E_i \rangle$. Note that $\langle W \rangle$ is always an upper bound on the free energy difference due to the reversible work theorem. However, we endeavor to obtain a better approximation to the free energy difference by considering the distribution of individual pseudowork values derived from the METTS ensemble.

In this framework, we let each METTS in the ensemble correspond to a trajectory. For each trajectory, we compute a pseudowork value by taking the difference of the measured initial and final energies of the sampled pseudothermal state before and after evolving it under the $\lambda(t)$ protocol. While the average over this ensemble of pseudowork values will converge to the correct value for average work $\langle W \rangle$, the individual values in the ensemble are not necessarily physical work values. This is because the METTS protocol only guarantees accurate averages over the ensemble of METTS. Nevertheless, we show that this distribution can be used in the Jarzynski equality to compute an approximate free energy difference $\Delta\tilde{F}$ as

$$e^{-\beta\Delta\tilde{F}} = \langle e^{-\beta\tilde{W}} \rangle, \tag{2}$$

where $\tilde{W}$ are the individual pseudowork values computed with the METTS ensemble. In the limit of $\beta \to 0$, this approximation to the free energy difference becomes exact. In the limit of $\beta \to \infty$, $\Delta\tilde{F}$ is exact for $\lambda(t)$ protocols that are adiabatic. For arbitrary β, $\Delta\tilde{F}$ upper bounds the true ΔF for adiabatic $\lambda(t)$ protocols, and is a better approximation to the free energy difference than $\langle W \rangle$ due to Jensen's inequality. See Sections V and VI of the Supplemental Material [20] for proofs of these statements. For nonadiabatic $\lambda(t)$ protocols, we empirically find that $\Delta F \leq \Delta\tilde{F} \leq \langle W \rangle$ for a range of β's and spin-model Hamiltonians; see Section VII of Supplemental Material [20]. Plugging the pseudowork distribution into the Jarzynski equality, therefore, provides a very good approximation to the free energy difference for closed quantum systems under certain conditions, and provides a tighter upper bound to the free energy difference than the average work in a broad range of cases. We emphasize that while our algorithm only approximates the free energy difference, it is one of the very few algorithms that can feasibly be performed on near-term quantum computers [19]; and in many instances, this approximation can provide a strict, and even tight, upper bound on the free energy difference.

Algorithm.—We now describe our algorithm, which provides a procedure for obtaining a pseudowork distribution from nonequilibrium dynamic simulations of a closed quantum system on a quantum computer, which in turn can be used to approximate free energy differences. The pseudocode is shown in Algorithm 1. The algorithm takes as input the parameter-dependent Hamiltonian $H(\lambda)$, the inverse temperature β of the initial system at equilibrium, the protocol $\lambda(t)$ to evolve the parameter from 0 to 1, and the total number of trajectories M. The algorithm generates a pseudowork distribution by looping over the M trajectories.

For each trajectory, a subcircuit is generated which prepares the sampled pseudothermal state at inverse temperature β (circ_TS), depicted by the red circuit in Fig. 2(a). According to the METTS protocol, this is accomplished by initializing the qubits into an initial product state (IPS) and evolving it for an imaginary time $\beta/2$ under the initial Hamiltonian. In this Letter, we use the QITE algorithm to implement the imaginary-time evolution, though alternative methods [47,92] could be substituted. For the first trajectory, IPS is a random product state, while for all subsequent trajectories the new IPS is determined by a projective measurement of the METTS from the previous trajectory.

Then, circ_TS is embedded into three separate circuits. The first circuit (circ_M) is used to determine IPS for the next trajectory, depicted by the green circuit in Fig. 2(a).

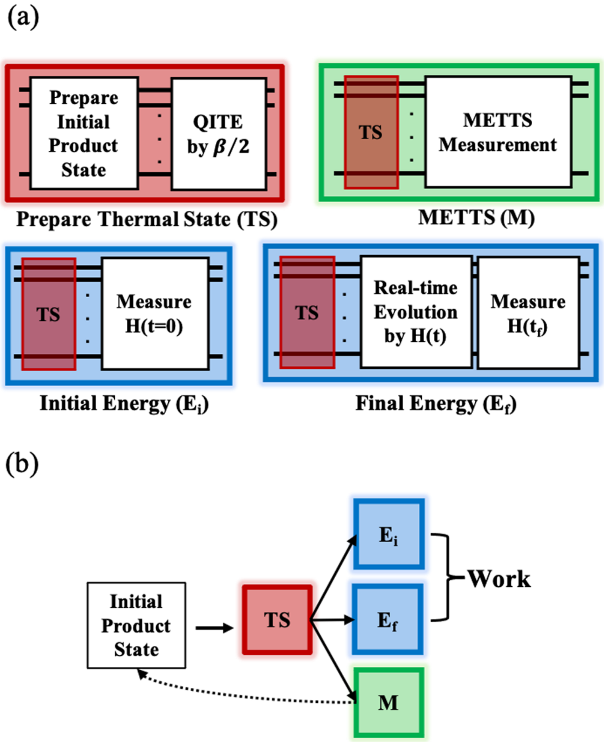

FIG. 2. Circuits generated and workflow diagram for the algorithm. (a) Quantum circuit diagrams for the thermal state preparation subcircuit (red), which is used in three separate circuits for measuring the initial and final energies (blue) as well as measuring the initial product state for the subsequent trajectory (green). (b) Workflow diagram depicting how the circuits above are integrated to produce a pseudowork distribution.

This circuit collapses the thermal state into a basis which depends on the parity of trajectory m. In order to ensure ergodicity and reduce autocorrelation times, it is helpful to switch between measurement bases throughout sampling [88]. Following the method proposed in Ref. [88] for spin-$\frac{1}{2}$ systems, we measure (i.e., collapse) along the z axis for odd trajectories, while for even trajectories we measure along the x axis.

The second circuit (circ_E_i) measures the expectation value of the initial Hamiltonian $H(\lambda = 0)$ in the pseudothermal state to give the initial energy. Finally, the third circuit (circ_E_f) measures the final energy. To generate this circuit, a subcircuit (circ_hamEvol) is first created to evolve the system under the time-dependent Hamiltonian according to the $\lambda(t)$ protocol. In this Letter, we use a recently proposed method for implementing the real-time evolution with short, constant-depth circuits, which works for a special subset of one-dimensional systems [44]. However, more general methods, such as standard Trotterization or variational techniques [93,94], can be substituted. This subcircuit is appended to (circ_TS) to generate the time-evolved pseudothermal state. The final energy is obtained by measuring the expectation value of the final Hamiltonian $H(\lambda = 1)$ in this state. The circuits for measuring initial and final energies are depicted by the blue circuits in Fig. 2(a). The difference between these energies gives the pseudowork for the given trajectory. The free energy difference can then be approximated by plugging the pseudowork ensemble into Eq. (2).

Figure 2(b) shows how a pseudowork value is derived from the three main circuits for each trajectory and how the measurement of the M circuit from the previous trajectory provides input to the TS subcircuit for the next trajectory. Note that the first few trajectories should be discarded as "warm-up" values [87].

Results.—We demonstrate our algorithm on real quantum hardware with a two- and three-qubit TFIM as a proof of concept. The Hamiltonian is defined as

$$H(\lambda) = J_z \sum_{i=1}^{N-1} \sigma_i^z \sigma_{i+1}^z + \left(1 + \frac{\lambda(t)}{2}\right) h_x \sum_{i=1}^{N} \sigma_i^x, \quad (3)$$

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, h_x is the strength of the transverse magnetic field, and σ_i^α is the α-Pauli operator acting on spin i. The system starts in thermal equilibrium at an inverse temperature β with an initial Hamiltonian $H_i = H(\lambda = 0) = J_z \sum_i \sigma_i^z \sigma_{i+1}^z + h_x \sum_i \sigma_i^x$. The parameter λ is then linearly increased from 0 to 1 over a total time τ, resulting in a system with a final Hamiltonian $H_f = H(\lambda = 1) = J_z \sum_i \sigma_i^z \sigma_{i+1}^z + 1.5 h_x \sum_i \sigma_i^x$. We set $J_z = 1$, $h_x = 1$, and $\tau = 10$, and set the number of trajectories $M = 100$ for the two-qubit system and $M = 300$ for the three-qubit system.

Figure 3 shows the approximate free energy differences at various inverse temperatures β computed using our algorithm on the IBM quantum processing unit (QPU) "ibmq_toronto" for a two-qubit system (a) and a three-qubit system (b). The black solid lines show the analytically computed free energy differences, which are possible to compute due to the small size of our systems. The blue dashed lines show raw results from the QPU. The quantum circuits for the three-qubit simulations are significantly larger than those for the two-qubit simulations, and thus accumulate more error due to hardware noise. This explains why the QPU results for the two-qubit system are significantly closer to the ground truth than those for the three-qubit system. To ameliorate this systematic noise, we implement two error mitigation techniques. The first is known as zero-noise extrapolation (ZNE) [95,96], which combats noise arising from two-qubit entangling gates, which are currently one of the largest sources of error on near-term quantum devices. We pair ZNE with a second error mitigation technique to combat readout error, which is error derived from the measurement operation. See Section VIII of the Supplemental Material [20] for more details on error mitigation. The QPU results after error

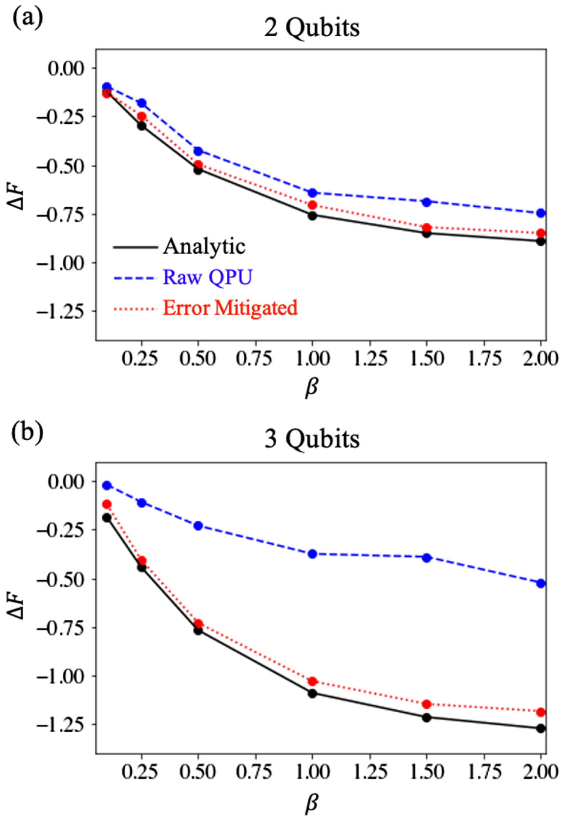

FIG. 3. Approximate free energy differences ($\Delta\tilde{F}$) for two- and three-qubit systems initialized at various inverse temperatures β performed on an IBM QPU. The solid black line gives the analytically computed values (ΔF) for reference. The blue dashed lines show raw results from the QPU, while the red dotted lines show these results after error mitigation has been performed.

mitigation are shown in the red dotted lines. The error mitigated results are in excellent agreement with the analytic results for both system sizes, demonstrating the ability of the two error mitigation techniques to combat major contributions to noise on the quantum computer.

In addition to the systematic errors derived from noisy near-term quantum devices, another source of error stems from using the QITE algorithm to approximate the imaginary time evolution required to generate the METTS. The size of this error depends on the step-size $\Delta\beta$ used to construct the QITE circuits for thermal state preparation at inverse temperature β. This error can systematically be made smaller by decreasing $\Delta\beta$ at the expense of complexity in building the quantum circuit. In general, Trotter error will be another source of error, which arises from the most commonly used approach to generate the real-time evolution operator used to evolve the system as λ is varied from 0 to 1. However, we were able to make this negligible using techniques developed in Ref. [44], which apply to the real-time evolution of TFIMs. See Section IX of the Supplemental Material [20] for more details.

Conclusion.—We have introduced an algorithm for computing free energy differences of quantum systems on quantum computers using fluctuation relations. We demonstrated our algorithm on IBM's quantum processor for the TFIM, resulting in free energy differences in excellent agreement with the ground truth after applying two simple error mitigation techniques. The main bottleneck to using our algorithm for larger systems is the limit on the size of quantum circuits that is feasible to execute on currently available quantum hardware. The imaginary- and real-time evolution components of our algorithm are the largest contributors to circuit depths. Thus, targeting more relevant systems with our algorithm can be addressed by developing new, shorter-depth implementations for imaginary- and real-time evolution. Due to the modularity of our algorithm, such implementations can easily be substituted in as they become available. Simultaneously, new methods for quantum error mitigation, as well as continued improvements made to quantum processors, will further extend the depths of circuits that are feasible to execute. Because of the significant progress in these areas over the last few years [44–50] we anticipate that our algorithm will become increasingly important as a means to compute free energy differences in scientifically relevant systems as quantum computers become more powerful.

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