Chapter 1

Introduction

1.1 *Quantum practicality*

The original concept of quantum computing traces its roots back to the 1980s when the legendary physicist, Richard P. Feynman [1, 2] and the Russian mathematician Yuri Manin [3] independently envisioned the idea of harnessing quantum mechanical systems for computational purposes. This revolutionary notion was spurred by the realization that solving the many-body Schrödinger equation for systems exhibiting strong correlation effects posed significant challenges [4] for classical computers. These problems arise from the exponential growth of the Hilbert space dimension of a quantum mechanical system with respect to the number of particles in this system; this requires exponential resources (space or time) for exact simulations as the size of the system increases. Consequently, classical computers face great difficulty in simulating general quantum systems, such as computing the ground state—also known as the eigenstate corresponding to the lowest en-

ergy/eigenvalue—which is a notoriously NP-complete problem [5]. However, not all quantum mechanical systems are equally demanding to simulate. This fact lays the physical foundation for the development of quantum computers. Quantum mechanical systems that are easily controllable and possess computable exact solutions or approximate solutions with arbitrary tight error bound, can be leveraged to perform the computation or the simulation of complex quantum systems that are otherwise intractable [6, 7].

With decades of groundbreaking advancements throughout the full quantum hardware/software stack, the applications of quantum computing have extended well beyond its initial purpose as a quantum simulator for other quantum systems. The vast potential of quantum computers is unlocked through the construction of full-stack quantum computer systems and the exploration of meaningful applications [8]. A wide range of complex problems of academic and/or commercial interest have been suggested to potentially benefit from *quantum speedup* (the time scaling for a quantum algorithm grows more slowly with the size of the problem than its classical counterpart), including cryptanalysis, chemistry, materials science, optimization, big data processing, machine learning, database search, drug design, protein folding, fluid dynamics, weather prediction, etc. However, not all applications can achieve a practical quantum advantage (***quantum practicality***) in practice even on a futuristic fault-tolerant quantum device.

In a recent commentary, researchers at Microsoft have suggested multiple guidelines for achieving ***quantum practicality*** and identified problems with realistic quantum speedup from many proposed applications [9]. The first consideration, the *I/O bottleneck* of quantum computers when accessing large

amounts of classical data, ruled out problems that relied on broad bandwidths of data input and output. Typical problems include database search and unstructured linear algebra systems [10]. The second criterion, *crossover time*, must be short enough to have the runtime advantage of quantum computers. The analysis shows that quantum algorithms that only promise quadratic quantum speedups (those based on Grover's search algorithm [11, 12]) are unlikely to show a practical advantage, which requires at least cubic or quartic speedups [13]. This guideline further eliminates several applications, including the utilization of quantum random walks for accelerating Monte Carlo simulations, employing Grover's algorithm-based optimization and machine learning algorithms to enhance protein structure prediction and drug discovery [14].

One particularly promising domain for achieving **quantum practicality** is the quantum simulation of quantum problems in chemistry and materials science. These are small-data problems that exhibit exponential quantum speedup. History goes back to the original proposal of quantum advantage. By simulating quantum chemical problems on quantum computers, significant advancements can be made in areas such as the design of new catalysts which enable more efficient nitrogen fixation or CO_2 reduction [15]. These breakthroughs have the potential to revolutionize the field and pave the way for new strategies and technologies with far-reaching implications.

1.2   Models of quantum simulation

There are two distinct models for quantum simulations [16]. Feynman's initial proposal of a quantum mechanical computer aligns more with **analog quantum simulation**, where the dynamics of a controlleable quantum simulator emulates the dynamics of a model quantum system that we are interested in. For instance, ultracold atoms can be manipulated to simulate electron dynamics by adjusting the interactions between these atoms via adjusting laser light, switching external electric and magnetic fields [17]. Analog simulators are typically regarded as more resilient to noise, making them easier to construct [6, 18].

Various physical implementations of analog quantum simulations have been successfully demonstrated for practical chemical applications. For example, simulators based on ultracold atoms and semiconductor quantum dots are utilized to simulate simple chemical reactions [19, 20]. Photonic analog simulators are applied to investigate molecular vibronic spectroscopy[21, 22, 23, 24] and to examine the time dynamics of vibrational excitations [25]. Trapped ion devices are employed to emulate both molecular vibronic spectra [26] and the many-body electron-electron Coulomb interaction of an electron gas [27]. Spin-lattice simulators are used to solve quantum chemical nuclear dynamics [28]. Superconducting simulators show the capability to generate generating molecular spectra for both equilibrium and non-equilibrium states of diatomic molecules [29]. These sophisticated analog quantum simulations achieved in condensed matter physics [30, 31, 32] and molecular quantum chemistry [17, 33] may

already exceed the capabilities of classical simulations.

However, analog quantum simulators always suffer from imperfect control, as the actual quantum system in the laboratory only provides a rough approximation of the specific quantum system of interest, no matter how precise the manipulations are. There is no systematic way to mitigate or correct such errors in large analog simulations. In another aspect, analog simulation is highly domain-specific, requiring distinct programs for various systems of interest. In this model, computations are articulated through technical protocols of experimental operations conducted at the hardware level, as opposed to an abstract algorithmic procedure commonly employed in classical computations.

In contrast, the more flexible **digital quantum simulation** is based on general-purpose (universal) circuit-based quantum computers that are capable of simulating any desired real system through appropriate programming, while also serving various other purposes. Digital quantum simulation maps the target problem onto a set of gates that can be executed on a quantum computer. Though digital quantum simulations are more sensitive to noise and device imperfections than analog simulations, systematic protocols have been established for error correction [34, 35] and error mitigation [36, **?**, 37].

Under the framework of universal quantum computers, computations in quantum chemical simulation utilize the same language as those for solving algebraic problems [38]. Layers of abstraction similar to classical digital computers make the evaluation of quantum algorithms more straightforward.

In the subsequent sections of this dissertation, we will focus exclusively on the digital quantum simulation of chemistry problems.

1.3   Problems in quantum chemistry

1.3.1   Electronic structure problem

The fundamental problem in molecular quantum chemistry is to solve the time-independent, non-relativistic electronic Schrödinger equation under the Born-Oppenheimer approximation

$$\hat{H}_{\text{elec}}(\mathbf{R}, \mathbf{r})\psi(\mathbf{R}, \mathbf{r}) = E_{\text{elec}}(\mathbf{R})\psi(\mathbf{R}, \mathbf{r}) \tag{1.1}$$

where we define the collective electronic $\mathbf{r} = \{\vec{r}_i\}$ and nuclear $\mathbf{R} = \{\vec{R}_A\}$ degrees of freedom, and the electronic Hamiltonian (in atomic units) is given by

$$\hat{H}_{\text{elec}} = -\frac{1}{2}\sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e}\sum_A^{N_{\text{nuc}}} \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \frac{1}{2}\sum_{i \neq j}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_j|} \tag{1.2}$$

where N_e and N_{nuc} are the number of electrons and nuclei in the system, $\vec{r}_i$ and $\vec{R}_A$ are the position of electron i, atomic nucleus A, and Z_A represents the charge of nucleus A.

Solving the electronic Schrödinger equation provides the electronic wavefunction and the corresponding energy levels, which yield valuable information about the electronic structure and the molecular properties. From a mathematical standpoint, the problem is to solve a coupled set of partial differential equations. To tackle this, the main numerical tool is to introduce a basis set, which encompasses a set of independent functions. These functions are utilized to expand the abstract wavefunction vectors either in position space when Gaussian functions are employed or in momentum space when plane

wave functions are used [39]. In this way, the electronic Hamiltonian is expressed as a Hermitian matrix. Resolving the eigenvalue problem associated with this matrix yields the electronic energy spectrum of the molecule.

For the scope of this dissertation, we work with the electronic Hamiltonian in the second-quantized formalism

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} \langle pq \| rs \rangle \, \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \tag{1.3}$$

where h_{pq} are the one-electron integrals and $\langle pq \| rs \rangle$ two-electron integrals, $\hat{a}^\dagger$ and $\hat{a}$ are creation and annihilation operators, respectively. The first term represents the kinetic and potential energy of the electrons in the presence of the molecular field, and the second term accounts for the electron-electron repulsion.

Slater determinants To solve the electronic Schrödinger equation for many-electron systems, the Slater determinant basis is a commonly used mathematical construct. It is particularly well-suited for describing the electronic wavefunction, because it enforces the correct fermionic symmetry by ensuring that the wavefunction remains antisymmetric under electron exchange.

The electronic wavefunction of a system with N electrons can be written as a product of one-electron wavefunctions, also known as molecular orbitals (MOs) or spin orbitals (SOs) when spin part is included. The Slater determinant is constructed by antisymmetrizing the product of spin orbitals, ensuring that the resulting wavefunction is antisymmetric with respect to the exchange of any two electrons. This antisymmetry is a direct consequence of the Pauli

exclusion principle and accurately reflects the quantum nature of electrons. The Slater determinant (electronic configuration) for an N-electron in M-spin-orbital system is given by:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \ldots & \phi_M(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \ldots & \phi_M(\mathbf{r}_2) \\ \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \ldots & \phi_M(\mathbf{r}_N) \end{vmatrix} \tag{1.4}$$

where $\mathbf{r}_i)$ represents the position of the i-th electron, and $\phi_i(\mathbf{r}_j)$ represents the i-th spin orbital evaluated at the position of the j-th electron. In the second-quantized formalism, we write each Slater determinant in a compact occupation number representation given by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = |f_M, \ldots, f_i, \ldots, f_1\rangle \tag{1.5}$$

where $f_i = 1$ if ϕ_i is occupied and $f_i = 0$ when ϕ_i is unoccupied.

Hartree-Fock method There is a full hierarchy of approximative numerical methods for solving the electronic Schrödinger equation with increasing accuracy and cost. The simplest approach, Hartree-Fock (HF) method, provides a way to obtain the most accurate single Slater determinant approximation for the system [40]. It is also known as the mean-field approach, since in Hartree-Fock theory the electrons are treated as if they were moving independently in an effective field created by the other electrons and the atomic nuclei.

We start by assuming a set of molecular orbitals (MOs), which are typically expanded as a linear combination of atomic orbitals (AOs) from the

constituent atoms

$$\psi_i = \sum_{\mu}^{\text{AO}} \chi_\mu C_{\mu i} \tag{1.6}$$

where ψ_i is the i-th molecular orbital, χ_μ is the μ-th atomic orbital and $C_{\mu i} = \langle \chi_\mu | \psi_i \rangle$ represents the expansion coefficients. The molecular orbitals are enforced to be orthonormal that satisfy the condition $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. The goal of Hartree-Fock theory is to determine the best set of expansion coefficients $C_{\mu i}$ that minimize the energy. This is done by solving a set of self-consistent field equations, which are derived by minimizing the electronic energy under the orthonormality constraint of the molecular orbitals based on the variational principle [41]. The Hartree-Fock equations can be written as:

$$\hat{F}\psi_i = \epsilon_i \psi_i \tag{1.7}$$

where the Fock operator is given by

$$\hat{F} = \hat{H}^{\text{core}} + \hat{J} - \hat{K} \tag{1.8}$$

Here, $\hat{H}^{\text{core}}$ is the one-electron term that describes the motion of electrons in the field of the atomic nuclei, $\hat{J}$ is the Coulomb operator that represents the classical electron-electron repulsion, and $\hat{K}$ is the exchange operator that accounts for the exchange correlation effect.

The Hartree-Fock equations in a finite computational basis (AO basis) $\{\chi_\mu\}$ are called Roothan equations [42] given by

$$\mathbf{FC} = \mathbf{SCE} \tag{1.9}$$

where $\mathbf{S}$ is the overlap matrix of atomic orbitals, E is a diagonal matrix containing the molecular orbital energies. Due to the presence of $\mathbf{S}$, this generalized eigenvalue problem is solved iteratively until the electronic energy and the density converge.

We refer to the set of molecular orbitals obtained from Hartree-Fock equations as the canonical orbitals. The set of canonical molecular orbitals is usually a good starting point for more advanced post-Hartree-Fock electronic structure methods.

Electron correlation One of the main issues with Hartree-Fock calculations is the neglect of electron correlation effects beyond the mean-field approximation. Electron correlation comes from the repulsion and attraction between electrons in a system. The correlation effects that cannot be adequately captured by the Hartree-Fock (single-determinant) approximation are by convention classified into two types:

- Dynamic correlation refers to the rapid, non-local fluctuations of electron positions due to their mutual repulsion. These fluctuations occur on a very short timescale and involve the exchange of electrons between different regions of space. Dynamic correlation effects are particularly important in transition metal complexes or molecules with highly delocalized electrons [43].

- Static correlation arises from the possibility of multiple Slater determinants (electronic configurations) with similar energies. In molecules with near-degenerate electronic states, the wavefunction cannot be accurately described by a single determinant. This is often the case in

molecules undergoing bond breaking or in photochemical processes that involve electronic excited states [44]. Static correlation effects require a proper treatment of the wavefunction to capture the mixing of multiple determinants.

The Full Configuration Interaction (FCI) gives the exact solution to the electronic Schrödinger equation within a given finite basis set. FCI includes all possible determinants, allowing for a complete treatment of electron correlation

$$\Psi_{\mathrm{FCI}} = \sum_I C_I \Psi_I \tag{1.10}$$

However, the number of determinants in the FCI space grows exponentially with the number of electrons N_e and the number of correlated spin orbitals M, making FCI computationally intractable for larger systems.

As a result, approximations and truncations are often employed to balance accuracy and computational cost. Various truncated CI methods and truncated coupled-cluster methods are commonly used approaches that include a subset of determinants based on excitation level. In practice, these methods usually truncated at double excitation level from the Hartree-Fock determinant [40, 41].

1.3.2   Quantum dynamics

The electronic energy spectra and wave functions obtained from Eqn. 1.1 describe stationary states of the system. Many complex processes in nature happen at finite temperature, which requires the time dynamics of the system. Dynamical properties are encoded in the time-dependent Schrödinger equa-

tion

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \hat{H}\Psi(\mathbf{r}, t). \tag{1.11}$$

When the Hamiltonian is time-independent, which is usually the case for a large class of dynamical processes that chemists are interested in, the time-evolved state can be written as

$$\Psi(\mathbf{r}, t) = e^{-i\hat{H}t}\Psi(\mathbf{r}, 0). \tag{1.12}$$

Expanding $\Psi(\mathbf{r}, 0)$ in the eigenstate basis $\{\varphi_J(\mathbf{r})\}$ of the time-independent Hamiltonian yields

$$\Psi(\mathbf{r}, t) = \sum_J C_J e^{-iE_J t}\varphi_J(\mathbf{r}) \tag{1.13}$$

where $C_J = \langle\varphi_J(\mathbf{r})|\Psi(\mathbf{r}, 0)\rangle$ is the expansion coefficient, and E_J is the energy of eigenstate $\varphi_J(\mathbf{r})$.

Eqn. 1.13 reveals that dynamic problems are considerably more complex than static problems. This complexity arises from the requirement of knowing the complete spectrum of the Hamiltonian, as well as the expansion coefficient of each eigenvector in the initial state, to execute the exact time evolution of the system. Such an exact solution is only possible for systems with very few electrons. Consequently, quantum dynamics for medium- to large-sized molecules becomes a class of problems that cannot be effectively solved using classical computers.

1.3.3 Computational complexity

Quantum computers have a considerable advantage for simulating the dynamics of how a highly-entangled quantum state evolves with time because it is intrinsically capable of maintaining the entangled state, which circumvents the exponential memory overhead of classical algorithms to store all the coefficients in the expansion. In the language of computational complexity class, simulating unitary time evolution is a **BQP** problem [45], while BQP refers to the set of problems that can be efficiently solved using a quantum computer with polynomial resources and a bounded probability of error. Other typical **BQP** problems in quantum chemistry include quantum phase estimation (QPE)[46] and approximating the time-dependent effective Kohn-Sham potential in density functional theory [47].

1.4 Quantum computing basics

1.4.1 Quantum building blocks

Qubit [48], also known as quantum bit, serves as the fundamental building block of quantum information in quantum computing. It is the quantum analog of the binary bit that is used to represent information in classical computers. In mathematics, a single qubit is a two-level quantum-mechanical system described by a unit state vector in a two-dimensional complex vector space $\mathcal{V}$, also known as Hilbert space

$$|q\rangle = \cos\frac{\theta}{2}|0\rangle + \sin\frac{\theta}{2}e^{i\phi}|1\rangle \tag{1.14}$$

Any stable two-state devices could be a potential candidate for the physical realization of a qubit. Typical two-state quantum systems include the spin-up and spin-down state of electron spin or atomic spin in optical lattices, the vertical and horizontal polarization of a single photon, the clockwise and counterclockwise current of a superconducting Josephson junction, etc. [49, 50, 51] Therefore, the development of quantum hardware has branched to different physical architectures.

A single qubit has the potential to hold significantly more information than a classical bit, although it requires multiple preparations and measurements to extract that information. However, the true power of quantum computing lies in the exponential growth of the computational space when entangling an increasing number of qubits. An arbitrary state of an n-qubit system is represented by a unit vector in the tensor product space of singlet-qubit Hilbert space.

$$|Q\rangle = a_0 |0\ldots00\rangle + a_1 |0\ldots01\rangle + \cdots + a_{2^n-1} |1\ldots11\rangle \tag{1.15}$$

where n qubits encode 2^n probability amplitudes and computational basis states that can be exploited to store the information.

A **quantum circuit** consists of a number of single and two qubit gates acted on the qubits. These qubit gates are all unitary transformation acting on the state vector of qubits. The most commonly used are Pauli gates

$$X = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad Y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad Z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{1.16}$$

the Hadamard gate

$$H = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \tag{1.17}$$

which is useful to create a superposition state, for example, $H\left|0\right\rangle = (\left|0\right\rangle + \left|1\right\rangle)/\sqrt{2}$. There are also single qubit rotation gates that contain parameters,

$$R_Y(\beta) = \begin{bmatrix} \cos\frac{\beta}{2} & -\sin\frac{\beta}{2} \\ \sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{bmatrix}, \quad R_Z(\beta) = \begin{bmatrix} e^{-i\beta/2} & 0 \\ 0 & e^{i\beta/2} \end{bmatrix}, \tag{1.18}$$

which can be used to construct a parametrized variational ansatz. To entangle qubits, the two qubit controlled-NOT (CNOT) gate is required, which is mathematically written as

$$\text{CNOT} = I_t \otimes \left|0\right\rangle \left\langle0\right|_c + X_t \otimes \left|1\right\rangle \left\langle1\right|_c \tag{1.19}$$

where t denotes the target qubit, c denotes the control qubit.

1.4.2 Encoding fermionic problems on quantum computers

We are interested in simulating chemical systems in the second-quantised representation (Eqn. 1.3). To preserve the antisymmetry condition of fermionic wave functions, the second-quantised creation and annihilation operators follow the anticommutation relations

$$\{\hat{a}_p, \hat{a}_q^\dagger\} = \delta_{pq}, \quad \{\hat{a}_p, \hat{a}_q\} = \{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = 0 \tag{1.20}$$

To encode these fermionic operators acting on indistinguishable fermions

into qubit operators acting on distinguishable qubits, the most common mapping is the Jordan-Wigner transformation [52, 53] given by

$$\hat{a}_p = \frac{\hat{X}_p + i\hat{Y}_p}{2} \otimes \hat{Z}_{p-1} \otimes \ldots \hat{Z}_0$$
$$\hat{a}_p^\dagger = \frac{\hat{X}_p - i\hat{Y}_p}{2} \otimes \hat{Z}_{p-1} \otimes \ldots \hat{Z}_0$$

(1.21)

For the state, the occupation number of an spin orbital is stored in the $|0\rangle$ or $|1\rangle$ state of a qubit

$$|f_M, \ldots, f_i, \ldots, f_1\rangle \rightarrow |q_M, \ldots, q_i, \ldots, q_1\rangle$$
$$q_i = f_i \in \{0, 1\}$$

(1.22)

In this way, every Slater determinant in the FCI wavefunction can be written as one of the computational basis states, so M qubits can efficiently store the FCI wavefunction in M spin orbitals, surpassing the exponential memeory scaling with respect to the system size. This quantum advantage also holds for any other second-quantised mappings [54, 53].

1.5   Quantum algorithms for quantum chemistry

In this section, we give an overview of several prototype quantum algorithms for quantum chemical applications.

1.5.1   Quantum phase estimation

Suppose we have a unitary operator U and one of its eigenvectors $|u\rangle$ with eigenvalue $e^{2\pi i\varphi}$ where φ is unknown. The value of φ can be obtained through the quantum phase estimation subroutine. A general circuit form of QPE can be found in Nielsen and Chuang's canon.[49]

In the case of quantum chemistry, phase estimation can be formulated to compute the lowest energy eigenstate $|E_0\rangle$ of a Hamiltonian.[55] Figure 1.1 shows a pedagogical example of how to construct a circuit for phase estimation using three ancillary qubits. When the ancillary qubits are in the state $|x\rangle$, a controlled rotation $e^{-2\pi iHx}$ is applied to the register of qubits that encodes $|\Psi\rangle$. After layers of controlled gates, an inverse quantum Fourier transform is performed over all ancillary qubits before measuring these qubits on the standard computational basis. The measurement outputs a bit-string $\mathrm{bin}(E_0)$ from the register of ancillary qubits which gives the binary representation of the eigenvalue/energy of interest. Meanwhile, the $|\psi\rangle$ register is projected into the corresponding eigenstate $|E_0\rangle$.

The application of phase estimation on the near-term quantum devices, with less than 100 qubits and shallow circuits, are limited in the foreseeable future, because it requires a large overhead of ancillary qubits to achieve a acceptable precision, gate with high-fidelity as well as long coherence time to get a asymptotic approximation of the exact dynamics.
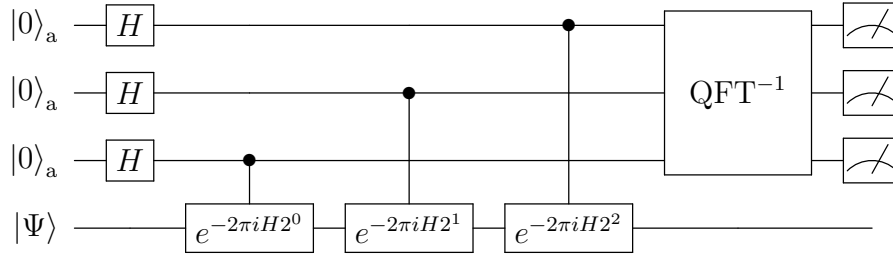
Figure 1.1: A circuit diagram for quantum phase estimation using three ancillary qubits. The circuit block labelled with QFT^{-1} executes the inverse quantum Fourier transformation. When the ancillary qubits are in state $|x\rangle$, a controlled rotation $e^{-2\pi i H x}$ is applied to the main register $|\Psi\rangle$. The ancillary qubits output an eigenvalue of H in binary when being measured in the computational basis; meanwhile the main register $|\Psi\rangle$ collapses to the corresponding eigenstate. The circuit diagram is adapted with permission from *Rev. Mod. Phys.*, 92(1):015003, 2020, DOI:10.1103/revmodphys.92.015003. Copyright 2020 American Physical Society.

1.5.2 Variational quantum eigensolver

The variational quantum eigensolver (VQE) [56, 57, 58] is a hybrid approach that combines classical and quantum computation to solve problems in quantum chemistry. It aims to find the lowest energy state (ground state) of a molecular system. In the VQE scheme, as shown in Fig. 1.2, a variational ansatz is employed to prepare a quantum state that approximates the ground state of the system. This ansatz is represented by a parameterized quantum circuit, where the parameters are adjusted iteratively to minimize the energy expectation value given by

$$E(\vec{\theta}) = \langle\psi_{\mathrm{ref}}|U^{\dagger}(\vec{\theta})\hat{H}U(\vec{\theta})|\psi_{\mathrm{ref}}\rangle. \tag{1.23}$$

where $\vec{\theta} = (\theta_1, \ldots, \theta_n)^T$ denotes a vector of independent parameters in the circuit, and $\psi_{\mathrm{ref}} = U_{\mathrm{ref}}|\bar{0}\rangle$ is usually taken to be a mean-field or multi-reference

state [59, 60, 61, 62, 63, 64] generated by non-parametrised gates on the initial all-zero state. The Rayleigh-Ritz variational principle guarantees that $E(\vec{\theta}) \geqslant E_0$ where E_0 is the exact ground-state energy. VQE harnesses the power of classical optimization algorithms to fine-tune the quantum circuit's parameters $\vec{\theta}$, while the energy expectation value is repeatedly measured on a quantum computer. Classical optimization algorithms, such as gradient-based methods [65], are employed to update the parameters and search for the optimal configuration that minimizes the energy expectation value.

VQE provides an efficient way to approximate the ground state energy without the need for complete diagonalization of the Hamiltonian, which is often computationally expensive for large systems. The main advantage of VQE is that it can utilize shallow circuits, which leads to less demanding coherence time, with the cost of a polynomial overhead of measurements and classical optimization.
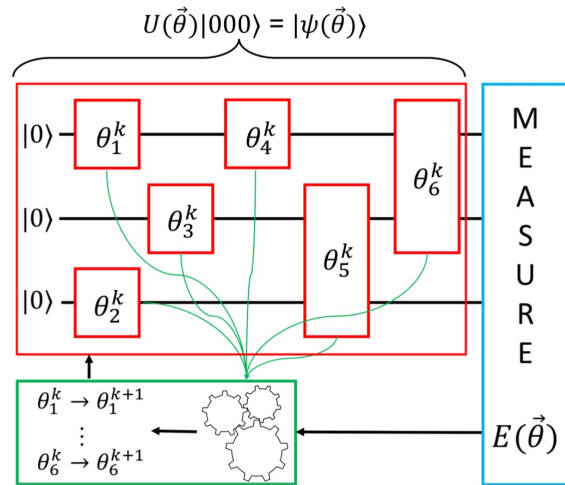

Figure 1.2: Scheme of the variational quantum eigensolver (VQE) using three qubits. The scheme is reprinted with permission from *Rev. Mod. Phys.*, 92(1):015003, March 2020, DOI:10.1103/revmodphys.92.015003. Copyright 2020 American Physical Society.

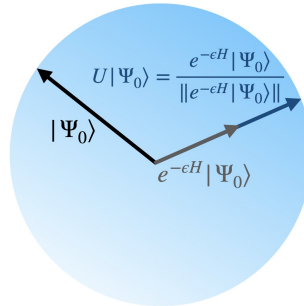### 1.5.3 Quantum imaginary time evolution

Figure 1.3: Schematic of the quantum imaginary time evolution (QITE) algorithm

As an alternative scheme to VQE, the quantum imaginary time evolution (QITE), an ansatz-independent optimization-free method, has been proposed to determine the eigenstates of a Hamiltonian on quantum computers [66]. QITE inherits the advantage of the classical imaginary time evolution method [67, 68], which allows correlations to build faster than the real-time evolution, which is limited by Lieb-Robinson bounds on the growth of correlation functions [69]. Propagating an initial state that has a non-zero overlap with the ground state in the imaginary time evolution path guarantees to converge to the exact ground state $|\Psi\rangle = \lim_{\beta\to\infty} \frac{|\Phi(\beta)\rangle}{\|\Phi(\beta)\|}$ (for $\langle\Phi(0)|\Psi\rangle \neq 0$. However, the imaginary-time propagator is nonunitary. As the basic operations allowed on quantum computers have to be unitary, the textbook implementation of a non-unitary operator is to use extra ancillary qubits with an increased number of measurements [49].

The key idea of QITE, as originally formalized by Motta and coworkers, is to map the action of the imaginary time evolution on the state to a rescaled real-time-propagated state by the least-square fitting [66]. The fitting proce-

dure involves solving linear equations in which matrix elements can be computed from projective measurement outcomes of the initial state without additional ancillary qubits.

The quantum imaginary time evolution algorithm is not limited to ground-state computations. Since its first proposal, it has been applied to estimate finite temperature properties [70], simulate open quantum systems [71], prepare thermal states [72], and even extended to perform prime factorization[73] and simulate quantum field theories [74].

The depth of the QITE circuit grows exponentially with the correlation length of the system and linearly with the number of imaginary time steps. As for the measurement cost, the number of Pauli terms (same as the dimension of the linear system to be solved in the fitting) scales exponentially with the correlation length. Thus, with increasing system size, this rapidly becomes the bottleneck of the algorithm. For practical implementations, many techniques have been proposed to reduce the circuit complexity and measurement overhead. Sun *et al.* introduced the circuit optimization by recompiling it using tensor networks [70]. Several works reported different strategies to combine unitary operators in the state preparation circuit effectively [75, 76, 77]. Some techniques have been developed to reduce the number of Pauli terms to be measured, such as exploiting Hamiltonian symmetries [70], randomized compiling [78], or utilizing a compact list of Pauli terms that arises in unitary-coupled-cluster-type exponential ansatz [75]. Another variant of QITE uses an adaptive scheme combining the variational ansatz simulation of imaginary time [79, 80] with the "action fitting" technique in QITE, which yields compact variational ansatz and a polynomial scaling of circuit depth with system

size [81].

1.6 Outline of the dissertation

In Chapter 2, we propose a novel quantum algorithm for practical chemical simulations, termed multireference selected quantum Krylov (MRSQK) algorithm, which use the efficient unitary time evolution on quantum computers to generate a very compact quantum Krylov subspaces. In Chapter 3, we introduce a hybrid quantum-classical unitary downfolding scheme based on the driven similarity renormalization group theory (QDSRG). This method effectively reduces the dimensionality of the problem and minimizes the required quantum resources, which enables resource-efficient simulations on small-scale quantum computers using large basis sets. In Chapter 4, we extend the QDSRG scheme to compute excited states via a state-averaged formalism (SA-QDSRG), specifically targeting the challenging cases of near-degenerate states (i.e. conical intersections) that play a crucial role in describing photodynamic processes.