Ab Initio Molecular Dynamics on Quantum Computers

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Abstract

Ab initio molecular dynamics (AIMD) is a valuable technique for studying molecules and materials at finite temperatures where the nuclei evolve on potential energy surfaces obtained from accurate electronic structure calculations. In this work, a quantum computer-based AIMD method is presented. The electronic energies are calculated on a quantum computer using the variational quantum eigensolver (VQE) method. We compute the energy gradients numerically using the Hellmann-Feynman theorem, finite differences, and a correlated sampling technique. Our method only requires additional classical calculations of electron integrals for each degree of freedom, without any additional computations on a quantum computer beyond the initial VQE run. To achieve comparable accuracy, our gradient calculation method requires three to five orders of magnitude fewer measurements than other brute force methods without correlated sampling. As a proof of concept, AIMD dynamics simulations are demonstrated for the H₂ molecule on IBM quantum devices. To the best of our knowledge, it is the first successful attempt to run AIMD on
quantum devices for a chemical system. In addition, we demonstrate the validity of the method for larger molecules using full configuration interaction (FCI) wave functions. As quantum hardware and noise mitigation techniques continue to improve, the method can be utilized for studying larger molecular and material systems.

Introduction

The time evolution of molecular and material systems has been carried out for decades on classical computers using molecular dynamics (MD) calculations.\textsuperscript{1–10} There are different levels of complexity and accuracy of such calculations. The most accurate and computationally demanding method is of course full quantum dynamics, where the time-dependent Schrödinger equation (TDSE) is solved for both electrons and nuclei. Often such approaches are formulated in terms of coupled Born-Oppenheimer potential energy surfaces for the electronic degrees of freedom, and various approximations are introduced to make the problem in question tractable.\textsuperscript{11} Such quantum dynamics calculations are limited to only a few degrees of freedom due to the high computational costs. On the other end of the complexity spectrum is the field of classical MD methods, which are capable of describing chemical systems consisting of thousands of atoms.\textsuperscript{2} The reason the classical MD of such large systems is possible is that the movement of atoms is described classically through the solution of Hamilton’s equations. One of the main aspects of classical MD simulations is the calculation of interatomic forces, which are often computed from empirical potential functions, also called force fields,\textsuperscript{3,4} parameterized from small model systems to reproduce experimental data. However, in many cases, the transferability of such potentials can be poor, and classical MD fails to describe even qualitatively many interesting chemical and physical phenomena that are intrinsically nonclassical. The field of ab initio molecular dynamics (AIMD),\textsuperscript{5–10} which is a quantum-classical approach, is between the two extremes (full quantum MD and
classical MD). In addition to numerous studies of molecular properties, AIMD has been successfully applied to modeling of materials, such as diffusion properties,\(^1\) reaction processes,\(^2\) vibrational frequencies,\(^3\) and amorphous materials.\(^4\) In AIMD, the nuclei are treated classically, but they are propagated on the potential energy surfaces (PESs) that are calculated quantum-mechanically through the solution of the time-independent Schrödinger equation (TISE) for the electrons. The interatomic forces are obtained as negative gradients of PESs. Compared to force fields, this approach allows for a better description of the time evolution of molecular systems as long as nuclear and electronic motions are not strongly coupled, and quantum effects between nuclei are not very strong.

The solution of TISE is central in the field of quantum chemistry. Unfortunately, it can be solved exactly only for very small systems due to the exponential growth of Hilbert space with molecular size. Many methods have been developed to find approximate solutions to TISE that can produce highly accurate results. However, they all require encoding quantum states on a classical computer, and without additional approximations, the computational cost of simulations scales exponentially. The classical full configuration interaction (FCI) method provides the exact solution for TISE for a given basis set but is not practical due to the exponential scaling. More computationally efficient methods, such as density matrix renormalization group\(^5\) or selected configuration interaction\(^6\), allow for larger simulations with FCI quality energies\(^7\), but these methods still scale exponentially. In recent years, a new field of quantum computational chemistry emerged with the idea of representing the state of a quantum chemical system on a quantum computer.\(^8\)–\(^2\) The idea to simulate quantum physics with quantum computers was theoretically proposed by Feynman.\(^9\) Later, it was shown that the time evolution of quantum systems could be efficiently simulated on a quantum computer.\(^10\) Small scale demonstrations of such simulations
have been performed on today’s quantum computers.\textsuperscript{27,28} When an error-free quantum computer with a large number qubits is available, the quantum phase estimation (QPE) algorithm should be able to provide the exact ground state energies in polynomial time for systems too large to be simulated exactly on classical computers.\textsuperscript{29,30} However, the number of qubits available on modern quantum computers is small, which limits the size of the system that can be simulated. Additionally, due to decoherence effects, the number of gates is also limited. Thus, the application of QPE for problems intractable on classical computers is arguably years away.\textsuperscript{31} For the noisy intermediate-scale quantum (NISQ)\textsuperscript{31} hardware, one of the promising directions in quantum computational chemistry is the Variational Quantum Eigensolver (VQE) method.\textsuperscript{32,33} It is based on the Rayleigh-Ritz variational principle that is widely used in quantum chemistry calculations on classical computers. VQE helps to avoid the problem of short coherence times of qubits in the NISQ quantum hardware devices by using classical variational optimization of the quantum circuit parameters.

In the present work, a quantum computer-based \textit{ab initio} molecular dynamics method is introduced. In this method, the nuclei are propagated classically on PESs that are computed on-the-fly on a quantum computer using the VQE method. The forces for nuclear propagation are calculated numerically using the Hellmann-Feynman theorem (HFT) and correlated sampling (CS) technique, a combination that simultaneously reduces the cost by orders of magnitude while improving the accuracy of calculations. The proposed method is extensively tested on IBM quantum hardware using a model H$_2$ system. Moreover, the accuracy of the proposed gradient calculation approach is also estimated for larger molecules. This proposed method can be extended to studying materials using periodic boundary conditions,\textsuperscript{34,35} and it is potentially a subject of our future work.
The paper is organized as follows. In Section 2, the used AIMD and VQE methodologies are described. In this section, we also describe our method for the calculation of accurate numerical gradients. In Section 3, the computational details are presented. Section 4 is devoted to the discussion of the results of AIMD dynamics for H₂ molecule and testing of the methods for larger molecules. In Section 5, the conclusions are presented.

Methods

Ab Initio Molecular Dynamics

The time evolution of a quantum molecular system described by the wave function \( \Psi(r, R; t) \) is defined by TDSE:

\[
i\hbar \frac{\partial}{\partial t} \Psi(r, R, t) = H(r, R)\Psi(r, R, t)
\]

(1)

where \( H(r, R) \) is the total molecular Hamiltonian that depends on electronic coordinates \( r \) and nuclear coordinates \( R \). In the present work, a standard quantum-classical approach is employed. First, the Born-Oppenheimer approximation (BOA)\(^{36} \) is applied to separate electronic and nuclear motions. Moreover, nuclear quantum effects are neglected, and the propagation of the nuclear wave function is reduced to a classical mechanics problem. Classical trajectories (positions and momenta of the \( N \) nuclei) are propagated on electronic PESs according to the classical Hamilton’s equations:

\[
\dot{R}_I = \frac{P_I}{M_I}
\]

(2a)

\[
\dot{P}_I = F_I = -\nabla_I \left( E_0(R) + V_{NN}(R) \right)
\]

(2b)

where \( R_I, P_I, M_I \) are positions, momenta, and masses along the nuclear coordinate \( I \) respectively. The force \( F_I \) is computed as a negative gradient of the sum of the electronic ground state energy
and nuclear repulsion energy $V_{NN}(R)$. Ground state electronic energy is computed “on-the-fly” at every step quantum mechanically through the solution of electronic TISE:

\begin{align}
H_{el} \psi(r; R) &= E \psi(r; R) \\
H_{el} &= T_e + V_{ee}(r) + V_{eN}(r, R) \\
H &= H_{el} + V_{NN}(R)
\end{align}

where $H_{el}$ is the electronic Hamiltonian, $T_e$ is the kinetic energy of electrons, $V_{ee}$ is the electron repulsion energy, and $V_{eN}$ is the potential energy of the electron-nuclear interaction. In the present work, we consider only the ground state of the system, which corresponds to the smallest eigenvalue of the electronic Hamiltonian. Each eigenvalue $E$ gives rise to a PES on which the nuclei can be propagated. In general, these PESs can be coupled through nonadiabatic effects, either due to the breakdown of BOA or if the PESs are coupled through other means, for example, spin-orbit coupling. Molecular dynamics for such systems is an object of study in the field of nonadiabatic molecular dynamics.\textsuperscript{11,37–40} Recently an algorithm to simulate nonadiabatic dynamics on quantum computers was proposed.\textsuperscript{41} In this work, the couplings between PESs are neglected and the simulations are restricted to the dynamics on the ground electronic state with energy $E_0$.

From the perspective of quantum chemistry, the computational aspect of AIMD simulations narrows down to the calculation of two quantities: gradients and energies. The former are used to carry out an MD trajectory by approximately solving Eq. (2), and the latter, along with the total kinetic energy, are used to evaluate the total energy as a check on the quality of the trajectory. The details of electronic structure calculations of energy and gradients are presented in the following sections. The classical propagation of the nuclei is straightforward and requires negligible computational resources compared to the electronic structure calculations. Since the dynamics simulations are performed “on-the-fly”, we do not have access to full analytical PESs.
and Eq. (2) needs to be integrated numerically with a finite time step size. The choice of the integration method can significantly affect the number of energy and gradient calculations and accuracy. In this work, we use the Verlet algorithm in the velocity formulation.\textsuperscript{42,43} This integration method requires only a single calculation of the forces per MD time step. Moreover, the Verlet algorithm has an extremely low drift of the total classical energy over long periods of time compared to other integrators, such as Runge-Kutta.\textsuperscript{44}

Ground state energy calculation

The exact solution of Eq. (3) is generally not available, and there are many quantum chemistry methods of varying accuracy and computational cost designed for classical computers to compute electronic energies and accurate analytical gradients. In this work, energies and gradients are computed using quantum computers. Due to the limitations of NISQ\textsuperscript{31} hardware, the quantum computational chemistry field is mostly based on using the VQE method and its variations. Calculation of the ground state energy $E_0$ for a system described by electronic Hamiltonian $H_{el}$ is performed using the variational principle that is widely used in quantum chemistry. When applied in VQE, this method optimizes the quantum circuit parameters that are used for quantum state preparation on a quantum computer:

$$E_0 \leq \frac{\langle \psi(\theta)|H_{el}|\psi(\theta)\rangle}{\langle \psi(\theta)|\psi(\theta)\rangle} \quad (4)$$

where $\psi(\theta)$ is the trial wave function, and the quantity on the right of Eq. (4) is minimized iteratively with respect to the parameter(s) $\theta$. The trial state $\psi(\theta)$ is obtained from the initial state by applying a unitary operator $\psi(\theta) = U(\theta)\psi$.

To find the ground state energy of the system $E_0$, the electronic Hamiltonian is represented in the second quantized form.\textsuperscript{45}
\[ H_{el} = \sum_{p,q} h_{pq} a_p^\dagger a_q + \sum_{p,q,r,s} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s \] (5)

where \( a^\dagger \) and \( a \) are creation and annihilation operators, respectively. \( h_{pq} \) are one-electron integrals representing the kinetic energy of the electrons and their Coulomb interaction with the nuclei. \( h_{pqrs} \) are two-electron integrals representing electron-electron Coulomb repulsion. One-electron and two-electron integrals can be efficiently computed on a classical computer in any quantum chemistry package. Next, the variational form of the wave function, an ansatz, needs to be chosen. The design of ansatzes for VQE calculation is an active area of research, varying from the so-called hardware-efficient\(^{32,46}\) (HE) ansatzes that are designed to be simpler and easier to run on NISQ hardware, to chemically inspired ones such as the unitary coupled cluster (UCC).\(^{33}\) An adaptive ansatz\(^{47}\) can significantly reduce the computational cost by addition and removal of operators in the set. The UCC method was initially applied to solve problems in physics\(^{48-50}\), and with the development of NISQ quantum hardware, it was proposed for solving quantum computational chemistry problems.\(^{21,32}\) In the UCC method, the initial state is obtained from a reference Hartree-Fock state by applying the exponential unitary operator:

\[ |\psi_{UCC}\rangle = e^{\hat{T}_1} e^{\hat{T}_2} |\psi_{HF}\rangle \] (6)

where \( T \) is the excitation operator that excites electrons from the occupied orbitals \( \alpha \) in the reference configuration into virtual (unoccupied) orbitals \( i \). In the truncated version (UCCSD), which is used in present work, only single and double excitations are considered:

\[ \hat{T} = \hat{T}_1(\theta) + \hat{T}_2(\theta) = \sum_{i \in \text{virt}, \alpha \in \text{occ}} \theta_{i\alpha} a_i^\dagger a_{\alpha} + \sum_{i,j \in \text{virt}, \alpha, \beta \in \text{occ}} \theta_{ij\alpha\beta} a_i^\dagger a_j^\dagger a_{\alpha} a_{\beta} \] (7)

The UCC method is intractable on classical computers due to exponential scaling, but it can be solved in polynomial time on a quantum computer.\(^{33}\) UCC is a modification of a classical coupled cluster (CC) method, which is considered a gold standard in quantum chemistry\(^{51}\) and can be
efficiently solved on a classical computer. In the standard CC method, the wave function is obtained by using the non-unitary $e^\hat{T}$ operator $|\psi_{CC}\rangle = e^\hat{T} |\psi_H\rangle$. The UCC method retains the advantages of CC method and has an additional beneficial property of being variational, unlike the standard CC method. In addition to standard UCCSD there are modified versions of the method, such as generalized UCCGSD.$^{52}$

To simulate a chemical system in the second quantized representation, the creation and annihilation operators acting on indistinguishable fermions need to be mapped to operators acting on distinguishable qubits. The most common encoding methods are Jordan-Wigner,$^{53}$ parity,$^{54}$ and Bravyi-Kitaev$^{55}$ encoding, all of which produce Hamiltonians of the following form:

$$H = \sum_j \alpha_j P_j = \sum_j \alpha_j \prod_i \sigma_i^j$$

(8)

where $P$ are Pauli strings, $\sigma_i^j$ are Pauli matrices, and $\alpha_j$ are coefficients that depend on the values of electron integrals $h_{pq}$ and $h_{pqrs}$. Each encoding type has its own advantages. For example, parity mapping takes advantage of the system symmetry and reduces the number of qubits required for the simulation. Jordan-Wigner encoding enforces the conservation of the number of particles. Bravyi-Kitaev mapping yields logarithmically shorter circuits compared to Jordan-Wigner and parity encodings.

The methodology for calculations of molecular ground electronic state energies described above can be extended to materials by using periodic boundary conditions.$^{34,35}$ Recently an embedding approach has been proposed to simulate properties of molecules and materials using quantum hardware.$^{56}$

Gradient calculation

The schemes for calculation of the analytical gradient on quantum computers have been proposed in recent studies.$^{57,58}$ However, from the standpoint of running simulations on NISQ
hardware, such schemes require prohibitively long circuits. An extensive study regarding computation of numerical gradients on a quantum computer has been performed by O’Brien et al.\textsuperscript{59} In the present work, the gradients are computed numerically using central differences. Three approaches are considered (see Table 1). In the first brute force approach, for each of the $3N$ nuclear degrees of freedom $x$, the energies at displaced geometries $x - d$ and $x + d$ are computed using full VQE optimization, therefore increasing computational cost at least by a factor of three compared to single point energy evaluation. In the second approach, the HFT allows us to optimize the wave function only once at point $x$, and use it to calculate energy at displaced geometries $x - d$ and $x + d$:

$$F = -\frac{d}{dx} \langle \psi(x) | H | \psi(x) \rangle \approx - \left( \psi(x) \right| \frac{dH}{dx} \left| \psi(x) \right)$$

$$\approx - \frac{\langle \psi(x) | H(x + d) | \psi(x) \rangle - \langle \psi(x) | H(x - d) | \psi(x) \rangle}{2d}.$$

(9)

As a result, we need to perform only one VQE optimization per one MD time step. In HFT approach, evaluating $\langle \psi(x) | H(x + d) | \psi(x) \rangle$ and $\langle \psi(x) | H(x - d) | \psi(x) \rangle$ on a quantum device involves two measurements, i.e. two different sets of a large number of shots to evaluate the expectation values of $H(x + d)$ and $H(x - d)$. The resulting two quantities have errors due to the stochastic nature of the quantum measurements, and these errors are independent. The displacement $d$ in the denominator of Eq. (9) typically has to be a number on the order of $10^{-3}$ $a_0$ to $10^{-4}$ $a_0$ so that the finite difference approximation is sufficiently accurate. However, the smaller the $d$ value, the more the stochastic gradient error is magnified if there is some inherent error in the numerator (the sum of the errors of the two independent measurements). As a result, the stochastic gradient error can be larger than the error in the energy by orders of magnitude. Obtaining highly accurate gradients using such a scheme would require millions of shots for each
energy evaluation to reduce the gradient error to the level that would ensure classical energy conservation. Instead, we employ a third approach with HFT and correlated sampling (CS), as shown in Fig. 1. In our scheme, the HFT is utilized by using the optimized circuit parameters at point $x$, $\theta(x)$, to evaluate energy at $x - d$ and $x + d$. In addition, instead of performing independent measurements, the results of sampling the Pauli strings of qubit-mapped Hamiltonian $\sum_j \alpha_j^x P_j^x$ (see Eq. (8) at the central point $x$ are used for energy evaluation at $x - d$ and $x + d$. In other words, the same set of shots is used to evaluate the expectation values of $H(x + d)$ and $H(x - d)$. This technique works because only coefficients $\alpha$ change, Pauli strings stay the same. Thus, the only extra calculations at displaced geometries are the computations of electron integrals $h_{pq}$ and $h_{pqrs}$ on a classical computer. Apart from the obvious advantage of performing a smaller number of computations (only one full VQE cycle) on a quantum computer, our scheme has a feature that is more important for numerical gradient calculation. The energies at $x - d$ and $x + d$ are obtained from the quantum measurements at the same point. Therefore, the corresponding energy errors are correlated. As a result, a much smaller error is expected from division by a small number in Eq. (9). The differences in the three approaches described above are presented in Table 1, and the cost associated with each approach is presented in Table 2.
Table 1. Different approaches to compute electronic energies required for the evaluation of numerical gradients. Energies are computed as expectation values of the Hamiltonian mapped to qubits (Eq. (8)), Hamiltonian is represented as a sum of Pauli strings $P_j$ with weights $\alpha_j$. In the first brute force approach, energies at displaced geometries $x - d$ and $x + d$ are computed using full VQE optimization. In the second HFT approach, parameters optimized for point $x$ are used to calculate energies for $x - d$ and $x + d$, performing only a single quantum measurement for each displaced geometry. In our third HFT + CS approach, no quantum measurements are performed at displaced geometries, only $1e^-$ and $2e^-$ are recomputed at $x - d$ and $x + d$.

|     | (1) Brute force | (2) HFT | (3) HFT + CS |
|-----|-----------------|---------|--------------|
| $x - d$ | $\langle \psi(x - d) | \sum_j \alpha_j^{x-d} P_j^{x-d} | \psi(x - d) \rangle$ | $\langle \psi(x) | \sum_j \alpha_j^{x-d} P_j^{x-d} | \psi(x) \rangle$ | $\langle \psi(x) | \sum_j \alpha_j^{x-d} P_j^{x-d} | \psi(x) \rangle$ |
| $x$   | $\langle \psi(x) | \sum_j \alpha_j^x P_j^x | \psi(x) \rangle$ | $\langle \psi(x) | \sum_j \alpha_j^x P_j^x | \psi(x) \rangle$ | $\langle \psi(x) | \sum_j \alpha_j^x P_j^x | \psi(x) \rangle$ |
| $x + d$ | $\langle \psi(x + d) | \sum_j \alpha_j^{x+d} P_j^{x+d} | \psi(x + d) \rangle$ | $\langle \psi(x) | \sum_j \alpha_j^{x+d} P_j^{x+d} | \psi(x) \rangle$ | $\langle \psi(x) | \sum_j \alpha_j^{x+d} P_j^{x+d} | \psi(x) \rangle$ |

It is important to note the errors associated with HFT gradients. First, if $\psi(x)$ is an exact eigenfunction of $H$, the HFT is an exact expression for the gradient (upper Eq. (9)). For typical quantum chemistry applications, as pointed out by Pulay, when $\psi(x)$ is not an exact eigenstate, there is a contribution to the gradient that is neglected in the HFT expression owing to the quantum chemistry bases being atom-centered and thus changing with $x$. This omitted term can be large, particularly for single determinant (e.g., Hartree Fock) approximations. Bakken et al. carried out a careful analysis and showed how increasing the basis set level and degree of configuration interaction can lead to significant improvements in HFT-based gradients. In our application to $H_2$, with minimal basis but with full configuration interaction, we have verified that the HFT errors (including those associated with the finite difference approximation) are insignificant regarding the generation of trajectories that conserve energy to a good degree. In the era beyond NISQ devices, when hardware capabilities allow deeper circuits and longer coherence times, analytical gradients, which do not have the discussed error, could be used in MD simulations. However,
these errors are negligible compared to the stochastic errors associated with limited samples on quantum computers.

Table 2. The number of shots required for numerical gradient calculation using different approaches. \( N \) is the number of degrees of freedom; \( N_{\text{iter}} \) is the number of VQE iterations in one cycle; \( N_{\text{shots}} \) represents the number of shots per single Pauli string measurement.

| Position | Approach          |
|----------|-------------------|
|          | (1) Brute force   |
|          | 6\(N \times N_{\text{iter}} \times N_{\text{shots}}\) |
| x - d    | 6\(N \times N_{\text{iter}} \times N_{\text{shots}}\) |
|          | (2) HFT           |
|          | 6\(N \times N_{\text{shots}}\) |
| x        | \(N_{\text{iter}} \times N_{\text{shots}}\) |
|          | (3) HFT + CS      |
|          | \(N_{\text{iter}} \times N_{\text{shots}}\) |
| x + d    | 6\(N \times N_{\text{iter}} \times N_{\text{shots}}\) |
|          | 6\(N \times N_{\text{shots}}\) |
| Total    | \(N_{\text{iter}} \times N_{\text{shots}} \times (1 + 12N)\) |
|          | \(N_{\text{shots}} (N_{\text{iter}} + 12N)\) |
|          | \(N_{\text{iter}} \times N_{\text{shots}}\) |

Although the number of evaluations of numerical gradients grows with the system size as \(6N\), where \(N\) is the number of nuclei, our CS procedure has a very low computational overhead compared to just the energy evaluation (see Table 2). There are no extra expensive VQE optimizations, and our approach only requires a calculation of electron integrals for each displaced geometry, the cost of which is significantly lower than additional energy evaluations.

Since the \(H_2\) molecule contains only 2 electrons, single and double excitations in UCCSD ansatz cover all possible electronic excitations. Thus, UCCSD method is equivalent to FCI for the studied system and, therefore, provides the exact solution of the TISE for a given basis set. We start by running UCCSD simulations using the state vector simulator Aer in Qiskit package,\(^{63}\) which calculates the full wave function and does not involve measurements. Such simulations are good for benchmarking because there is no noise present, either stochastic, from the probabilistic nature of quantum measurements, or noise from the quantum hardware due to decoherence effects.

It has been shown by McClean \textit{et al.}\(^{33}\) and by Romero \textit{et al.}\(^{64}\) that the number of quantum measurements \(N_{\text{shots}}\) required to estimate the energy to precision \(\varepsilon\) has an upper bound of
\[ N_{\text{shots}} = \frac{\left( \sum_{i} |\alpha_{ij}| \right)^2}{\varepsilon^2} \]  

where \( \alpha_{ij} \) are the Pauli string coefficients in the Hamiltonian, and \( M \) is the number of orbitals. For the Gaussian basis orbital basis used in present work, the resulting scaling is \( O(M^6/\varepsilon^2) \). The \( M^6 \) scaling can be reduced down to \( M^3 \) by grouping the commuting terms and measuring them simultaneously.\(^{65} \) For the 1-qubit H\(_2\) system \( M = 1 \) and therefore achieving chemical accuracy of \( \sim 10^{-3} \) Ha for estimation of the energy will require at most \( 10^6 \) measurements.

| M\(_x\) | VQE loop |
|---|---|
| \( N_{\text{vec.} \text{circuit evaluations}} \) | \( \langle \psi(\theta)|H|\psi(\theta) \rangle \geq E_0 \) |
| \( h_{pq, x} \) | \( h_{pq, x} \) and \( 2e^- \) integrals |
| Measurement result | Measurement result |
| M\(_x\) | \( E_{x-d} \) | \( E_{x+d} \) |
| no circuit evaluations | no circuit evaluations |

Fig. 1. Schematic representation of correlated sampling approach for numerical gradient calculations. When computing energies at displaced geometries \( x - d \) and \( x + d \), the sampling and circuit parameters are taken from the middle geometry \( x \); only integrals \( h_{pq} \) and \( h_{pqrs} \) are calculated at displaced geometries.

There are multiple sources of error involved in the gradient calculation. First, VQE optimization might converge to a local minimum instead of the global one, which leads to variational parameters that overestimate the energy. Second, the chosen ansatz might not be able to recover all electron correlation energy and, therefore, be unable to recover the exact energy for
a given basis. To eliminate all errors not related to the gradient calculation procedure and to assess
the accuracy of the utilized gradient calculation, we use the following strategy. First, direct
diagonalization of the Hamiltonian is performed to obtain the exact wave function. Then fermionic
operators are mapped to qubit operators and the resulting Hamiltonian is of the form as in Eq. (8).
Consequently, Pauli strings of the mapped Hamiltonian are used to compute the matrix elements
\[ \langle \psi(x) | \sum_j \alpha_j^{x-d} P_j^x | \psi(x) \rangle \] and \[ \langle \psi(x) | \sum_j \alpha_j^{x+d} P_j^x | \psi(x) \rangle \]. Then, all matrix elements are sampled.
Note that Pauli strings indicated \(P_j\) are sampled at point \(x\) for all geometries \((x, x + d\) and \(x - d\).
Only the weights \(\alpha_j^{x-d}\) and \(\alpha_j^{x+d}\) vary due to different electron integrals \(h_{pq}\) and \(h_{pqrs}\) at displaced geometries. Finally, all sampled matrix elements are added up to obtain total energies at \(x - d\) and \(x + d\) to compute the gradient at \(x\).

**Computational Details**

In this study, all VQE calculations were performed using Qiskit 0.19.6 package.\(^{63}\) This package is developed by IBM and used to run calculations on IBM quantum devices or simulators. IBM quantum devices are provided by the Quantum Computing User Program located in Oak Ridge Leadership Computing Facility (OLCF).\(^{66}\) We used a slightly modified version of Qiskit, which adds the implementation of the CS technique. The optimization of variational parameters \(\theta\) in VQE was done using the COBYLA optimizer. Calculations on hardware were done on IBM 5-qubit quantum device Vigo. One- and two-electron integrals were computed using PySCF\(^{67}\) electronic structure program, which is interfaced with Qiskit. All calculations were performed using STO-3G Gaussian basis set. The Hamiltonian was mapped to qubits using parity mapping.\(^{68}\) It was previously shown\(^{69,70}\) how the number of qubits required for describing a fermionic system could be reduced by using symmetry, effectively reducing the size of Hilbert space. For example, the \(\text{H}_2\) molecule in a minimal basis set has been studied before with the number of qubits reduced to two from the standard four qubits. We use an approach developed by Bravyi \textit{et al.} to further
reduce the number qubits needed to run calculations on a quantum computer down to only one qubit.\textsuperscript{54}

**Results and Discussion**

**Accuracy of energies and gradients**

Before running the circuits on the real quantum hardware, we start with the calculations using the QASM simulator. This simulator mimics the measurement on actual quantum hardware by using a random number generator to obtain the result of measurement (0 or 1) for each qubit. QASM calculations allow us to estimate the actual stochastic error for the H\textsubscript{2} molecule. We ran VQE simulations with the number of shots ranging from 8 \times 10\textsuperscript{3} to 512 \times 10\textsuperscript{3}. The energy errors were calculated as the difference between the VQE energy and the exact energy obtained from direct Hamiltonian diagonalization. It can be seen from Fig. 2 that at least 256 \times 10\textsuperscript{3} shots are needed to keep the error in energy within the chemical accuracy range of 1.6 mHa (1 kcal/mol). For a smaller number of measurements, chemical accuracy cannot be guaranteed. The errors are expected to increase on real quantum hardware due to the device noise.

![Graph showing energy errors for H\textsubscript{2} molecule](image)

Fig. 2. Errors in the potential energy of H\textsubscript{2} molecule computed on a QASM simulator for the 1-qubit UCCSD/STO-3G circuit. Colors represent the number of shots, from 8 \times 10\textsuperscript{3} to 512 \times 10\textsuperscript{3}. Error bars correspond to one standard deviation. Black horizontal line represents the error threshold for chemical accuracy $\varepsilon = 1.6 \times 10\textsuperscript{-3}$ Ha (1 kcal/mol).
Implementation of the numerical gradients requires a careful choice of the displacement parameter $d$ in Eq. (9) because division by a number much smaller than 1 significantly amplifies the errors in energy. The errors in gradients computed with different $d$ values are presented in Fig. 3. In Fig. 3a, the black line corresponds to the gradients calculated using energies obtained from the state vector simulator, where the wave function was optimized at displaced geometries (by $d$), i.e. without application of HFT. The lines related to the state vector calculation using HFT for different $d$ values are indistinguishable from the black line. The insert in Fig. 3 shows the errors in gradients for state vector simulations. Smaller $d$ values produce more accurate gradients, but for all $d$ values in this range, the errors are on the order of $10^{-6} \text{ Ha}/a_0$, which is three orders of magnitude smaller than the errors introduced by stochastic noise in calculations using QASM simulator with $512 \times 10^3$ shots (Fig. S1a in Supplementary Information). Fig. S1a suggests that stochastic noise is significantly larger compared to the noise coming from $d$ even when CS is used. As expected, the error decreases with an increasing number of shots consistent with $1/\sqrt{N}$ estimate using Eq. (10) (see Fig. S1b).

Fig. 3. Numerical gradient for 2 qubit UCCSD circuit computed with statevector simulator for different values of displacement $d$ after application of the HFT. The black line corresponds to the calculation without the HFT application, which was used to calculate absolute errors of the gradient (colored dots in the insert).
Simulations of large molecules

The scalability of our approach to calculate gradients using HFT and CS for larger molecular systems was tested by performing gradient calculations using FCI with STO-3G basis set for the following molecules: H\(_2\), H\(_4\), LiH, BeH\(^+\). The number of qubits increases from 1-qubit H\(_2\) system up to 12-qubit BeH\(^+\) molecule. Systems with a different number of qubits for a given molecule correspond to simulations with and without symmetry application to reduce the number of qubits. In Fig. 4, we compare the number of shots per Pauli string per VQE iteration required to reach accuracy in gradients of \(\varepsilon = 1\text{mHa}/a_0\) using three different approaches: without application of HFT and CS, using HFT but without CS, and finally with HFT and CS application (see Table 1 for details). To obtain the number of shots required to achieve a certain accuracy, the errors were calculated for the number of shots ranging from 64 to \(6.5 \times 10^7\), fitted using least squares method according to the \(\varepsilon = \alpha/\sqrt{N_{\text{shots}}}\) formula. After that, the number of shots was extrapolated to achieve a required accuracy (see Fig. S4 for details). The first important conclusion from these simulations is that the application of HFT without CS does not affect the accuracy of calculated gradients for all studied molecules. However, HFT saves two VQE optimization loops for every MD step. The VQE optimization loop is the most time-consuming step in the full quantum AIMD cycle. When CS is used, the number of shots required is lower by 4 orders of magnitude across all studied molecules. The smallest number of shots required without CS is on the order of \(10^7\). This is a very large number of shots to execute on NISQ hardware. To make it worse, it is multiplied by the number of Pauli strings in the Hamiltonian, which grows with system size, and by the number of iterations in the VQE optimization. The scaling of such calculations makes it impractical even for a single point energy calculation, and it is cost-prohibitive for AIMD simulations on NISQ-era hardware.
Fig. 4. The number of shots per Pauli string required to achieve accuracy $\varepsilon = 1\text{mHa}/a_0$ for different molecules computed at $R = 4.0\ a_0$. Green color corresponds to calculations with HFT and CS. Blue represents calculations with applied HFT but without CS, while red corresponds to calculations without HFT and CS. Arrows represent error bars.

CS is a known technique that has been applied in different fields, for example, in Monte Carlo simulations. HFT is also a popular approximation that is used in various problems to reduce the cost of simulation of quantum systems. However, to the best of our knowledge, HFT and CS have not been applied together for gradient calculations. As it was shown for multiple systems in Fig. 4, this technique improves the accuracy with very low overhead, essentially providing higher accuracy at a lower cost. It is possible because the errors introduced by CS technique are negligible compared to stochastic uncertainties. On actual quantum hardware, the advantage of this technique becomes even more clear. HFT+CS technique was tested only on VQE simulations, but the
applicability of this technique is much broader. It can be applied in other algorithms; for example, the QPE algorithm, as long as the ground state wave function is available. Our HFT and CS scheme provides not only a constant, four orders of magnitude decrease in the number of shots, but also a scaling advantage, allowing quantum AIMD simulations to be scaled to a larger number of atoms. The number of derivatives needed for a number of atoms \( N \) is \( 6N \). Without CS, each of these \( 6N \) directions would need to be sampled independently, with the number of shots growing as \( 6N \cdot O(M^{6}) \) (where the \( O(M^{6}) \) comes from the number of terms in the Hamiltonian). With our CS scheme, we only need to sample at position \( x \), and then calculate the Hamiltonian at the displaced geometries in all dimensions. Since we reuse the shots from position \( x \) for all other positions, the number of shots only grows with the number of terms in the Hamiltonian, not with the number of dimensions of the gradient, leading to advantage in scaling.

**H\(_2\)** simulations on IBM Q devices

The quality of an MD trajectory for a 1D system can be represented by plotting positions vs. momenta (Fig. 5). When a molecule returns to its starting position, the trajectory is represented by the full ellipse and covers the whole configuration space. If the initial and final points coincide with each other, the total energy is conserved, and therefore accurate simulation of longer trajectories is possible. When the total energy decreases over time due to accumulated errors, the trajectory drifts from the ellipse towards the center, and two atoms collapse on each other. If the total energy increases, the ellipse spirals out, and the molecule eventually dissociates. Thus, the goal of an accurate MD scheme is to minimize the total energy drift over time.

For simulations on hardware, IBM Q Vigo was chosen due to the low readout and single-qubit errors. A single MD trajectory for \( \text{H}_2 \) molecule computed on the IBM Q Vigo machine with \( 295 \times 10^3 \) shots and measurement error mitigation, as implemented in Qiskit Ignis\(^{63}\) package, is shown in Fig. 5. Fig. 5a presents the trajectory corresponding to a complete vibration of \( \text{H}_2 \) in
phase space. The trajectory calculated on a classical computer using state vector simulator is represented by orange lines. The green line corresponds to simulations without VQE optimization where the variational parameters are preoptimized using the state vector simulator, essentially reducing the use of a quantum computer for sampling quantum circuits with optimal parameters. The blue lines correspond to the trajectory obtained using full VQE optimization at every step. The starting geometry for MD trajectory is $x = 2a_0$ and initial velocity is $v_0 = 0$. The deviation of the total energy of the trajectory obtained using state vector simulator from the ideal trajectory is minimal with a slight increase of 0.03 mHa in the region of short internuclear distances, which happens around $t = 5$ fs. However, when the molecule leaves a short internuclear distances region, the total energy goes back to the initial value. This error is attributed to the finite time step numerical integration, and the accuracy can be systematically improved by decreasing the time step. Due to the noise, stochastic and noise from the quantum device, in trajectories calculated on the quantum device (green and blue lines) the total energy value oscillates around zero with the amplitude around 6 mHa (see Fig. 5b); however, there is no drift during the simulation. The potential energy and gradient values obtained from hardware simulations oscillate around the FCI values and reproduce the exact results well (see Fig. S2). It is important to point out that the relative error of circuit parameter $\theta$ along the trajectory is much larger than the errors in energies and gradients, which can be seen in Fig. 5b. This can be explained by the fact that the parameters optimized using the noiseless state vector simulator might not correspond to the minimal energy of the system with noise on an actual quantum device. Also, the gradient of energy with respect to parameter $\theta$ is small, i.e. the deviation of $\theta$ from optimal values does not translate into energy deviations comparable with hardware noise error.
Fig. 5. A single loop MD trajectory for a 1-qubit H$_2$ system computed using UCCSD ansatz. The orange line corresponds to the state vector simulation: a) position vs. velocity, b) total energy vs. time, c) parameter $\theta$ vs. time. Blue lines represent the simulation on IBM Q Vigo machine using $295 \times 10^3$ shots with measurement error mitigation. Green lines correspond to simulations on IBM Q Vigo machine where parameters were optimized using statevector simulator, and sampling was done using $295 \times 10^3$ shots with measurement error mitigation.
In addition to the 1-qubit $\text{H}_2$ system, we performed simulations on a 2-qubit system with 1 parameter $\theta$ on IBM Q Vigo machine. The 2-qubit system does not produce more accurate results compared to a 1-qubit system, even if the hardware error rate was much lower, because the symmetry reduction used to obtain a 1-qubit system does not affect accuracy. However, we provide results for a 2-qubit system to estimate how feasible MD simulations are for non-trivial circuits.

From Fig. 6b, it can be seen that the conservation of energy for 2-qubit systems is significantly worse than for 1-qubit system. However, in the 2-qubit system trajectory, the potential energy is significantly overestimated, and the deviation from FCI energy is relatively constant over all internuclear distances. This potential energy shift in the 2-qubit system is easily explained by the hardware noise from four CNOT gates, which are not present in the 1-qubit system; each of CNOT gates has an error rate on the order of 1%. This noise can be mitigated using various techniques, for example, zero-noise extrapolation,$^{72-74}$ symmetry verification$^{75}$, or reduced density matrix purification.$^{76}$ However, such simulations on modern NISQ hardware for the whole MD trajectory would be prohibitively time-consuming.

![Diagram](image-url)
Fig. 6. A single loop MD trajectory for a H₂ system computed using UCCSD ansatz on IBMQ Vigo machine using $295 \times 10^3$ shots with measurement error mitigation: a) position vs. velocity, b) total energy vs. time, c) potential energy vs. time. The orange line corresponds to the state vector simulation (solutions for 2-qubit and 1-qubit systems match). Red and green lines represent the hardware simulations of the 2-qubit and 1-qubit systems, respectively. Parameters used in simulations on hardware were optimized with state vector simulation, VQE optimization was not performed.

Conclusions

We presented a quantum computer-based AIMD method suitable for NISQ-era quantum hardware, which relies on the VQE method for the calculation of ground-state electronic energies. The energy gradients were computed using HFT and CS approaches. Using HFT in combination with CS drastically improves the accuracy of the numerical gradient. To achieve the same level of accuracy as the standard approach without HFT and CS, our method with HFT and CS requires
four orders of magnitude less quantum measurements. Moreover, it scales extremely well with the increasing degrees of freedom number since it only requires extra electron integrals computation instead of linearly increasing the number of full energy evaluations. Based on simulations for the set of different molecules considered in this paper, we conclude that HFT does not affect the gradient accuracy but significantly lowers the computational cost.

As a proof of concept, the AIMD simulations for the H$_2$ test system were performed on IBM quantum hardware using 1-qubit and 2-qubit circuits. Although the total classical energy fluctuates by several mHa over the course of simulations, there is no total energy drift overall, and trajectories return to the initial positions. This might not be the case for longer trajectories, but quantum hardware with lower error rates in the future would improve the quality of energies and gradients, and therefore provide more accurate trajectories. As expected, the simulations based on 2-qubit circuits provide trajectories of inferior quality and show that additional error mitigation is required to simulate AIMD of larger systems on modern NISQ quantum hardware. We also demonstrated that the technique for numerical gradient computation using HFT and CS could be applied to larger molecules, and it does not require any additional calculations on a quantum computer.

To the best of our knowledge, this work is the first successful attempt to run AIMD on quantum devices. Although our example of vibrational motion in H$_2$ is elementary, it demonstrates that AIMD simulations on NISQ quantum hardware are possible. Our work paves the way for new opportunities for simulating molecular and materials dynamics problems intractable on classical computers as the size and fidelity of quantum computers improve in the future. In particular, our work can be extended to studying materials using periodic boundary conditions, and it is potentially a subject of our future work. While we employed the VQE method as the basis for our
energy and gradient evaluations, the CS approach introduced for the gradient procedure could be used with other quantum algorithms, e.g., the more accurate/scalable QPE method, as long as the electronic wave function is available.

Data Availability
Data that support the findings of this study are available upon request.

Code Availability
Modified version of Qiskit package is available upon request.

References
1. Meyer, H.-D., Manthe, U. & Cederbaum, L. S. The multi-configurational time-dependent Hartree approach. *Chem. Phys. Lett.* **165**, 73–78 (1990).
2. Adcock, S. A. & McCammon, J. A. Molecular Dynamics: Survey of Methods for Simulating the Activity of Proteins. *Chem. Rev.* **106**, 1589–1615 (2006).
3. Mackerell, A. D. Empirical force fields for biological macromolecules: Overview and issues. *J. Comput. Chem.* **25**, 1584–1604 (2004).
4. Chmiela, S. *et al.* Machine learning of accurate energy-conserving molecular force fields. *Sci. Adv.* **3**, e1603015 (2017).
5. Marx, D. & Hutter, J. *Ab Initio Molecular Dynamics.* (Cambridge University Press, 2009). doi:10.1017/CBO9780511609633.
6. Tuckerman, M. E. Ab initio molecular dynamics: basic concepts, current trends and novel applications. *J. Phys. Condens. Matter* **14**, R1297–R1355 (2002).
7. Paquet, E. & Viktor, H. L. Computational Methods for Ab Initio Molecular Dynamics. *Adv. Chem.* **2018**, 1–14 (2018).
8. Carloni, P., Rothlisberger, U. & Parrinello, M. The Role and Perspective of Ab Initio Molecular Dynamics in the Study of Biological Systems. *Acc. Chem. Res.* **35**, 455–464 (2002).
9. Iftimie, R., Minary, P. & Tuckerman, M. E. Ab initio molecular dynamics: Concepts, recent developments, and future trends. *Proc. Natl. Acad. Sci.* **102**, 6654–6659 (2005).
10. He, X., Zhu, Y., Epstein, A. & Mo, Y. Statistical variances of diffusional properties from ab initio molecular dynamics simulations. *npj Comput. Mater.* **4**, 18 (2018).
11. Tully, J. C. Perspective: Nonadiabatic dynamics theory. *J. Chem. Phys.* **137**, 22A301 (2012).
12. Mosconi, E., Azpiroz, J. M. & De Angelis, F. Ab Initio Molecular Dynamics Simulations of Methylammonium Lead Iodide Perovskite Degradation by Water. *Chem. Mater.* **27**, 4885–4892 (2015).
13. Zhang, C., Wu, J., Galli, G. & Gygi, F. Structural and Vibrational Properties of Liquid Water from van der Waals Density Functionals. *J. Chem. Theory Comput.* **7**, 3054–3061 (2011).
14. Johari, P., Qi, Y. & Shenoy, V. B. The Mixing Mechanism during Lithiation of Si Negative Electrode in Li-Ion Batteries: An Ab Initio Molecular Dynamics Study. *Nano Lett.* **11**, 5494–5500 (2011).
15. Chan, G. K.-L. & Sharma, S. The Density Matrix Renormalization Group in Quantum Chemistry. *Annu. Rev. Phys. Chem.* **62**, 465–481 (2011).
16. Li, J. *et al.* Accurate many-body electronic structure near the basis set limit: Application to the chromium dimer. *Phys. Rev. Res.* **2**, 012015 (2020).
17. Li, J., Otten, M., Holmes, A. A., Sharma, S. & Umrigar, C. J. Fast semistochastic heat-bath configuration interaction. *J. Chem. Phys.* **149**, 214110 (2018).
18. Kassal, I., Whitfield, J. D., Perdomo-Ortiz, A., Yung, M.-H. & Aspuru-Guzik, A. Simulating Chemistry Using Quantum Computers. *Annu. Rev. Phys. Chem.* **62**, 185–207 (2011).
19. Lu, D. *et al.* Quantum chemistry simulation on quantum computers: theories and experiments. *Phys. Chem. Chem. Phys.* **14**, 9411 (2012).
20. Quantum Information and Computation for Chemistry. (John Wiley & Sons, Inc., 2014). doi:10.1002/9781118742631.
21. Yung, M.-H. *et al.* From transistor to trapped-ion computers for quantum chemistry. *Sci. Rep.* **4**, 3589 (2015).
22. Cao, Y. *et al.* Quantum Chemistry in the Age of Quantum Computing. *Chem. Rev.* **119**, 10856–10915 (2019).
23. McArdle, S., Endo, S., Aspuru-Guzik, A., Benjamin, S. C. & Yuan, X. Quantum computational chemistry. *Rev. Mod. Phys.* **92**, 015003 (2020).
24. Bauer, B., Bravyi, S., Motta, M. & Chan, G. K.-L. Quantum algorithms for quantum chemistry and quantum materials science. Preprint at arXiv:2001.03685v2 (2020).
25. Feynman, R. P. Simulating Physics with Computers. *Int. J. Theor. Phys.* **21**, 467–488 (1982).
26. Lloyd, S. Universal Quantum Simulators. *Science* **273**, 1073–1078 (1996).
27. Chiesa, A. *et al.* Quantum hardware simulating four-dimensional inelastic neutron scattering. *Nat. Phys.* **15**, 455–459 (2019).
28. Otten, M., Cortes, C. L. & Gray, S. K. Noise-Resilient Quantum Dynamics Using Symmetry-Preserving Ansatzes. Preprint at arXiv:1910.06284 (2019).
29. Abrams, D. S. & Lloyd, S. Simulation of Many-Body Fermi Systems on a Universal Quantum Computer. *Phys. Rev. Lett.* **79**, 2586–2589 (1997).
30. Abrams, D. S. & Lloyd, S. Quantum Algorithm Providing Exponential Speed Increase for Finding Eigenvalues and Eigenvectors. *Phys. Rev. Lett.* **83**, 5162–5165 (1999).
31. Preskill, J. Quantum Computing in the NISQ era and beyond. *Quantum* **2**, 79 (2018).
32. Peruzzo, A. *et al.* A variational eigenvalue solver on a photonic quantum processor. *Nat. Commun.* **5**, 4213 (2014).
33. McClean, J. R., Romero, J., Babbush, R. & Aspuru-Guzik, A. The theory of variational hybrid quantum-classical algorithms. *New J. Phys.* **18**, 023023 (2016).
34. McClain, J., Sun, Q., Chan, G. K.-L. & Berkelbach, T. C. Gaussian-Based Coupled-Cluster Theory for the Ground-State and Band Structure of Solids. *J. Chem. Theory Comput.* **13**, 1209–1218 (2017).
35. Sun, Q., Berkelbach, T. C., McClain, J. D. & Chan, G. K.-L. Gaussian and plane-wave mixed density fitting for periodic systems. *J. Chem. Phys.* **147**, 164119 (2017).
36. Born, M. & Oppenheimer, R. Zur Quantentheorie der Molekeln. *Ann. Phys.* **389**, 457–484 (1927).
37. Curchod, B. F. E. & Martinez, T. J. Ab Initio Nonadiabatic Quantum Molecular Dynamics. *Chem. Rev.* **118**, 3305–3336 (2018).
38. Fedorov, D. A., Pruitt, S. R., Keipert, K., Gordon, M. S. & Varganov, S. A. Ab Initio Multiple Spawning Method for Intersystem Crossing Dynamics: Spin-Forbidden Transitions between $^3\text{B}_1$ and $^1\text{A}_1$ States of GeH$_2$. *J. Phys. Chem. A* **120**, 2911–2919 (2016).
39. Fedorov, D. A., Seritan, S., Fales, B. S., Martínez, T. J. & Levine, B. G. PySpawn: Software for Nonadiabatic Quantum Molecular Dynamics. *J. Chem. Theory Comput.* acs.jctc.0c00575 (2020) doi:10.1021/acs.jctc.0c00575.
40. Fedorov, D. A. & Levine, B. G. Nonadiabatic Quantum Molecular Dynamics in Dense Manifolds of Electronic States. *J. Phys. Chem. Lett.* **10**, 4542–4548 (2019).
41. Ollitrault, P. J., Mazzola, G. & Tavernelli, I. Non-adiabatic molecular quantum dynamics with quantum computers. Preprint at arXiv:2006.09405 (2020).
42. Verlet, L. Computer ‘Experiments’ on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Phys. Rev.* **159**, 98–103 (1967).
43. Swope, W. C., Andersen, H. C., Berens, P. H. & Wilson, K. R. A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters. *J. Chem. Phys.* **76**, 637–649 (1982).
44. Faou, E., Hairer, E. & Pham, T.-L. Energy Conservation with Non-Symplectic Methods: Examples and Counter-Examples. *BIT Numer. Math.* **44**, 699–709 (2004).
45. Szabo, A. & Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. (Dover Publications, 2012).
46. Kandala, A. *et al.* Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets. *Nature* **549**, 242–246 (2017).
47. Grimsley, H. R., Economou, S. E., Barnes, E. & Mayhall, N. J. An adaptive variational algorithm for exact molecular simulations on a quantum computer. *Nat. Commun.* **10**, 3007 (2019).
48. Bartlett, R. J., Kucharski, S. A. & Noga, J. Alternative coupled-cluster ansätze II. The unitary coupled-cluster method. *Chem. Phys. Lett.* **155**, 133–140 (1989).
49. Hoffmann, M. R. & Simons, J. A unitary multiconfigurational coupled-cluster method: Theory and applications. *J. Chem. Phys.* **88**, 993–1002 (1988).
50. Taube, A. G. & Bartlett, R. J. New perspectives on unitary coupled-cluster theory. *Int. J. Quantum Chem.* **106**, 3393–3401 (2006).
51. Purvis, G. D. & Bartlett, R. J. A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. *J. Chem. Phys.* **76**, 1910–1918 (1982).
52. Lee, J., Huggins, W. J., Head-Gordon, M. & Whaley, K. B. Generalized Unitary Coupled Cluster Wave functions for Quantum Computation. *J. Chem. Theory Comput.* **15**, 311–324 (2019).
53. Jordan, P. & Wigner, E. Über das Paulische Äquivalenzverbot. *Zeitschrift für Physik.* **47**, 631–651 (1928).
54. Bravyi, S., Gambetta, J. M., Mezzacapo, A. & Temme, K. Tapering off qubits to simulate fermionic Hamiltonians. Preprint at arXiv:1701.08213 (2017).
55. Bravyi, S. B. & Kitaev, A. Y. Fermionic Quantum Computation. *Ann. Phys. (N. Y.)* **298**, 210–226 (2002).
56. Ma, H., Govoni, M. & Galli, G. Quantum simulations of materials on near-term quantum computers. *npj Comput. Mater.* **6**, 85 (2020).
57. Parrish, R. M., Hohenstein, E. G., McMahon, P. L. & Martinez, T. J. Hybrid Quantum/Classical Derivative Theory: Analytical Gradients and Excited-State Dynamics
for the Multistate Contracted Variational Quantum Eigensolver. Preprint at arXiv:1906.08728 (2019).

58. Mitarai, K., Nakagawa, Y. O. & Mizukami, W. Theory of analytical energy derivatives for the variational quantum eigensolver. Phys. Rev. Res. 2, 013129 (2020).

59. O’Brien, T. E. et al. Calculating energy derivatives for quantum chemistry on a quantum computer. npj Quantum Inf. 5, 113 (2019).

60. Pulay, P. Ab initio calculation of force constants and equilibrium geometries in polyatomic molecules. Mol. Phys. 17, 197–204 (1969).

61. Pulay, P. Analytical derivatives, forces, force constants, molecular geometries, and related response properties in electronic structure theory. Wiley Interdiscip. Rev. Comput. Mol. Sci. 4, 169–181 (2014).

62. Bakken, V., Helgaker, T., Klopper, W. & Ruud, K. The calculation of molecular geometrical properties in the Hellmann—Feynman approximation. Mol. Phys. 96, 653–671 (1999).

63. Abraham, H. et al. Qiskit: An Open-source Framework for Quantum Computing. (2019) doi:10.5281/zenodo.2562110.

64. Romero, J. et al. Strategies for quantum computing molecular energies using the unitary coupled cluster ansatz. Quantum Sci. Technol. 4, 014008 (2018).

65. Gokhale, P. et al. Minimizing State Preparations in Variational Quantum Eigensolver by Partitioning into Commuting Families. Preprint at arXiv:1907.13623 (2019).

66. Oak Ridge Leadership Computing Facility: Quantum Computing. https://www.olcf.ornl.gov/tag/quantum-computing/.

67. Sun, Q. et al. PySCF: the Python-based simulations of chemistry framework. WIREs Comput. Mol. Sci. 8, (2018).

68. Seeley, J. T., Richard, M. J. & Love, P. J. The Bravyi-Kitaev transformation for quantum computation of electronic structure. J. Chem. Phys. 137, 224109 (2012).

69. O’Malley, P. J. J. et al. Scalable Quantum Simulation of Molecular Energies. Phys. Rev. X 6, 031007 (2016).

70. Moll, N., Fuhrer, A., Staar, P. & Tavernelli, I. Optimizing qubit resources for quantum chemistry simulations in second quantization on a quantum computer. J. Phys. A Math. Theor. 49, 295301 (2016).

71. Filippi, C. & Umrigar, C. J. Correlated sampling in quantum Monte Carlo: A route to forces. Phys. Rev. B 61, R16291–R16294 (2000).

72. Li, Y. & Benjamin, S. C. Efficient Variational Quantum Simulator Incorporating Active Error Minimization. Phys. Rev. X 7, 021050 (2017).

73. Otten, M. & Gray, S. K. Accounting for errors in quantum algorithms via individual error reduction. npj Quantum Inf. 5, 11 (2019).

74. Otten, M. & Gray, S. K. Recovering noise-free quantum observables. Phys. Rev. A 99, 012338 (2019).

75. Bonet-Monroig, X., Sagastizabal, R., Singh, M. & O’Brien, T. E. Low-cost error mitigation by symmetry verification. Phys. Rev. A 98, 062339 (2018).

76. Truflandier, L. A., Dianzinga, R. M. & Bowler, D. R. Communication: Generalized canonical purification for density matrix minimization. J. Chem. Phys. 144, 091102 (2016).
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Author Contributions
D.A.F., M.J.O., S.K.G. and Y.A. designed the research. D.A.F. wrote the code, performed simulations on simulator and hardware and analyzed the results. All authors wrote the manuscript.

Competing Interests
The authors declare no competing interests

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Ab Initio Molecular Dynamics on Quantum Computers
Supplemental Information

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Figure S1. a) RMS gradient errors over $R = 0.8 \ a_0$ through $R = 7.0 \ a_0$ for 2-qubit UCCSD circuit computed for different $d$ values using QASM simulator with $512 \times 10^3$ shots. b) RMS gradient error computed over distances from 0.8 to 7.0 $a_0$ and displacement $d = 10^{-2} \ a_0$ for number of measurements ranging from $8 \times 10^3$ to $512 \times 10^3$. 
Figure S2. Potential energies (a) and gradients (b) of MD trajectory for a 1-qubit H$_2$ system computed using UCCSD ansatz. Orange line corresponds to the statevector simulation. Blue lines represent the full VQE simulation on IBMQ Vigo machine using $295 \times 10^3$ shots with measurement error mitigation. Green lines correspond to simulations on IBMQ Vigo machine simulation where parameters were optimized using state vector simulator and sampling was done using 294,912 shots with measurement error mitigation.
Figure S3. Gradients for a single loop MD trajectory for a H$_2$ system computed using UCCSD ansatz on IBMQ Vigo machine using $295 \times 10^3$ shots with measurement error mitigation: a) forces vs. time, b) variational parameter $\theta$ vs. time. Orange line correspond to the state vector simulation. Red and green lines represent the simulation of the 2-qubit and 1-qubit systems respectively. Parameters used in simulations on hardware were optimized with state vector simulation, VQE optimization was not performed.
Figure S4. Gradient error for 8-qubit LiH system computed with different number of shots using three approaches: green circles represent the errors computed with HFT+CS approach, red circles represent HFT errors, and blue circles represent brute force approach. The lines of corresponding colors are obtained by fitting the errors using $\varepsilon = a/\sqrt{N_{\text{shots}}}$ law.