

Quantum Information and Algorithms for Correlated Quantum Matter

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Cite This: <https://dx.doi.org/10.1021/acs.chemrev.0c00620>



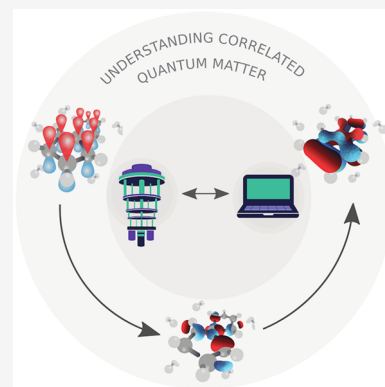
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ABSTRACT: Discoveries in quantum materials, which are characterized by the strongly quantum-mechanical nature of electrons and atoms, have revealed exotic properties that arise from correlations. It is the promise of quantum materials for quantum information science superimposed with the potential of new computational quantum algorithms to discover new quantum materials that inspires this Review. We anticipate that quantum materials to be discovered and developed in the next years will transform the areas of quantum information processing including communication, storage, and computing. Simultaneously, efforts toward developing new quantum algorithmic approaches for quantum simulation and advanced calculation methods for many-body quantum systems enable major advances toward functional quantum materials and their deployment. The advent of quantum computing brings new possibilities for eliminating the exponential complexity that has stymied simulation of correlated quantum systems on high-performance classical computers. Here, we review new algorithms and computational approaches to predict and understand the behavior of correlated quantum matter. The strongly interdisciplinary nature of the topics covered necessitates a common language to integrate ideas from these fields. We aim to provide this common language while weaving together fields across electronic structure theory, quantum electrodynamics, algorithm design, and open quantum systems. Our Review is timely in presenting the state-of-the-art in the field toward algorithms with nonexponential complexity for correlated quantum matter with applications in grand-challenge problems. Looking to the future, at the intersection of quantum information science and algorithms for correlated quantum matter, we envision seminal advances in predicting many-body quantum states and describing excitonic quantum matter and large-scale entangled states, a better understanding of high-temperature superconductivity, and quantifying open quantum system dynamics.



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Special Issue: Quantum Materials

Received: June 16, 2020

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1. INTRODUCTION

Accurate and efficient prediction of molecules and materials is one of the most important outstanding problems in science and engineering. Discoveries in quantum materials, which are characterized by the strongly quantum-mechanical nature of electrons and atoms, have revealed exotic properties that arise from correlations, including unconventional superconductors, topological insulators, spin liquids, and new phases of matter induced via strong light–matter interactions. These systems exhibit remarkable effects including quantum interference, tunneling, fluctuations, entanglement, and topological quantum states. However, the physics of quantum materials has conventionally been inaccessible to numerical modeling, so many of their interesting phenomena remain poorly understood, and technological applications are elusive. For example, electronic structure simulations of molecules with long-range interactions are beyond the capabilities of the best supercomputers and are extremely challenging when collective quantum effects become important, as in strongly correlated electron systems. Further, real quantum materials have heterogeneity and disorder that are challenging to model.

We anticipate that quantum materials to be discovered and developed in the near future will transform the areas of quantum information processing, which encompasses communication, storage, computing, sensing, and metrology. Simultaneously, efforts toward developing new quantum algorithmic approaches for quantum simulation and advanced calculation methods for

many-body quantum systems will enable major advances toward functional quantum materials and their deployment. It is the promise of quantum materials for quantum information science at the same time as the potential of new quantum algorithms to discover entirely unexplored quantum matter that has inspired this Review. Over the past few years, there has been substantial activity in establishing the prediction of molecules as the primary near-term application of quantum computation. There are similarly impressive discoveries to come in quantum computation of quantum materials. Our Review is therefore timely and presents the state-of-the-art in the field toward algorithms with nonexponential complexity for strongly correlated quantum systems, with applications in excitonic quantum matter and many-body quantum states, large-scale entangled states, and high-temperature superconductivity.

The challenge for classical approaches is the treatment of the intrinsically quantum mechanical nature of the problem, in particular for highly entangled or correlated states. The advent of quantum computing raises new possibilities for eliminating the exponential complexity that has stymied simulation of strongly correlated quantum systems on high-performance classical computers. Despite this promise, the current challenge for quantum approaches is the limited size and coherence of available quantum hardware. While the promise of quantum computing for quantum materials is large, the current state of the field is best described as “noisy intermediate-scale quantum” (NISQ). Heuristically, in this regime quantum computers are too large to be directly simulated on classical computers but remain too small to perform useful error correction. Utilizing various hardware realizations such as superconducting qubits, trapped ions, cold atoms, or photonic systems, academic groups and commercial ventures have demonstrated various levels of operational control and entanglement on tens of qubits. Here, we aim to review new algorithms and computational approaches to predict and understand the behavior of correlated quantum matter, utilizing both quantum and classical resources.

In 2020, the field of quantum information processing is on the cusp of a critical moment: special-purpose NISQ devices have become capable of solving certain problems that classical computers cannot solve, and quantum computers are poised to show practical “quantum advantage”. This is in part due to the breakthrough announced in 2019, showing that a quantum device can perform calculations that are classically intractable, benchmarked on the large supercomputer Summit.¹ Researchers at Google and NASA presented heuristic benchmarking showing that their 54-qubit superconducting (SC) circuit quantum computer performs certain sampling algorithms much faster than classical computers,² though these algorithms have no known practical application. However, Google’s SC quantum computer is still firmly in the regime of NISQ devices, as its components are so noisy that the chances of completing a task vanish exponentially with task size. That this “quantum advantage” achievement would be first realized by a SC architecture is not surprising, as staggering progress in recent decades has enabled high-fidelity and high-speed qubit initialization and logic gates. This result is an important step toward incorporating quantum information as a general purpose tool for scientific problems. Researchers at Google proceeded a step further and utilized their superconducting processor to determine molecular energies using experimentally implemented Hartree–Fock theory,^{3–5} illuminating the pathway toward practical quantum advantage for molecular and material problems.

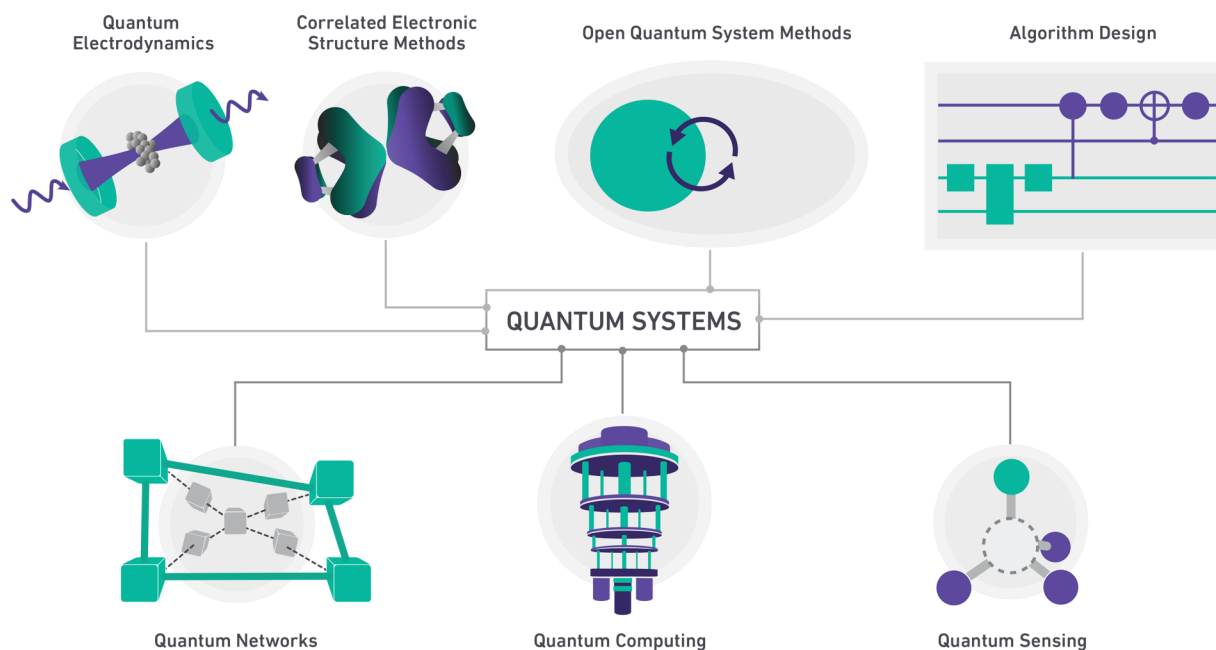


Figure 1. Scalable quantum systems have been the focus for many different fields including quantum optics, quantum chemistry, materials science, and computer science. For instance, method development in quantum electrodynamics, correlated electronic structure, open quantum systems, computational algorithms, and the interplay between these fields have provided a better understanding of quantum systems. Their progress has enabled physical realizations of novel quantum information technologies including quantum networks, quantum computers, and quantum sensors.

In parallel, over the past few years, the ability to connect quantum information processors by quantum communication channels, toward a future “quantum internet”, has enabled a wide variety of multiparty computation and decision making protocols that go beyond classical secure communication. In 2020, we saw the first demonstration of a quantum repeater, an important step toward enabling large-scale quantum networks. This would allow secure communication of information over long distances using matter and photonic based quantum information systems.⁶ Quantum technologies for precision measurement already form the basis for the world’s most accurate clocks and sensors. We expect that the next generation of sensing technologies will use large-scale quantum coherence and entanglement to increase accuracy and precision by many orders of magnitude. There is inherent synergy between a better understanding of quantum many-body dynamics and developing new quantum information technologies. Therefore, in this Review, we emphasize quantum materials for quantum information science, enabling the development of physical systems that can coherently store and manipulate quantum states well enough for error correction.

In the NISQ-era, quantum devices with increasing complexity are emerging rapidly. Multiple different hardware platforms have become available recently that are intrinsically capable of simulating quantum systems due to their quantum nature. Ideas in quantum simulation have been realized in a wide range of systems, including superconducting qubits, molecular qubits, defect systems, photonic platforms, and topological systems. With a plethora of these novel platforms, there is now an opportunity for the realization of functional quantum resources: quantum devices that offer practical quantum advantage in simulations.

A significant focus of the community has been creating robust and resilient quantum devices, many based on new materials. Therefore, an accurate description of the electronic structure of molecules and quantum materials is critical for predicting the

properties of these quantum devices. The electronic structure gives rise to quantum mechanical states, which can then be entangled and used as a “quantum resource” or more directly lead to novel applications, such as the optimization of molecular energy storage. The electronic structure of such systems is a good candidate for quantum computation since the inherent quantum nature of quantum devices provides natural benefits for predicting quantum behavior. However, the realization of quantum algorithms on quantum devices faces the major challenge of susceptibility to noise, leading to sizable error effects. These error rates are due to multiple factors: qubits can only stay in a mixed state for a certain period of time, the qubit operations are susceptible to accuracy errors, and subtle changes in the environment can affect accuracy. To consider quantum matter beyond small-scale model Hamiltonians, reducing the error rates is essential for maximizing the reliability of the results produced by current hardware.

This discussion shows that the description, prediction, and optimization of these quantum devices requires the intersections of methodologies from different fields including but not limited to quantum electrodynamics, electronic structure theory, open quantum systems, and algorithm design, as depicted across the top row of Figure 1. Quantum electrodynamics focuses on the accurate description of quantum systems under light–matter interaction, their optical properties, and experimental realization. Electronic structure theory, including methods such as Hartree–Fock, density-functional, many-body perturbation and coupled cluster theories, aims to accurately predict electronic configurations within general molecular and material systems. Open quantum systems focus on systems whose behavior and dynamics are dictated by system–environment interactions, including environmental noise. Computational algorithm design draws ideas from classical computing and computer science while exploiting the quantum properties of the hardware for universal quantum computation. These fields are well-established and have produced accurate and general methods

for predicting behavior in quantum systems. Combining recent breakthroughs from these fields with ideas from computer science to optimally design quantum algorithms has led to physical realizations and novel application of a wide range of quantum technologies including quantum networks, quantum computers, and quantum sensors. Beyond the field of quantum information, these platforms promise a new perspective on some of the longstanding problems in chemistry such as improvements in the design of molecules for catalysis, photosynthetic light-harvesting, and energy storage.

1.1. Layout and Sections

In this Review, part of a Thematic Issue on Quantum Materials, we provide a fresh look at classical and quantum algorithms to approach novel quantum systems. With increased understanding and remarkable experimental imaging of quantum behavior of molecules and materials, these systems are becoming technologically relevant. Researchers have made tremendous progress toward the accurate treatment of the electronic structure of quantum mechanical systems, tailoring and controlling correlations, thereby allowing the design of novel molecules and materials.^{7–11} In section 2, we discuss classical methods in electronic structure theory that use the wave function as the primary variable of interest to accurately treat quantum systems where electronic correlation is critical. In section 2.1, we discuss the definition and importance of electronic correlation in molecules and materials. In section 2.2, we discuss classical electronic structure theory methods including Hartree–Fock, configuration interaction, and coupled cluster theories. We then highlight molecular qubit candidates as both an independent and exciting active field of experimental research and as a potential application of these classical methods.

An alternative approach from using the wave function as the primary variable of interest is to consider a density perspective, which we discuss in section 3. In section 3.1, we highlight reduced density matrix techniques, with an emphasis on the variational method to capture correlation in molecular and material compounds. We then discuss physically motivated density matrix constraints that can be used as error mitigation on quantum devices. We briefly discuss reduced density matrix functional theory, leading into the remainder of this section, which focuses on density functional approaches.

Density functional based methods have been extensively developed and utilized for describing aspects of molecular and solid-state quantum systems. Research advances have extended DFT methods to be time-dependent and, importantly, have allowed for direct inclusion of correlations with electrons, phonons, and photons. There have also been method developments such as the quasiparticle *GW* approach, which builds upon DFT. Altogether these methods have been timely, as experimental work has expanded to include novel materials and chemical systems, along with the inclusion of light-mediated and cavity-driven interactions. Light-mediated manipulation of quantum matter is particularly attractive, as it enables control at fundamental time scales and access to novel nonequilibrium states of matter. Ultrafast and quantum electrodynamic methods have been recently used as a new tuning knob to induce insulator-to-metal transitions, topological phases, and ferroelectricity, as well as transient superconductivity in copper oxides and organic crystals. While this provides a tantalizing opportunity to explore new quantum phases, particularly in the case of transient superconductivity, key questions remain on the

underlying excitation mechanisms and computational approaches to describe such systems.

With these as motivating factors, we discuss DFT methods in section 3.2. In particular, we highlight in section 3.2.1 the theoretical approaches for describing atomic point defects in crystals. These defects, which can behave as “artificial atom” qubits or “color center” qubits, serve also to highlight opportunities for algorithmic advances to capture correlated electron–nuclear dynamics in these and other quantum matter systems. Going beyond conventional DFT, section 3.3 covers time-dependent density functional theory and quasiparticle methods for correlated quantum matter. In section 3.4, we introduce algorithmic advances toward describing “driven quantum matter”. In particular, we highlight *ab initio* quantum electrodynamic methods that can model inherently correlated quantum interactions, where photon, nuclear, and electron degrees of freedom are treated at the same level of quantization.

We then review, in section 4, the recent progress in quantum algorithms and how the realization of quantum devices has allowed for an alternative pathway for reducing the scaling of the *N*-body problem of interacting quantum mechanical particles. In section 4.1, we consider the inception of quantum algorithms and early progress in their application to chemical and material systems. In section 4.2, we discuss an important class of quantum–classical approaches where a limited number of atoms or orbitals are mapped on the quantum computer, while the remaining part of the material system is treated using the strength of classical supercomputing platforms. In section 4.3, we present error mitigation ideas to aid in successful simulation of large quantum systems as NISQ platforms of appropriate qubit size and coherence times become available. The diversity of hardware including gates, connectivity, control schemes, and noise characteristics are both a challenge and an opportunity; as much as one algorithmic approach may not succeed on one platform, it might be adjusted to succeed on another, as the community has recently shown. Validation and verification of the quantum hardware is important as we establish a new computational paradigm, especially with the high error rates and initially unknown nature of errors of NISQ hardware.

In section 5, we will discuss the field of open quantum systems and how this perspective can be used as a lens to think about quantum systems of interest, from atoms and molecules to quantum networks. The control of quantum systems requires coupling diverse subsystems together while simultaneously driving them and minimizing the detrimental effects of the environment. The inherent contradiction in using external classical fields for control while limiting the deleterious effect of the environment requires a fundamental understanding of a quantum system that is open to its environment. Modeling and controlling quantum systems that operate with some degree of decoherence is an interdisciplinary problem, as we will illustrate. In the simplest case where the system is well isolated and the coupling to the environment is weak, methods such as the Lindblad–Kossakowski formalism can be used to capture decoherence and loss due to the environment. While this alone is challenging, certain regimes, such as strong system–bath coupling, are much more complex. Strides toward defining and distinguishing between different regimes and capturing the resulting dynamical properties are discussed in sections 5.1 and 5.2, respectively. Further, in section 5.3, we will present advances in the treatment of open quantum systems through a myriad of applications from correlated materials physics to descriptions of hybrid quantum systems.

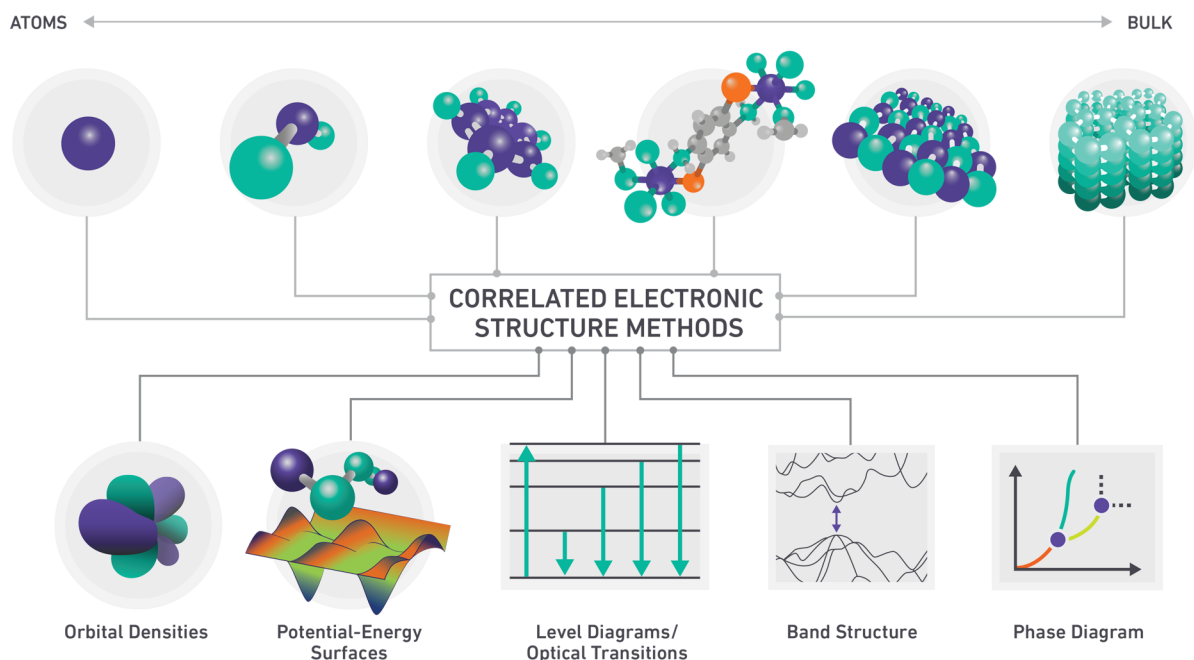


Figure 2. Electronic structure methods are a computational backbone for building quantum matter. From atoms to bulk material, correlated electronic structure methods are used to investigate properties including orbital densities, potential-energy surfaces, level diagrams and optical transitions, band structures, and phase diagrams.

We acknowledge that the strongly interdisciplinary nature of the topics covered is unprecedented and there is a need for a common language to integrate ideas from these fields. In this Review, we aim to provide this common language while weaving these fields together. Taken together with the other reviews in this Thematic Issue on Quantum Materials, including those by Zunger et al.,¹² Felser et al.,¹³ and Nguyen and Cava,¹⁴ we present a comprehensive foundation for those entering the fields of correlated quantum matter and quantum information science.

We conclude the Review in section 6 with open questions in quantum simulations and algorithms for correlated quantum matter. In particular, we highlight directions beyond variational quantum eigensolvers and discuss recently developed algorithms to capture correlations, entanglement, and excited states in quantum materials. Further, we present forward-looking ideas in predicting and controlling driven quantum matter.

2. WAVE FUNCTION-BASED ELECTRONIC STRUCTURE METHODS FOR QUANTUM MATTER

Ever-increasing computational power, theoretical advances, and improvements in algorithm design have opened new frontiers in 21st century quantum chemistry and quantum materials science. Treating atoms, molecules, and materials using computational methods involves solving a many-body problem of interacting electrons and nuclei and possibly also coupled electromagnetic fields. Due to the vast configuration space, this problem is exponentially complex and can only be solved exactly for very small systems. Therefore, all practical methods for real systems rely on approximations, and balancing the computational costs of these methods with the accuracy of the prediction is a constant challenge. The simplest methods to treat interacting multicomponent systems are adiabatic and semiclassical approximations. Examples include the Born–Oppenheimer approximation, which simplifies electron–nuclei problems, or a semiclassical Schrödinger–Maxwell treatment, which simplifies the problem of the electromagnetic field interacting with

electronic systems. In each method, the many-body problem is reduced to a problem of interacting electrons, which are treated as quantized, and a separate problem of nuclei or the electromagnetic field governed by Maxwell’s equations. The different time scales of nuclear, electronic, and photonic motion provide justification for these approximations. When considering the electronic degrees of freedom, relatively accurate treatment for electronic correlation is often critical for obtaining important molecular and material properties such as those depicted in Figure 2. In this section, we will focus on the development of electronic structure methods and how these theories can enable future experiments in quantum materials and quantum information.

2.1. Introduction to Electronic Correlation Effects

The correlation energy of a general molecular electronic system can be given by

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \quad (1)$$

where E_{exact} is the exact total electronic energy and E_{HF} is the Hartree–Fock or mean-field energy. Generally the correlation energy is the energy associated with the interaction between electrons beyond a single-particle picture or the part of the electronic energy that the Hartree–Fock method fails to capture.¹⁵ For quantum matter applications, electronic correlation can be divided into two categories, static and dynamic.¹⁶ Static or multireference electronic correlation arises when the low-energy configurations are degenerate or nearly degenerate with the reference Slater determinant, as in stretched molecular configurations.¹⁷ In other words, a single molecular-orbital diagram is insufficient to describe the wave function and more determinants must be included.¹⁸ Dynamic correlation arises from the repulsion due to the relative motion of electrons and often requires the need to mix higher-order excited configurations with the reference Slater determinant.¹⁶ As an example of these energies, the total energy, Hartree–Fock

energy, and correlation energy of hydrogen fluoride at varying bond distances are shown in Figure 3.

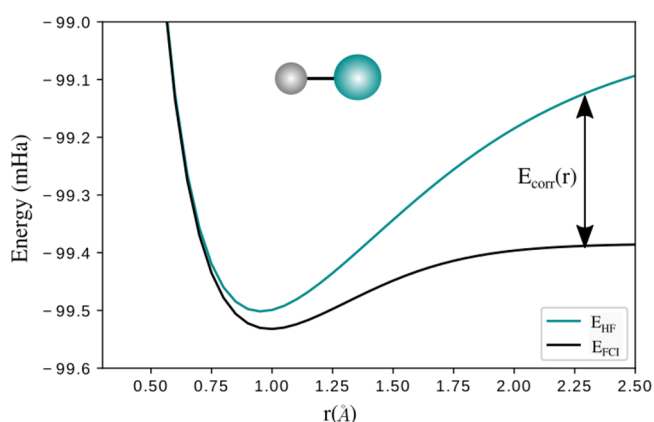


Figure 3. Hartree–Fock (teal) and full-configuration interaction (gray) energies versus atomic distance r for the dissociation of hydrogen fluoride in the STO-6G basis set¹⁹ calculated using PySCF.²⁰ The separation dependent correlation energy is shown as $E_{\text{corr}}(r)$ as the difference between E_{HF} and E_{FCI} .

There are several popular methods of approximating the correlation energy, including Møller–Plesset perturbation theory (MPT), configuration interaction (CI) theory, and coupled cluster (CC) theory. When using any approximate or perturbative method, there are a few important properties to preserve while considering the electronic structure of a system, including size consistency and size extensivity. Size consistency refers to the energy of a molecular system being equivalent to the sum of its individual parts at infinite separation, whereas size extensivity refers to the energy scaling with the system size.²¹ Due to the physical nature of size consistency and size extensivity, methods that satisfy these properties are generally preferable. Accurate calculation of strong electronic correlation in molecular and extended material systems is critical for a variety of applications. Predicting and controlling the electronic entanglement is essential to designing large molecular systems for use as qubits or to store information or energy.^{22–32} Traditional formulation of the electronic correlation problem leads to exponential scaling in system size; however, current progress in the field is producing novel methods for treating electron correlation with improved scaling.

In section 2.2, we will discuss the traditional quantum chemistry methods as relevant to predictions of correlated quantum matter. In section 3, we will then discuss other routes such as density functional and time-dependent density functional theory and its extensions, quasi-particle and reduced density matrix based methods, and other recent techniques including machine learning-based approaches in computational condensed matter physics.

2.2. Quantum Chemistry Approaches to Correlated Quantum Matter

The simplest approximation to intuitively consider electronic behavior is to ignore explicit treatment of electron–electron correlation and instead consider the energy and configuration of a single electron in the average field of other electrons. This class of approaches is referred to as mean-field methods and the Hartree–Fock method is the most commonly used in quantum chemistry. In the Hartree–Fock method, the solution of the

interacting many-body problem of N electrons is approximated by a single Slater determinant,

$$|\Psi_0\rangle = |\chi_1\chi_2 \dots \chi_N\rangle \quad (2)$$

where χ_i are single-particle wave functions. The variational principle can be used to determine the optimal wave function $|\Psi_0\rangle$ that leads to the lowest energy, E_0 :

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (3)$$

where \hat{H} denotes the Hamiltonian of the system.³³

The Hartree–Fock approximation leads to a set of single-particle equations, known as the Hartree–Fock eigenvalue problem. The ground state is composed out of the N lowest occupied orbitals, while the other orbitals are unoccupied or virtual orbitals. By choosing a single Slater determinant and therefore only considering occupied orbitals and by ignoring the correlated nature of electron–electron interactions, Hartree–Fock scales as N_{orb}^3 , where N_{orb} is the basis set size, while capturing 99% of the electronic energy for a wide range of atoms, molecules, and materials.³³ As a mean-field approximation, the Hartree–Fock method fails to capture the electronic structure of strongly correlated systems. This critical failure has led to the development of many methods to include electronic correlation, commonly referred to as post-Hartree–Fock methods.

A standard approach for improving upon the Hartree–Fock method is by including an increasing number of Slater determinants, consequently increasing the size of the Hilbert space. Many of these extensions use active spaces as a method of decreasing the space of chemical interest and therefore decreasing the computational cost, allowing for the treatment of larger quantum systems. Using an active space involves selecting a subset of orbitals to be treated with a high level of theory, while the remainder of the orbitals are treated at a mean field level of theory.³⁴ Generally the valence orbitals near the HOMO–LUMO gap are selected as the active space, while the lower energy occupied orbitals (core orbitals) and the high energy unoccupied orbitals (virtual orbitals) are treated at a lower level of theory. Active spaces are incorporated into many of the post-Hartree–Fock methods discussed below.

An important class of post-Hartree–Fock methods is the multiconfigurational self-consistent field (MC-SCF) methods.^{35–37} In MC-SCF, the wave function is written as a linear combination of Slater determinants with coefficients that are determined variationally through minimizing the energy of the MC-SCF wave function. MC-SCF methods have been used to accurately treat static correlation in a variety of molecular systems, including transition metal and actinide chemistry.^{38–40} An important subset of MC-SCF methods are the complete active space self-consistent field (CASSCF) methods. These involve generating a full configuration interaction wave function within the active space and then variationally optimizing the orbitals and configuration coefficients.³⁴ A more recently developed subset of MC-SCF methods is the generalized active space (GAS) method where multiple active spaces are chosen and controlled such that insignificant configurations are neglected.^{41–43} Restricted active space (RAS) and localized active space (LAS) methods are other directions that have been explored,^{44,45} the latter being introduced recently to improve the use of active space methods in the density matrix embedding framework.^{46,47}

There are a variety of perturbative techniques for adding electronic correlation to the Hartree–Fock energy in molecular

systems. Møller–Plesset perturbation theory is a systematic way of adding correlation energy to the total electronic energy of a system.⁴⁸ This method is generally used to second order in correlation potential, denoted as MP2, and while this method originated in the 1930s, much progress has been made since then, which has allowed it to become a popular method for capturing electronic correlation.⁴⁹ Methods such as the resolution of identity (RI) or density fitting,^{50–55} Cholesky decomposition,^{56–60} local correlation,^{61,62} and combinations therein have reduced the complexity of the MP2 method and introduced efficient computational schemes allowing for its use to treat molecular systems with hundreds of atoms.⁶³ The advantages of MP2 include polynomial scaling, from $O(N_{\text{orb}}^5)$ down to $O(N_{\text{orb}})$ with the correct approximations,^{64–69} size-consistency, and the ability to capture dynamic correlation. However, the treatment of electronic correlation is incomplete and therefore inaccuracies arise when treating systems that include stacking or hydrogen bonding.^{70–72} Many method extensions based on MP2 have been developed to overcome such drawbacks, notably spin component scaled MP2, which has been shown to improve the ground-state energies in non-covalent interactions,^{73–78} orbital-optimized MP2,^{79–82} spin-network-scaled MP2, which relies on the inclusion of neural nets to weight interaction energy terms,⁸³ the use of natural orbital functionals to include static correlation,⁸⁴ and many more.^{85–87} Other perturbative techniques include the complete active space perturbative approach to second order (CASPT2)^{88,89} and the restricted active space perturbative approach to second order (RASPT2).⁹⁰ Both of these perturbative methods improve the CASSCF energy by including dynamical correlation through the use of perturbation theory. These methods have been successful in the description of excited states,⁹¹ dissociation energies,⁹² and magnetic properties.⁹³ A specific example of the use of CASSCF and CASPT2 was for the investigation of the spin density on the metal centers of a variety of molecular qubit candidates.³¹ Alongside experimental investigation, the ability to theoretically investigate molecular properties of these novel qubit candidates allows for improved design and efficiency.

Another possible avenue for including electronic correlation is through using the configuration interaction method. In the full configuration interaction (FCI) method, all determinants contribute to the wave function, and in the limit of an infinite basis set, the exact energies could be calculated.³³ The wave function can be written as

$$|\Psi\rangle = (I + \hat{T})|\Psi_0\rangle \quad (4)$$

with

$$\hat{T} = \sum_i \hat{T}_i \quad (5)$$

where \hat{T}_i is the operator that creates all particle excitations of order i and $|\Psi_0\rangle$ denotes a reference state, which is commonly the Hartree–Fock wave function. The prominent drawback of this method is that the scaling is exponential in terms of system size. Due to the exponential scaling, even with small basis sets the FCI method can only capture the electronic configuration for cases in which no more than around 18 orbitals are necessary.³³ Although the scaling of this method is computationally unfavorable, multiple flavors of configuration interaction have been explored. The simplest approximation is to truncate the level of excitations, starting with including all determinants that represent a single excitation (CIS), then single

and double excitations (CISD), then single, double, and triple (CISDT), and so on until the desired accuracy is obtained.⁹⁴ Another method is considering the seniority number of the wave functions or determinants to include. Notably, the doubly occupied configuration interaction (DOCI) method restricts the FCI space to the double occupied space or to the seniority zero space, where only determinants that represent paired configurations are included.⁹⁵ While this produces a reduced scaling, it is still exponential and therefore limited in a similar way to the FCI. Numerous different seniority schemes have been studied and applied successfully to treat small molecular systems.⁹⁶ Recently, machine learning techniques have been implemented using artificial neural networks to select which configurations are important contributions to the electronic wave function.^{97,98}

A major drawback of the CI method is that when the level of excitations is truncated, it is no longer size-extensive.⁹⁹ Using an exponential excitation operator ansatz to include higher order excitation determinants to the wave function allows for size extensivity to be recovered, in a method referred to as coupled cluster. The wave function in coupled cluster theory is often written as

$$|\Psi\rangle = e^{\hat{T}}|\Psi_0\rangle \quad (6)$$

with

$$\hat{T} = \sum_{i=1}^N \hat{T}_i \quad (7)$$

where $|\Psi_0\rangle$ denotes a reference state and \hat{T}_i is the operator that creates all particle excitations of order i . For instance, \hat{T}_1 is the operator that creates all possible single particle excitations and \hat{T}_2 double excitations. The highest possible excitation operator is \hat{T}_N , where N is the number of electrons in the system. Typically the Hartree–Fock wave function is used as the reference state; however other options also exist.

Analogous to the CI expansions, coupled cluster methods fall into classes according to excitation order by including single and double excitations (CCSD), including triple excitations (CCSDT), and so on.¹⁰⁰ Using a single reference state, the Baker–Campbell–Hausdorff (BCH) formula can be used to determine the ground-state energy. Due to the commutation properties of the excitation operators, the similarity-transformed Hamiltonian expansion is truncated at fourth order, thus allowing for efficient energy calculations.^{99,101} While this allows for low computational cost, the BCH formula only holds for single reference states, and in this sense can not capture strong static correlation. In addition, the coupled cluster ansatz is not variational and is therefore similar to a perturbation theory.

A further reformulation of the CC ansatz involves ensuring that the excitation operator is unitary such that

$$|\Psi\rangle = e^{\hat{T} - \hat{T}^\dagger}|\Psi_0\rangle \quad (8)$$

where \hat{T}^\dagger is the conjugate transpose of the excitation operator \hat{T} . The unitary coupled cluster (UCC) formulation has the benefit of being variational; however, the calculation proves to be challenging as the BCH formula no longer truncates.^{102,103} Method development^{104,105} and computational improvements¹⁰⁶ have allowed coupled cluster methods to accurately predict dynamic electronic correlation¹⁰¹ in molecular and solid-state systems.¹⁰⁷ Moreover, there has been a renewed interest in UCC as it can be used in conjunction with a classical

optimization strategy in variational quantum eigensolver (VQE) algorithms for quantum devices, a class of methods that will be discussed in section 4.

In the following, we want to briefly comment on the validity of the different approximations in the context of correlated quantum matter. To this end, the scaling and performance in capturing the dissociation of hydrogen fluoride for a sampling of the above methods including Hartree–Fock, MP2, CCSD, FCI, and DOCI is shown in Figure 4a,b, respectively. The scaling and

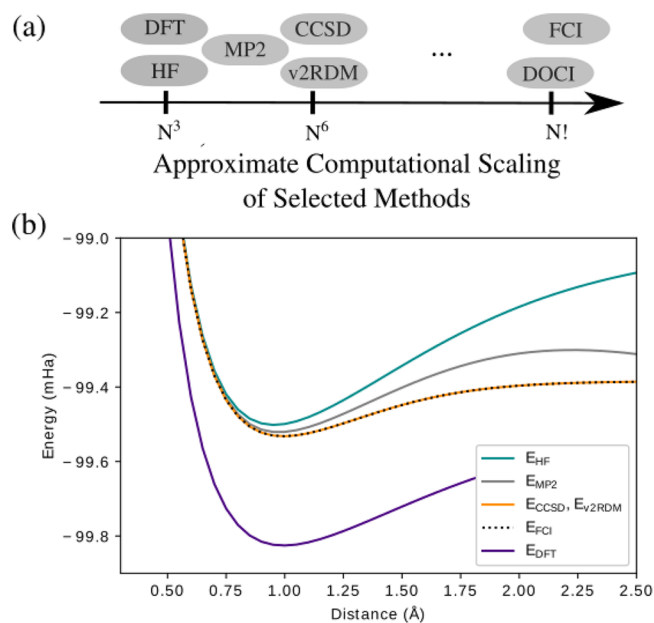


Figure 4. (a) Approximate computational scaling of a variety of electronic structure methods including Hartree–Fock (HF), density functional theory (DFT), Møller–Plesset perturbation theory to second order (MP2), variational 2-electron reduced density matrix (v2RDM), coupled cluster single doubles (CCSD), and full and double occupied configuration interaction (FCI and DOCI, respectively) where N is the basis set size. (b) Dissociation curve of hydrogen fluoride, comparing the accuracy of the Hartree–Fock, MP2, CCSD, v2-RDM, DFT, and FCI methods.

performance of density functional^{108,109} and reduced density matrix methods are also included and will be discussed in section 3. It should be noted that a minimal basis of STO-6G was used for these dissociation curves and improved results could be obtained by using a more complete basis.

Many of these methods have been in use for decades, and there continues to be an abundance of research dedicated to extensions, improvements, and applications in prediction of new quantum materials and phases of quantum matter. As discussed above, one such recent development is mapping these methods from classical high-performance computing onto quantum devices. While this will be discussed in detail in section 4, methods such as Hartree–Fock,^{1,3} full configuration interaction, and coupled cluster theory have all been used as ansätze in hybrid quantum algorithms on quantum devices. A considerable amount of research is currently being dedicated to adapting classical electronic structure theory methods to be amenable to the framework of gate-based quantum computing.

Another approach to overcome the computational challenges in the methods presented above is dividing the system into smaller computationally cheaper subsystems and then combining these subsystems. When one or some subsystems and the

surrounding environment are treated at different levels of theory, this is often referred to as quantum embedding.¹¹⁰ Embedding theories aim to predict properties of interest of the subsystem or impurity without having to perform a costly calculation on the whole quantum system. A plethora of embedding models exist, each focusing on different methods for dividing up the system and utilizing different computational techniques for treating each part.^{110–113} For example, in chemical quantum systems it is often natural to focus on geometry-based approaches, carefully avoiding breaking chemical bonds that contribute to the strong correlation of the system.¹¹⁰ The computational techniques differ based on the primary variable of interest. There are three main options leading to three main types of embedding theories:^{110,114} Green’s function embedding,¹¹⁵ density functional embedding,^{116–118} and density matrix embedding.¹¹⁹ Excellent and comprehensive reviews of embedding theories are presented in refs 114 and 110.

One of the most well-known embedding theories for the treatment of strong correlation is dynamical mean-field theory (DMFT) in which the infinite bulk system is mapped to an impurity model that consists of a subsystem embedded in a noninteracting environment.^{120–124} The correlated frequency-dependent Green’s function of the impurity is determined self-consistently, often resulting in predictions that approximate the bulk limit. Since the calculation of Green’s functions is a more complex task than the calculation of stationary states, DMFT is more computationally costly than necessary for ground-state calculations. An alternative embedding approach referred to as density matrix embedding theory (DMET) utilizes the 1-body density matrix as the variable of interest instead of the 1-body Green’s function.¹¹⁹ In the noninteracting limit, this theory is formally exact.^{110,119} Through the DMET correlation potential, DMET self-consistently optimizes the impurity embedded in an approximate many-body Schmidt basis for the environment.^{119,125} To treat the environment, often low-level theories such as Hartree–Fock^{119,126} are utilized. The impurity or subsystem is treated at a high-level of theory using methods such as coupled cluster¹²⁷ or complete active space self-consistent field.¹²⁸

DMET has been successfully applied to a variety of spin models, including 1D^{119,127,129,130} and 2D Hubbard models,^{119,131–134} and in chemical systems. A few chemical examples include small molecular configurations such as hydrogen rings, hydrogen sheets, and beryllium rings^{126,135} and extended molecular systems including boron-nitride sheets, polymers, and diamond structures.¹²⁷ Moreover, DMET has been successful at capturing and predicting chemical processes including hydrogen chain dissociation¹³⁶ and organic substitution reactions.¹³⁵ While DMET has shown to be an efficient technique for solving ground-state properties, successful extensions have also been developed for calculating excited-state properties through response theory formulations.^{131,137,138}

2.2.1. Predicting Molecular Qubits. A promising application for these classical wave function electronic structure methods, extensions, and the density methods, which will be discussed in section 3, is in the investigation of molecular qubit candidates. While many different types of qubits are being experimentally prepared, verified, and utilized, spin-based molecular qubits show great promise due to recent advances led by experimental groups.²⁹ The design of molecular spin qubits is gaining interest due to their chemical properties, which allow for ease of initialization into a well-defined quantum state,

enhanced quantum coherence, natural implementation as quantum logic gates, ease of integration into devices, and potential for creation of quantum networks.^{139,140} Their atomic precision, magnetic properties, and synthetic tunability make them excellent candidates for quantum computing applications, quantum sensors, and environmental probes.^{31,141–143} Moreover, through synthetic design and theoretical insight, molecular qubits can be relatively easily produced, tuned, and controlled.¹⁴²

When considering molecular spin based qubits, nuclear or electronic spins can be considered. While nuclear spins tend to have longer coherence times, electronic spins offer a few unique advantages, including precise spatial control due to their confinement to molecular structures and ease of tunability due to improved manipulation technology such as pulsed electron paramagnetic resonance.^{144,145} Electronic spins can be found in radical, diradical, or coordination complexes spanning the periodic table,¹⁴⁵ including transition metal²⁷ and lanthanoid complexes.^{139,146} A few examples of such molecular qubit compounds are shown in Figure 5.²⁷

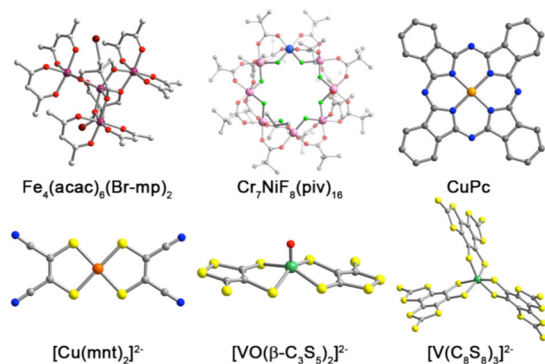


Figure 5. Crystal structures of a variety of the most relevant spin qubits made from transition metal ions where purple, orange, pink, light blue, green, maroon, light green, blue, yellow, red, and gray spheres represent iron, copper, chromium, nickel, vanadium, bromine, fluorine, nitrogen, sulfur, oxygen, and carbon atoms, respectively. Reprinted with permission from ref 27. Copyright 2017 American Chemical Society.

Like many other platforms for quantum computation, one of the biggest challenges that molecular qubits face is in extending and controlling coherence times.¹⁴² The coupling to environmental degrees of freedom can impact decoherence;¹⁴⁷ however, due to the quality of current synthetic techniques and the flexibility of molecular compounds, the structure of molecular qubits can be tuned to mitigate these detrimental effects.^{25,148,149} Other challenges in the field consist of improving the control of molecular excited states and entanglement processes.¹⁴²

The potential advantages of molecules as qubit candidates would be in the versatility of molecular structures and bonding. Utilizing different chemical types could allow for the tuning of properties critical for their performance and application in quantum information science. For example, organic molecules offer advantages such as weak spin–orbit coupling,¹⁴⁹ while transition metal complexes offer the advantage of additional flexibility through the choice of both metal center and ligands, and additional vibronic degrees of freedom.^{27,142} While the chemical components of individual molecular qubit candidates are important, another key advantage of these specimens lies in

their intermolecular interactions. These bonds can be exploited to construct molecular arrays and therefore qubit arrays.¹⁴²

Going beyond single molecules, one study set out to verify a theory that predicted that long coherence times should exist in defects in conjugated carbon materials.^{30,150} In these works, the molecular bonding structure was used as a form of qubit engineering to create unpaired electronic spins in molecular graphene nanostructures. Another experimental study extended the concept of molecular qubits through use of metal–organic framework chemistry to create an array of qubit candidates and investigate their properties. This work demonstrates considerable progress toward the creation of a quantum network based on molecular qubits that could have wide reaching applications in quantum information sciences.³²

The majority of the progress in spin molecular qubits has been driven by experiments; however, there is great potential for theoretically and computationally guided search for the ideal molecular qubits. One such example utilized CASPT2 to predict the pulse electron paramagnetic resonance spectrum of the spin density on the metal centers in molecular qubit candidates.³¹ Other work has utilized a combination of electronic structure methods to investigate the spin–vibrational coupling in lanthanide complexes¹⁵¹ and vibronic evolution in transition metal complexes.¹⁵² As this field progresses, theory has the potential to aid in the experimental efforts to design, tune, and control interesting molecular properties in these spin qubit candidates.

While classical electronic structure methods can be used to investigate, predict, and optimize the chemical properties of small- to medium-sized molecular compounds, they face challenges in terms of computational cost when trying to predict properties in larger material structures and molecular networks. We recognize that molecular qubits are a nascent platform, yet they represent a good model system for many of the methods in correlated quantum matter discussed in this Review. The remainder of this Review discusses alternative methods to predict properties of such systems, including density based approaches as discussed in section 3 for systems such as molecular graphene nanostructures, algorithm developments on quantum devices as discussed in section 4, and open quantum system based approaches as discussed in section 5 for systems such as molecular networks.

3. DENSITY-BASED ELECTRONIC STRUCTURE TO PREDICT QUANTUM MATTER

In the previous section, we presented solutions to quantum many-body problems in terms of a ground-state or excited-state many-body wave function Ψ . While wave functions provide a natural path to obtain observables, it is usually not feasible to construct many-body wave functions due to the exponential scaling of the parameter space. Other approaches to describe the electronic ground and excited states of a quantum system can be based on reduced quantities, such as the density matrix, the electron density, or the Greens function, which will be discussed in the following.

3.1. Reduced Density Matrix Methods for Correlated Quantum Matter

An alternate approach for considering the electronic state of a system is to consider the density matrix,

$${}^N D = |\Psi\rangle\langle\Psi| \quad (9)$$

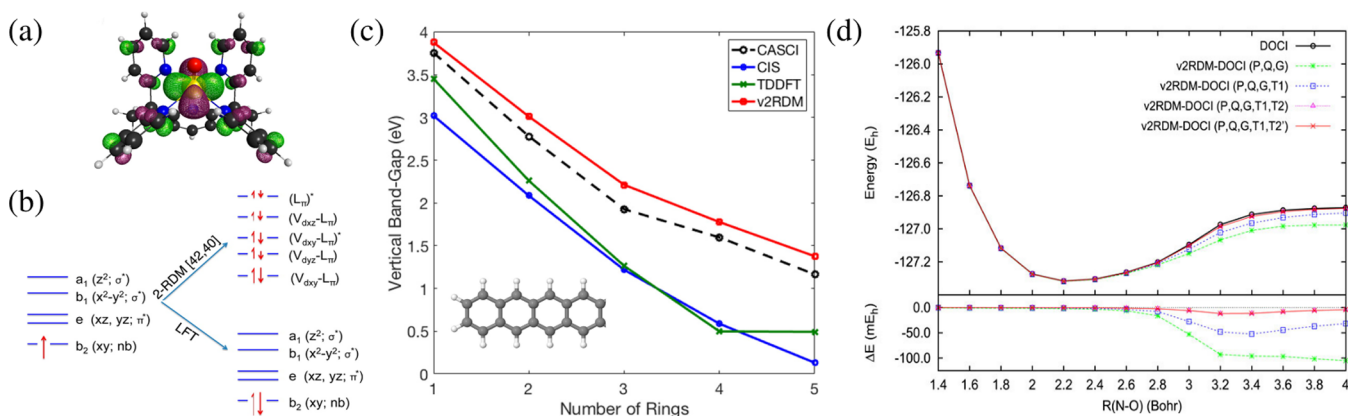


Figure 6. Applications of different flavors of the variational 2-RDM method and N -representability conditions. (a) Electron density contour plot of the highest occupied molecular orbital in vanadium(III) oxo determined from a [42,40] active space variational 2-RDM method showing the additional electron distributed over the ligands. Reprinted with permission from ref 7. Copyright 2016 American Chemical Society. (b) Electronic pictures for the vanadium(IV) oxo complex (left) and vanadium(III) oxo complex (right) with the upper panel showing the results from the [42,40] active space variational 2-RDM calculation and the lower panel showing the traditional results from ligand field theory. Reprinted with permission from ref 7. Copyright 2016 American Chemical Society. (c) Vertical band gap for the acene chains of length one to five comparing CASCI, CIS, TDDFT, and the ES-2RDM method using a π orbital active space. Reprinted with permission from ref 215. Copyright 2018 American Chemical Society. (d) Dissociation curve of the NO^+ molecule comparing the doubly occupied configuration interaction method with the variational pair 2-RDM method using DQG and various DQGT constraints. Reproduced with permission from ref 216. Copyright 2018 AIP Publishing.

where ${}^N D$ is the N -particle density matrix and Ψ is the wave function. The N -particle density matrix is the same size as the wave function, so it would provide few computational advantages over using the wave function directly; however, since electrons interact pairwise, a natural object to consider is the 2-electron reduced density matrix (2-RDM),¹⁵³

$${}^2 D(1, 2; 1', 2') = \int \Psi(1, 2, \dots, N) \Psi^*(1', 2', \dots, N) d3 \dots dN \quad (10)$$

where the elements are given by

$${}^2 D_{kl}^{ij} = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | \Psi \rangle \quad (11)$$

where second quantization notation is used and \hat{a}^\dagger and \hat{a} are the fermionic creation and annihilation operators, respectively. The 2-RDM represents the probability of two electrons interacting in a field of $N - 2$ electrons. While one can obtain a 2-RDM from any wave function by contraction or integration, not every general two-electron density matrix corresponds to an N -representable wave function. To ensure that a 2-RDM represents a physical N -particle system, the 2-RDM must satisfy additional constraints known as N -representability conditions.^{154–160} Advances in semidefinite programming (SDP) and the derivation of a formal hierarchy of ensemble N -representability conditions on the 2-RDM have led to recent applications of 2-RDM theory to important problems in the study of strongly correlated molecules. Progress has also been made in the study of pure N -representability conditions of the 1- and 2-RDMs.^{161,161–170}

For practical applications, an approximate set of necessary constraints are the 2-positivity DQG constraints,^{157,171}

$${}^2 D \geq 0 \quad (12)$$

$${}^2 Q \geq 0 \quad (13)$$

$${}^2 G \geq 0 \quad (14)$$

where ${}^2 Q$ is the two-hole RDM, ${}^2 G$ is the particle–hole RDM, and $M \geq 0$ implies that the matrix M has non-negative

eigenvalues or that the matrix must be positive-semidefinite. These constraints are physically motivated as the probability of finding two particles, two holes, or one particle and one hole must always be non-negative. It should be noted that while the DQG-positivity constraints are often sufficient for relatively accurate electronic structure calculations, they are a subset of the exact N -representability conditions.^{160,171}

Several methods utilize the 2-RDM to determine ground and excited electronic states, including variational and parametric^{172–186} 2-RDM methods as well the solution to the anti-Hermitian contracted Schrödinger equation.^{187–197} Here, we will focus on the variational 2-RDM method, which is particularly useful in capturing strong correlation in systems important to molecular chemistry and condensed-matter physics.^{15,198–205}

The variational 2-RDM method consists of variationally minimizing the energy of a system as a linear functional of the 2-RDM,

$$E = \text{Tr}({}^2 K {}^2 D) \quad (15)$$

where ${}^2 K$ is the two-body Hamiltonian under N -representability constraints.^{155–160,206–211} The energy produced from this constrained variational minimization is a lower bound on the ground-state energy.¹⁶¹ While the DQG constraints in eqs 12–14 are generally sufficient for relatively accurate electronic structure calculations, more complete sets of constraints have also been explored, including the three-index T_2 constraint which requires that $T_2 \geq 0$.^{158,160,212} Constraining these matrices to be positive-semidefinite requires the use of a form of convex optimization known as semidefinite programming.^{159,213,214} Beyond this application to electronic structure theory, SDPs are important in several applications, including the max-cut problem, economics, and combinatorics.²⁰³ In the context of variational 2-RDM methods, recent advances in SDP algorithms²⁰³ yield a scaling of N_{orb}^6 and N_{orb}^9 , for DQG and DQG with T_2 conditions respectively, providing a substantial improvement over wave function approaches to electronic structure calculations with exponential scaling.

The variational 2-RDM method has also been implemented as a replacement for the wave function calculation in active space methods such as CASSCF^{34,217,218} and DOCI.^{219–221} In the CASSCF framework, partitioning the orbitals into core, active, and valence allows for the variational algorithm to consider only a subset of the total electronic space and consequently treat significantly larger systems. There are several examples of this in recent literature, including applications to quantum dots,^{201,222} organometallic compounds,^{7,223,224} conductivity and transport in molecular junctions,^{225–228} exciton condensation,²²⁹ and molecular periodic systems.²³⁰ One specific example is the investigation and explanation of experimental phenomena such as the reduction of a vanadium oxo complex.⁷ An active space consisting of 42 electrons in 40 orbitals, which approximates 10^{21} variables in the wave function framework, reveals a ligand-centered reduction produced through electron entanglement.⁷ The highest occupied molecular orbital (HOMO) for the vanadium(III) oxo complexes, shown in Figure 6a, demonstrates that the electron density is delocalized across the pyridine ligands. This result contradicts both ligand field theory and smaller active space calculations, which predicted metal-centered reduction as shown in the level diagrams of Figure 6b where the vanadium(IV) complex is shown on the left and the vanadium(III) complex on the right. This result demonstrates the capacity of the active-space variational 2-RDM method to predict electron transfer in chemical systems accurately when multireference effects are important in the ground-state wave function.

For many transformations in matter including photo-excitation processes, ground-state calculations are insufficient and capturing excited-state phenomena is critical. While some early work in the RDM community studied excited-state spectra for small molecular systems,^{231–234} recently these methods have been improved to accurately capture optical band gaps in larger strongly correlated molecules. Based on previous theories that use the ground-state 2-RDM along with the Hermitian operator method to calculate excited-state energies,^{231–233,235–238} a recent study provides an improvement through the use of a Hamiltonian-shifted regularization algorithm.²¹⁵ The excited-state 2-RDM method (ES-2RDM) was used to calculate the band gaps of acene chains of varying lengths, which are in closer agreement to the CASCI gaps than those from the time-dependent density functional theory (TDDFT) and configuration interaction singles (CIS), as shown in Figure 6c. Moreover, this method allows for the determination of excitation energies for larger molecules, such as optical dyes, which are important for optically sensing voltage in neurons²³⁹ with greater accuracy than comparable excited-state methods.²¹⁵ ES-2RDM has since been applied to the band gap trend in graphene nanoribbons,²⁴⁰ and shows promise for investigation into excited-state phenomena in large molecular and quantum material systems.

In addition the variational 2-RDM method has been used in the pairing framework, also known as DOCI or seniority zero, where only doubly occupied configurations are considered.^{95,216,219–221,241–244} While in the configuration interaction context, restriction to the doubly occupied space maintains exponential scaling, a similar restriction under the variational framework reduces the scaling from N_{orb}^6 to N_{orb}^3 .^{219,220} The computational advantage comes from increased simplicity of the structure of the positivity constraints under the pair restriction.²²⁰ Early work was dedicated to considering benchmark small molecules to test the limitations of such a stringent

approximation, showing that despite the importance of orbital selection and potential need for orbital optimization or rotation, the pair approximation in conjunction with the variational 2-RDM has the potential to be a powerful method.²¹⁹ There are two areas on which current research is focusing to improve the pair variational 2-RDM method. The first area of focus is determining the effects of utilizing N -representability constraints beyond the DQG conditions. Extensions from the two-index N -representability constraints to the three- and four-index N -representability constraints have been considered, the latter being used to consider the Heisenberg XXZ spin model of quantum magnetism.^{216,220,245,246} An example of the effect of increasing the order of the N -representability constraints on the variational 2-RDM method in the seniority zero space can be seen in the dissociation curve for the NO^+ molecule in Figure 6d.²¹⁶ As the molecule dissociates, all presented DOCI methods capture the correlation; however, it can be seen that with increasing N -representability constraints, the energy becomes increasingly similar to the full DOCI solution. This shows that increasing the N -representability constraints, and hence the computational cost, can systematically increase the accuracy of this method.²¹⁶ The second area of focus is orbital selection. Early work focused on orbital optimization;²¹⁹ however, this adds cost to the calculation, negating some of the speedup due to the pair approximation. One study replaced the orbital optimization procedure with an orbital localization procedure to treat hydrogen chains, acene chains, and cadmium telluride chains.²²⁰ The localization of the molecular orbitals allowed the pair variational 2-RDM method to be approximately size extensive, a trait that is lost when using the canonical molecular orbitals.

From extensions to CASSCF and DOCI, variational 2-RDM approaches leverage their polynomial scaling to reveal electronic structure, which can aid in the design and understanding of quantum correlated matter for applications in energy storage, qubits, and catalysis, among others. An exciting direction for the variational 2-RDM method is its recent adaptation for use on a quantum simulator.²⁴⁷ While there has been plenty of focus on the development of variational quantum eigensolver (VQE) algorithms, which will be discussed further in section 4.2, the majority of methods focus on the variational principle for wave functions. The analogous RDM variational principle requires N -representability constraints, which were shown to reduce the number of measurements required in VQE calculations²⁴⁸ and act as an error mitigation scheme.²⁴⁷ The N -representability constraints are imposed on the 1-RDM and the 2-RDM is then reconstructed. The pure N -representability constraints for the 1-RDM are sometimes referred to as the generalized Pauli constraints (GPCs), and have been an area of intensive research over the past decade. Coleman's ensemble N -representability conditions for the 1-RDM¹⁵⁴ mimic the Pauli exclusion principle,²⁴⁹

$$\sum_{j=1}^{\infty} n_j = N \quad (16)$$

and

$$0 \leq n_j \leq 1 \quad (17)$$

where n_j are the eigenvalues and N is the particle number. This means that the eigenvalues, or the natural orbital occupation numbers, must remain between 0 and 1, while their sum must equal the total number of particles in the system. While these are

fairly simple constraints, the pure state N -representability conditions have proven to be a more challenging topic. The pure state N -representability conditions are necessary and sufficient constraints placed upon the 1-RDM such that it represents a pure state, or a state that can be represented by a single wave function. The development of these pure N -representability constraints has been a topic of much interest due to their importance in quantum chemistry and quantum information theory. Early work was dedicated to these constraints for specific systems,^{250,251} such as the work of Borland and Dennis, which derived conditions for three fermions in six orbitals.²⁵¹ These constraints are

$$n_5 + n_6 - n_4 \geq 0 \quad (18)$$

with

$$n_1 + n_6 = n_2 + n_5 = n_3 + n_4 = 1 \quad (19)$$

where n_i are the occupation numbers of the 1-RDM from largest n_1 to smallest n_6 . These constraints are an empirical rule that are useful for three electron systems, such as H_3 or the lithium atom,^{16,164} but they do not provide a framework for systematic generalization. More recently, a systematic method for generating these 1-RDM constraints for systems beyond the three fermion case was proposed,^{252,253} as well as for the 2-RDM and general p -RDM.¹⁶¹ The geometry and physical relevance of these constraints have been studied,^{163,254,255} as well as the effects of the GPCs on the occupation numbers of atoms and small molecules,^{16,163,168,256,257} spin systems,^{258,259} control of entanglement,^{260,261} and methods such as the variational 2-RDM optimization¹⁶² and reduced-density-matrix functional theory (RDMFT).²⁵⁶ Recently, the three fermion constraints were verified on a quantum device as shown in Figure 7.¹⁷⁰ The

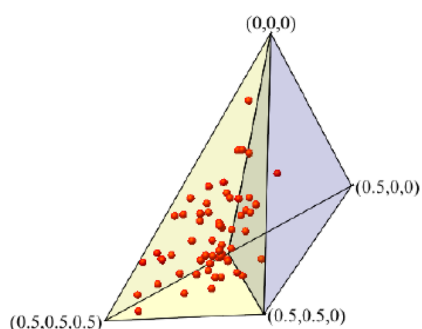


Figure 7. The entire convex polytope represents the orbital occupations of the 1-RDM allowed by the ordinary Pauli constraint, the yellow polytope represents the orbital occupations allowed by the Generalized Pauli Constraints. Each red point represents the three highest eigenvalues of a 1-RDM generated experimentally by a quantum computer. Reproduced with permission from ref 170. Copyright 2019 Springer Nature.

entire convex polytope represents the occupation numbers available for the 1-RDM under the ordinary Pauli constraints, while the yellow polytope represents the possible occupation numbers for the 1-RDM under the generalized Pauli constraints. The three highest eigenvalues of the 1-RDM as calculated on a quantum device are shown to be within the polytope defined by the Borland–Dennis constraints. This work was a novel demonstration that the GPCs on the 1-RDM are obeyed on a quantum device. The investigation into both ensemble and pure N -representability conditions is critical for variational 2-RDM

methods and reducing the errors of chemical calculations on quantum devices.

The generalized Pauli constraints have also been explored in the context of minimizing the energy functional in reduced density matrix functional theory.²⁵⁶ RDMFT is an alternative approach to electronic structure, which combines density functional theory, discussed in section 3.2 below, and the reduced density matrix methods discussed above.²⁶² In RDMFT, the energy is expressed as a function of the 1-RDM, though this energy functional is often minimized with respect to the eigenvalues, n_i , and eigenfunctions, ϕ_i , of the 1-RDM instead of the 1-RDM as a whole. This subset of RDMFT calculations is often referred to as natural orbital functional theory since the eigenfunctions and eigenvalues of the 1-RDM are the natural orbitals and natural orbital occupations, respectively. An advantage of this method over traditional density functional theory includes the explicit dependence of the kinetic energy term on the 1-RDM, the introduction of fractional occupation numbers,²⁶³ and the storage of more information in the 1-RDM.²⁶⁴ A notable drawback of this method is that instead of an eigenvalue equation, in the RDMFT framework the determination of orbitals is done through a computationally expensive minimization. Many methods have been considered to address the issue of natural orbital selection, including the use of nonlocal potentials to obtain natural orbitals;^{265,266} however the orbital determination is still the bottleneck of the calculation. Similar to traditional DFT, a plethora of research has been dedicated to designing and improving functionals.^{262,264,267–269,269–274} Through use of these improved and novel functionals, RDMFT has successfully been used to capture the dissociation of molecules,^{269,271,275,276} accurate band gaps,^{277–280} and phase transitions.^{277,279} Since its inception, many methods have extended the RDMFT framework²⁸¹ including local RDMFT,^{256,282,283} excited-state RDMFT, and time-dependent RDMFT.^{284–286} While we do not cover this method and its impact in-depth here, the references and reviews cited in this section are a good starting point for the interested reader.

3.2. Density-Functional Theory Approaches to Compute Quantum Materials

Another attractive wave function alternative is the method of density-functional theory. By exploiting the Hohenberg–Kohn theorem²⁸⁷ with the one-to-one correspondence between the ground-state density given by

$$n_0(\mathbf{r}) = \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_{n_c} \Psi^*(\mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_{n_c}) \Psi(\mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_{n_c}) \quad (20)$$

and the static external potential $v_0(\mathbf{r})$, it is possible to avoid the explicit construction of the many-body wave function and directly obtain observables by expressing them in terms of functionals of the electron density. Although formally DFT is an exact reformulation of Schrödinger's equation, in practice these functionals often remain unknown. The most prominent example that has to be approximated in practical calculations is the exchange–correlation (xc) functional. The quality and accuracy of the calculation is therefore determined by the underlying approximation for the xc potential.²⁸⁸

Many different routes have been explored to find approximations for this xc potential; however, we include limited discussion here as pertinent to the scope of this Review, and we refer the reader to refs 289 and 290 for comprehensive overviews of existing approximations. The local-density approximation (LDA)²⁹¹ is the most basic approximation of the xc potential,

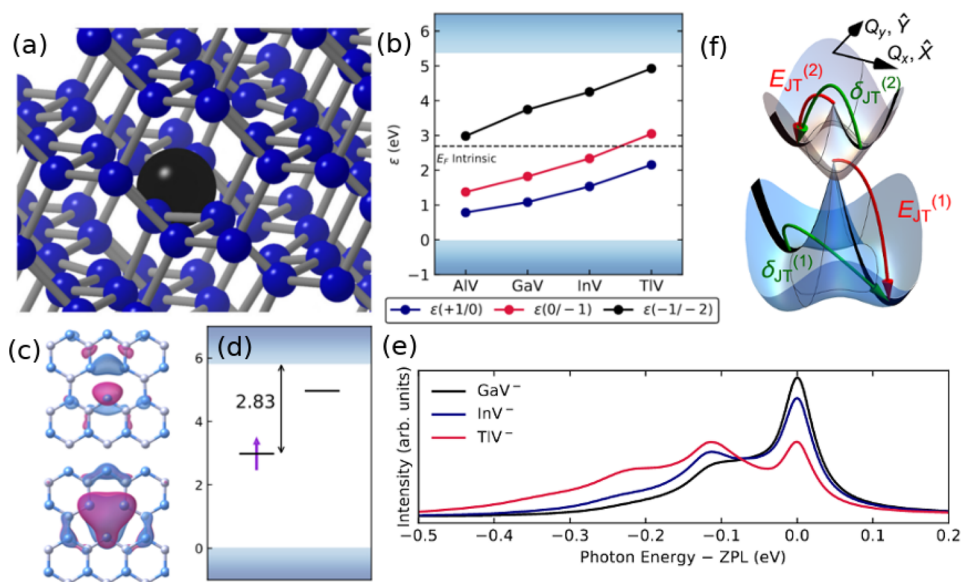


Figure 8. Defects in diamond and hBN using density-functional theory. (a) Pb atom shown in black in a split-vacancy configuration within the diamond lattice, consisting of carbon atoms shown in blue. Reprinted with permission from ref 305. Copyright 2019 by the American Physical Society. (b) Predicted thermodynamic charge transition levels for group III defect centers. GaV, InV, and TiV are found to be likely stable in the negative charge state for diamond samples with naturally occurring nitrogen doping, while AlV is more likely to exist in the neutral charge state. Reprinted with permission from ref 306. (c) Defect wave functions for ground and excited states in multilayer hBN for a nitrogen-vacancy defect (V_N) with the corresponding HSE based predictions shown in panel d reveal that complexes are found to offer more optically relevant defect bands within the gap. Reprinted with permission from ref 307. Copyright 2020 Springer Nature. (e) Predicted luminescence spectra for the group III emitters in diamond near room temperature conditions. Reprinted with permission from ref 306. (f) Potential energy surfaces computed for the product Jahn–Teller system in the excited state of group IV neutral defects in diamond. Reprinted with permission from ref 308.

where the electronic structure is considered as homogeneous and the functional dependency of the electron gas is then used. For the homogeneous electron gas, the exchange contribution can be calculated analytically, while the correlation contribution can be obtained to high accuracy by Monte Carlo methods.²⁹²

A natural extension to the LDA are approximations in which spatial derivatives or gradients of the density are also considered. Since the spatial derivatives are included in addition to the density at a particular point, this level of treatment is called “semi-local” and also referred to as a generalized gradient approximation (GGA). Popular functionals here are the PBE²⁹³ approximation including its extension to solids (PBEsol),²⁹⁴ which is currently one of the most widely used functionals in DFT calculations of quantum materials. With the development of the first semilocal functionals, DFT became popular for quantum chemistry applications.²⁹⁵ One way to systematically include more information into the xc functional leads to the inclusion of the kinetic energy component and is known as “meta-GGA”, with realizations such as the recent SCAN functional,²⁹⁶ which promises the accuracy of more computationally expensive approximations, such as hybrid-functional calculations, which effectively mix Hartree–Fock and DFT calculations with similar costs to a GGA functional.

Other recent developments with the design of efficient numerical algorithms have pushed the field toward the direct use of hybrid functionals. Well-known functionals include the HSE06²⁹⁷ and the PBE0 functionals^{293,298} for solid-state quantum material predictions, and the B3LYP^{108,109} functional for molecular quantum systems. Further developments pertinent to predicting quantum materials include dispersion functionals,^{299–302} which can account for dispersion or van der Waals interactions, range-separated functionals,³⁰³ and double hybrid functionals,³⁰⁴ which mix together Hartree–Fock

exchange, a GGA functional, and a many-body perturbation correction.

A recent and prominent example for a class of systems where density-functional theory has been successful but also displayed serious limitations, is in the understanding of the microscopic structure and dynamics of quantum defects in wide-bandgap semiconductor materials or “artificial atom qubits.” We show in Figure 8, numerical results obtained using DFT for defect emitters in diamond and monolayer hBN.

In this Thematic Issue, reviews by Zunger and Malý¹² on “Doping Quantum Materials” and by Kagan and Bassett³⁰⁹ on “Quantum Optical Nanostructures” discuss the recent progress in this field in more detail, and we refer the reader to these excellent reviews. Here we will focus on the computational and algorithmic advances and opportunities in this growing field.

3.2.1. Predicting Artificial Atom Qubits in Solids. Point defects in solids, including defect centers in silicon carbide (SiC),^{310–334} point defects and dopants in 2D transition metal dichalcogenides,^{335–352} nitrogen vacancy (NV)^{353–356} and silicon vacancy (SiV)^{357,358} centers in diamond, or single defects in hexagonal boron nitride (hBN),^{307,359–380} among others,^{381–383} have seen rising attention in recent years.^{384–388}

These systems have been identified as promising systems for a wide range of quantum information applications, such as sensing and metrology,³⁸⁹ computing,^{390,391} and use as quantum repeaters for long-range quantum networks.³⁹² The negatively charged nitrogen vacancy center in diamond with a spin triplet ground state is probably the most prominent one out of this list and has been long studied and demonstrated in many applications, including refs 354 and 393–419. The NV center possesses both long-lived spin states and high-fidelity spin–photon interfaces, which can enable quantum networking protocols, and has been theoretically studied, for example, in

refs 420 and 421. Despite these successes, there are also some drawbacks connected to the NV center. In particular, the optical applications of the NV center remain a challenge due to low quantum efficiencies, with weak emission into the zero-phonon line (ZPL). These limitations have spurred a theory-driven search for alternative quantum emitters.

In the diamond host lattice, in addition to the NV center, group IV quantum defects have been recently reported sparking experimental and theoretical studies. Both the NV center and the group IV centers replace one of the carbon atoms by a vacancy and an additional carbon atom by the corresponding element. While in the NV center, the nitrogen atom stays at the position of a carbon site, in group IV elements, the substitutional atom moves between those two carbon sites, as shown in Figure 8a for the PbV defect. The inversion-symmetric split-vacancy structure of the group IV elements results from the defect adopting a D_{3d} point-group symmetry. The inversion symmetry means the defect has no permanent electric dipole moment, which makes their optical transition frequencies less sensitive to electric field noise, which is often found for defects near surfaces.⁴²² In addition, they show more efficient emission into the zero-phonon line than the NV. Recent experimental advances have observed the negative charge state of these defect complexes, that is, SiV^- , GeV^- , SnV^- , and PbV^- ,^{305,423–438} which have also been characterized theoretically.^{439–441} The neutral charge state of the SiV has also been observed experimentally.^{358,442–444} One fewer electron than the SiV^- gives rise to a spin triplet ground state reminiscent of the NV center. A recent study also explores the excitonic excitations of SiV^0 and SiV^- .⁴⁴⁵ While SiV^0 requires the doping of the diamond host with boron impurities for thermodynamical stability, more recently, group III-related complexes in diamond have been theoretically proposed³⁰⁶ some of which are predicted to be stable in diamond intrinsically without the need for additional doping, as shown in Figure 8b. Single photon emission has also been explored for defects in 2D materials, in particular for hBN.^{359–361} We show a representative example, the V_N defect, in Figure 8c,d, where the defect is the result of a missing nitrogen atom.

From a computational perspective, these systems can be described using density-functional theory on the PBE or HSE06 level, using large supercells to characterize their ground-state behavior. With the inclusion of excited-state properties, photoluminescence spectra can be predicted,^{446–450} as shown in Figure 8e for the group III defects in diamond. Descriptions of other prominent interactions, for example, electron–phonon coupling, may be necessary for accurate predictions of ground- and excited-state properties. In particular, some of these systems show a prominent Jahn–Teller effect,^{308,420,421,439,451–453} demonstrated in Figure 8f. To include these electron–phonon coupling interactions, these systems have been described by model Hamiltonians parametrized using DFT data. To describe the excited-state manifold, the method of constrained DFT (ΔSCF), which consists of promoting an occupied to an unoccupied orbital, can be used but is limited to weak correlations and low-lying excited states.^{308,439}

The Jahn–Teller interaction is one instance of electron–phonon coupling and can be extremely important for accurate predictions of solid state defects and periodic structures, as well as molecules. In the diamond defects mentioned, such as NV and SiV, localized electronic orbitals can be energetically degenerate. When such degenerate orbitals are unequally occupied, there exists the possibility that a symmetry-lowering

nuclear distortion can push the system to an overall lower energy state, as first outlined by Jahn and Teller.⁴⁵⁴ The potential energy surface depicted in Figure 8f shows one type of Jahn–Teller landscape, where the coordinate axes represent directions along particular nuclear displacements associated with the Jahn–Teller distortion. The basic idea of this potential energy surface is common for all Jahn–Teller-related phenomena: at the high-symmetry configuration (where $Q_x = Q_y = 0$), the total energy is a local maximum, and a low-symmetry configuration is energetically preferable. There can exist distinct energy minima, as shown in Figure 8f; however in general the potential energy landscape resembles a Mexican hat. The distortion requires coupling of associated vibrational modes and overall the interaction is formulated as a case of electron–vibrational (or electron–phonon) coupling.

The correlated nature of the electronic and nuclear degrees of freedom in Jahn–Teller systems can be especially important for correct predictions of not only energy levels but also observables. As described in ref 455, *dynamic* Jahn–Teller distortions, in which case the system effectively exists in a superposition of the low-symmetry minima, can lead to quenching of observables associated with electronic operators. This is due to the strongly correlated nature of the electronic and nuclear degrees of freedom, which strongly couple to form a hybrid vibrational and electronic (“vibronic”) system. Electronic observables can be strongly altered when acting on such vibronic states, for example, the quenching of spin–orbit interaction. Accurate modeling of this Jahn–Teller problem has been crucial to predicting level structures and splittings consistent with experiment,^{439,456} and likewise will be important for predicting properties of novel emitters^{306,308} and molecular qubits going forward.

The Jahn–Teller interaction is one example of a variety of important electron–phonon interactions that can be critical for correct prediction and understanding of correlated quantum materials. In these electron–nuclear correlated systems, the nuclear degrees of freedom cannot be ignored. Phenomena that can emerge from this include things like charge density wave (CDW) distortions, which can result in a symmetry-breaking distortion in periodic systems that can alter the electronic properties.^{457–462} Laser-induced phonon excitation can be used to induce novel electronic properties and phenomena in general (see section 3.4). Electron–phonon interactions can also be crucial for understanding superconductivity in quantum materials.^{463–470} These phenomena can also be modulated by doping, which is covered in greater detail in the corresponding Review by Zunger et al.¹²

Importantly, these phonon-related effects are often temperature dependent. Thus, accurate models and understanding of these phenomena are important for understanding possible finite temperature effects associated with these systems. Theoretically describing these types of interactions is challenging, as at the heart of most quantum chemistry and materials calculations is the Born–Oppenheimer approximation⁴⁷¹ that allows the separation of the electron and nuclear degrees of freedom. In situations where nonadiabatic effects are important, these effects can be included in dynamical and time-dependent cases by explicitly including the nuclei in the calculation, for example, with the Ehrenfest or surface hopping approaches or other methods, such as the exact factorization approach⁴⁷² or conditional wave function approach.⁴⁷³ More generally, a variety of theoretical approaches based on first-principles frameworks to describe electron–nuclear interactions exist, such as generalized

density-functional theories,^{474–479} the nuclear-electron orbital (NEO) DFT,⁴⁸⁰ coupled cluster,⁴⁸¹ or density-functional perturbation theory for electron–phonon interactions.^{468,482–484}

For systems where strong electronic interactions become important, a different approach is essential. One augmented DFT method to treat more strongly electron-correlated materials within a density-functional theory framework is the LDA+U approach. In its standard formulation, the DFT+U method is an empirical method, in which the effective on-site Hubbard U parameter is chosen prior to the calculation. More recently, this approach has been extended, and it became possible to evaluate the values of U and J *ab initio* and self-consistently through linear-response techniques^{485–488} and with the ACBN0 functional.^{489,490} Along similar lines, in recent years the idea to combine the method of DFT and DMFT^{122,491} has seen attention to describe strongly correlated materials, in particular the strong Coulomb repulsion for materials that feature partially filled d or f shells. This hybrid method is based on the assumption that for the specific material it is possible to separate the electronic degrees of freedom into a weakly correlated part that can be treated on the DFT level and a correlated part, which has to be treated with a different method. These two methods are then combined in a self-consistent way. Such a treatment can be expected to be important for systems, where these stronger correlations induce a redistribution of the electronic structure.⁴⁹²

Excited and nonequilibrium states play a fundamental role in quantum materials. The following section will focus on classical approaches that allow access to excited-state properties of quantum materials. Later in this Review, we will discuss approaches for computing relevant excited states of quantum materials on quantum computers.

3.3. Time-Dependent Density-Functional Theory and Quasiparticle Methods for Correlated Quantum Matter

In many cases of experimental relevance, it is necessary not only to obtain ground-state properties of the system of interest but also to access excited-state properties. A straightforward calculation of some of the properties of low-lying excited states, such as ionization energies, can be obtained by the Δ SCF or constrained DFT approaches mentioned in section 3.2. In general, a constrained DFT calculation can be used to calculate the lowest state of a specific symmetry. Therefore for ionization energies, Δ SCF is strictly defined. However, for charge neutral excitations, Δ SCF is only strictly defined for the lowest states of different symmetries. Nevertheless, Δ SCF may also be applied to sets of low-lying excited states by promoting occupied orbitals to unoccupied orbitals. In practice, such a procedure can work well for triplet states that are well described by a single Slater determinant, while it may fail for singlet states that show multiconfigurational character.

A more general density-functional approach to access excited-state properties is time-dependent density-functional theory (TDDFT).^{493,494} Although TDDFT is in principle valid for any out-of-equilibrium system, in practice TDDFT has been particularly successful in the linear-response regime, from which excitation energies and transition dipole elements for many-body systems can be obtained. The solution of these equations can either be obtained in the time-domain by an explicit time-propagation⁴⁹⁵ or in frequency-domain by solving a pseudoeigenvalue equation.⁴⁹⁶ Practically, to calculate the time-dependent properties of real systems, we rely on approximations

for the exchange–correlation potential $v_{xc}(\mathbf{r}, t)$, and the validity of the calculation depends on these underlying approximations.⁴⁹⁷

In TDDFT, the simplest but also most widely used approximation is the adiabatic approximation.⁴⁹⁵ In the adiabatic approximation, we assume that the system adiabatically follows the external perturbation and uses functionals that have originally been developed for static or ground-state cases. The adiabatic approximation is justified for certain quantum systems, where the time-dependent density does not change too rapidly. TDDFT is most successful in the linear response regime^{496,498} where the change in the electron density, $\delta n(\mathbf{r}t)$, and the external perturbation, $\delta v(\mathbf{r}t)$, are connected via response functions $\chi_R^{(1)}(\mathbf{r}t, \mathbf{r}'t) = [n(\mathbf{r}t), n(\mathbf{r}'t)]$. In linear-response theory, the adiabatic approximation restricts the calculation to the single excitation manifold and practical calculations can be performed using the eigenvalue (Casida) equation.^{496,498} These equations have also found application for artificial atom qubits, for example, in diamond⁴⁹⁹ and hBN.⁵⁰⁰ The latter study compares the accuracy of a variety of different exchange–correlation functionals and quantum chemistry methods for defects with the conclusion that simpler GGA functionals are typically not accurate, but hybrid functionals such as HSE06 can accurately capture the energetics of such states, if the system is a triplet state. To accurately describe the dynamics of strongly correlated systems out-of-equilibrium using TDDFT, recently the ACBN0 functional has been extended to the time domain. For example in ref 501, it has been shown that the absorption spectra of transition metal oxides, such as NiO or MnO, are well reproduced by TDDFT+U simulations. DFT and TD-DFT methods have been shown to be effective at describing out-of-equilibrium plasmonic excitations.^{502–509}

Beyond linear response, there remain different challenges within TDDFT. A key open problem is extending beyond the adiabatic approximation.⁵¹⁰ Although many studies have been devoted to the analysis and construction of the exact time-dependent exchange–correlation functional for one-dimensional⁵¹¹ and real-space systems,^{512,513} a simple, intuitive approximation remains unknown. More general DFT approaches are known to fundamentally underestimate the fundamental band gap, also called the band gap problem of DFT.^{514,515} Recent approaches such as the use of hybrid functionals or generalized Kohn–Sham approaches⁵¹⁵ have been successful in improving the accuracy of the band gap description. An additional challenge for DFT approaches is a correct description of excitons, the bound states of electrons and holes. Some studies have shown that in principle those excitations can be described with TDDFT.^{516,517} Recent work has included the development of stochastic approaches⁵¹⁸ to make TDDFT more computationally efficient.

A more rigorous framework to calculate excited-state properties and obtain a more accurate description of the band gap and excitonic effects of molecular systems is the many-body perturbation approach using the interacting Green's function (GW).^{519–527} The Green's function can be defined for a specific number of particles, for instance, the one-particle and two-particle Green's function are sufficient to extract information about the quasiparticle excitations and the optical responses of an interacting system. In practice, the Green's function can be defined in terms of the electron field operators, which leads to the Martin–Schwinger hierarchy. This can be reformulated formally by introducing the electronic self-energy $\Sigma(1,2)$. In a similar spirit as density-functional methods, the self-energy $\Sigma(1,2)$ can be divided into Hartree and exchange–correlation

parts by using the Hartree potential, v_H , and numerically approximating Σ_{xc} . In many-body perturbation theory the self-energy is routinely expanded using Feynman diagrams.⁵²⁸ By formulating the vertex correction to second-order, one finds an equation that can be seen as the linear-response formalism of the self-energy to a change in external potential leading to the so-called Bethe–Salpeter equation (BSE).^{521,529,530} These vertex corrections account for exchange–correlation effects between electrons and also includes electron–hole interactions.

Aside from shifts in predicted transition energies^{531–533} relative to DFT, electron–hole interactions can lead to bound collective excitations known as excitons. These may coalesce into more complex subsystems, such as bound pairs of excitons, biexcitons, and singly charged excitons or trions. The relevance of these collective states depends on the strength of the electron–hole interaction. In many two-dimensional systems, such as transition metal dichalcogenides, the importance of excitonic effects is very prominent, as the exciton binding energies can be on the order of electronvolts and both exciton and trion peaks have been observed experimentally.⁵³⁴ These interactions can be important for looking at behavior of the “bulk” electronic states across the 2D flake as well as localized defect-induced states and their excited-state transitions.⁵³⁵ While excitonic effects are particularly prominent in these 2D monolayers, they can also be important for considering optoelectronic properties in other materials and chemical systems.

Another useful aspect of *GW* with BSE is access to multireference excited states in quantum matter. One particularly interesting and timely application is in the case of defect states with excited-state singlets. The energetic positioning and interaction with the triplet subspace of these singlet states can be critical for understanding optical efficiency as well as achieving controllable spin-readout^{536,537} of defect states. Due to the inherent multireference nature of these states, methods beyond conventional DFT, such as *GW*(+BSE)⁵³⁸ or TDDFT are required to capture them. Altogether, these unique types of quantum interactions accessible within a *GW* framework makes it an intriguing method for future study and characterization of a variety of quantum materials. We anticipate many contributions in quantum materials for quantum information to emerge from these methods in future.

With this, recent theoretical and computational developments have made *GW*-based methods more computationally accessible. Conventional *GW* calculations require that the screened Coulomb interaction W and the noninteracting Green's function G are determined by a perturbative expansion over Kohn–Sham electronic states. The expansion requires explicit treatment of both occupied and unoccupied states, and often the expansion over unoccupied states yields slow convergence, such that hundreds of unoccupied states may need to be considered for converging a particular system.^{539,540} Recent work that achieves convergence without the need for treating so many excited states, done by solving self-consistent linear Sternheimer equations, has been theoretically demonstrated⁵⁴¹ and implemented in available codes.^{542,543} In addition, advances have been made using stochastic methods such that the computational cost of a “single-shot” G_0W_0 calculation scales linearly with the number of electrons ($\sim O(N_e)$).^{544,545} This is a notable improvement over standard approaches, where the scaling is between $O(N_e^3)$ and $O(N_e^4)$. With this improvement, efficient G_0W_0 calculations have been demonstrated for large systems

consisting of 10^4 electrons.⁵⁴⁶ The use of stochastic orbitals has also been applied to solving the Bethe–Salpeter equation,⁵⁴⁷ where again explicit calculations have been demonstrated with systems consisting of thousands of electrons.

In addition to bulk-like structures, *GW* and BSE approaches have also been developed and applied for finite molecular systems, including refs 548–554. Similar to periodic systems, these techniques generally improve excited-state quasiparticle energy predictions compared to conventional DFT and TD-DFT methods and can also reveal the importance of electron–hole correlations.⁵⁵⁵ *GW*-based methods can also be useful in understanding electronic interactions with other perturbations in a given system, such as phonons. The quasiparticle self-energy due to external perturbations can shift the eigenenergy of the state via the real part of Σ and can also contribute to the line width of the electronic state via the imaginary part of Σ . In all practical calculations of these self-energy contributions, a many-body perturbation theory approach is needed to describe the interaction. However, often the interaction itself is evaluated using semilocal, DFT-based techniques,^{468,556} which is not strictly translatable to a many-body description or quasiparticle self-energies. On the other hand, *GW* methods are naturally written in terms of self-energies and include nonlocal electronic effects. Recent work has outlined methods that incorporate phonon interactions into a *GW* framework in both periodic systems⁵⁵⁷ (denoted as *GWPT*) and molecules.⁵⁵⁸ The periodic case demonstrates that for the correlated superconductor $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, typical DFT-based approaches cannot capture the significant (>50%) enhancement of the electron–phonon interaction strength resulting from many-electron correlations.⁵⁵⁷

In general, the prediction of novel bulk quantum materials, point defects, or molecules requires methods that give an unbiased physical description of the system. The *GW*-based techniques can offer a powerful toolkit for accessing the optoelectronic response of these systems, including prediction of band gaps and effects of electron–hole correlations. In particularly correlated systems, the use of *GW* techniques extended to look at interactions with other perturbations such as phonons or electric fields may be critical, as possible correlations might have important feedback on the associated interaction strengths, which would not be otherwise captured in DFT-based approaches.

3.4. Light–Matter Control of Correlations in Quantum Materials

Driven by new experimental and theoretical advances, recently there has been a push to explore the strong coupling regime of light and matter, that is, a regime where quantum chemical systems and quantum matter are strongly coupled to the electromagnetic field. This regime of strong light–matter coupling opens many new directions by creating novel polaritonic quasiparticles and new states of matter, with promises such as the on-demand control of quantum systems.^{559–561} For a detailed discussion of opportunities in strong light–matter coupling from a photonics and optics perspective, we refer the reader to the reviews in refs 8 and 562–570. Our discussion is centered on theoretical and algorithmic advances in treatment of strong light–quantum matter interactions and opportunities to use such coupling in quantum information science.

Driven by experimental demonstrations in optical cavities⁵⁶² and nanophotonic resonators,⁵⁷¹ the strong coupling regime of

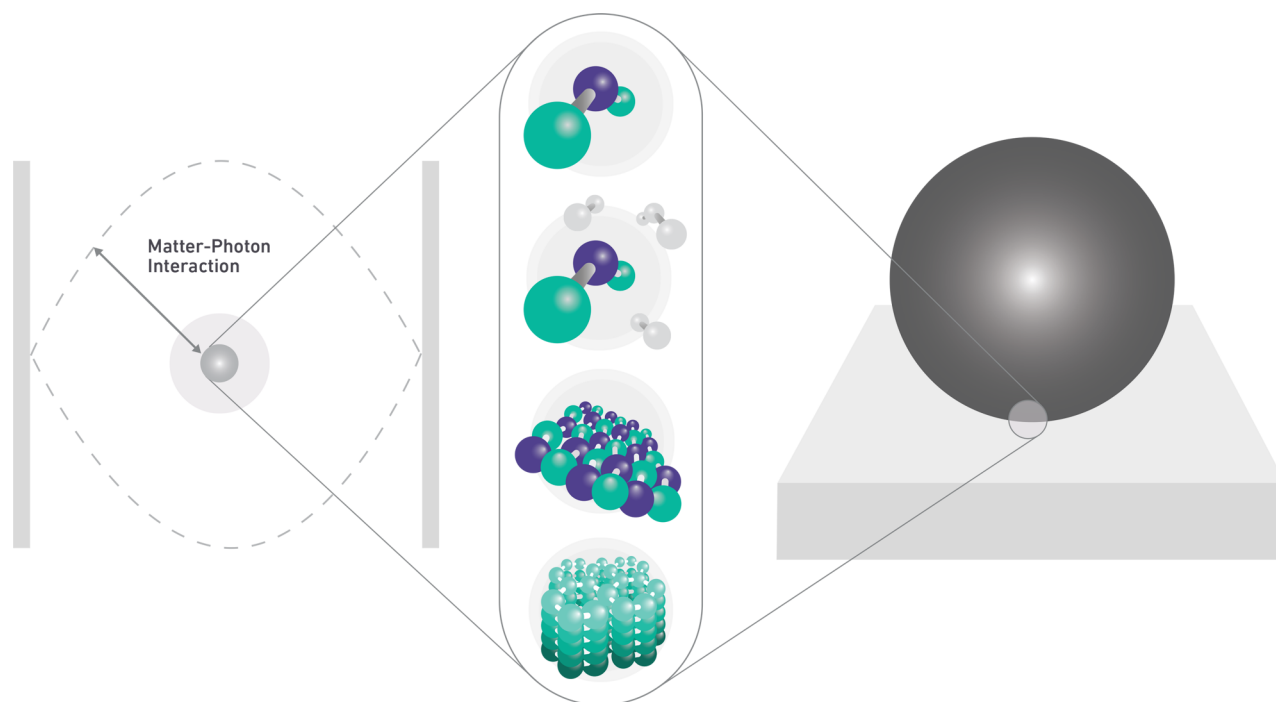


Figure 9. Schematics of prototypical configurations that reach strong light–matter coupling with an optical cavity on the left and a nanogap strongly coupled to nanophotonic excitations on the right. Strong light–matter coupling has been achieved experimentally for single molecules, collective coupling in ensembles of molecules, and two-dimensional and three-dimensional quantum materials as indicated in the middle.

many emitters has been explored, leading to a collective enhancement of the light–matter coupling and strong coupling down to the level of single emitters (Figure 9).⁵⁷² Different experiments have shown that this regime can be realized for a wide range of systems of chemical, physical, or biological interest. Examples of relevant recent studies include the demonstration of changes in chemical reactivity under strong light–matter coupling, such as the chemical reactivity for ground-state reactions⁵⁷³ and excited-state photochemical reactions⁵⁷⁴ and the suppression of photo-oxidation processes.⁵⁷⁵ Other examples besides reactivity examples include the realizations of hybrid organic–inorganic polariton LEDs,⁵⁷⁶ single-molecule tautomerization,⁵⁷⁷ the inversion of singlet and triplet excited states,^{578,579} femtosecond transient absorption spectra under ultrastrong coupling,⁵⁸⁰ the deep strong coupling limit in plasmonic nanoparticle crystals,⁵⁸¹ and intermolecular vibrational energy transfer.⁵⁸²

Recent theoretical studies in this field include the study of the effects of anharmonicity of vibrational modes on strong light–matter coupling,⁵⁸³ effects beyond the dipole approximation,⁵⁸⁴ surface-enhanced Raman spectroscopy,^{585,586} or the origin of asymmetric emission.⁵⁸⁷ Other effects studied are ensemble-induced strong light–matter coupling of single emitters,⁵⁸⁸ polariton-assisted remote energy transfer,⁵⁸⁹ electron transfer,⁵⁹⁰ or excitation transfer,⁵⁹¹ among others. The broad spectrum of effects seen in such light–matter control of quantum systems necessitates novel theoretical and computational approaches.

Previously many of these experimental results were described by using effective Hamiltonians inspired by work in the established quantum optics community. More recently, the field has seen a push toward the use of *ab initio* methods in quantum electrodynamics to describe electron–photon interactions. While traditional *ab initio* methods, such as those described in the prior sections, are capable of accurately

describing the electronic structure, the electromagnetic field is typically not accounted for. In cases of strong light–matter coupling, the treatments of electronic and photonic degrees of freedom become equally important, making it essential to go beyond conventional electronic *ab initio* methods.

The nonrelativistic electronic Hamiltonian can be formulated to account for transverse electron–photon interactions by changing to the length gauge and in dipole approximation as follows:^{592,593}

$$\hat{H} = \hat{H}_0 + \frac{1}{2} \sum_{\alpha} \hat{p}_{\alpha}^2 + \frac{1}{2} \sum_{\alpha} (\omega_{\alpha} \hat{q}_{\alpha} - \lambda_{\alpha} \cdot \mathbf{R})^2 + \frac{j_{\text{ext}}^{(\alpha)}(t)}{\omega_{\alpha}} \hat{q}_{\alpha} \quad (21)$$

where \hat{H}_0 represents the electronic Hamiltonian and \mathbf{R} represents the electronic dipole operator with $\mathbf{R} = \int d\mathbf{r} n(\mathbf{r})\mathbf{r}$. In the length gauge, the conjugated variable to the magnetic field is the electric displacement field that is given by $\hat{\mathbf{D}} = \sum_{\alpha} \sqrt{4\pi} \omega_{\alpha} \hat{q}_{\alpha}$. The electronic displacement field is coupled here in the dipole approximation where the bosonic operators $\hat{q}_{\alpha} = \sqrt{\frac{1}{2\omega_{\alpha}}} (\hat{a}^{\dagger} + \hat{a})$ and $\hat{p}_{\alpha} = i\sqrt{\frac{\omega_{\alpha}}{2}} (\hat{a}^{\dagger} - \hat{a})$ are connected to the electric field at the center of charge by $\hat{\mathbf{E}} = \sum_{\alpha} \sqrt{4\pi} (\omega_{\alpha} \hat{q}_{\alpha} - \lambda_{\alpha} \cdot \mathbf{R})$. The operators \hat{a}^{\dagger} (\hat{a}) create (destroy) one photon in mode α .

Starting from the Hamiltonian in eq 21, one can define a density-functional theory for electron–photon coupled problems as follows: Analogous to the electronic problem, a basic set of variables has to be chosen. In this case, these are the electron density, $n(\mathbf{r})$, and the electric displacement field, q_{α} . These basic variables then can be used to formulate a one-to-one correspondence between the basic (internal) variables and the

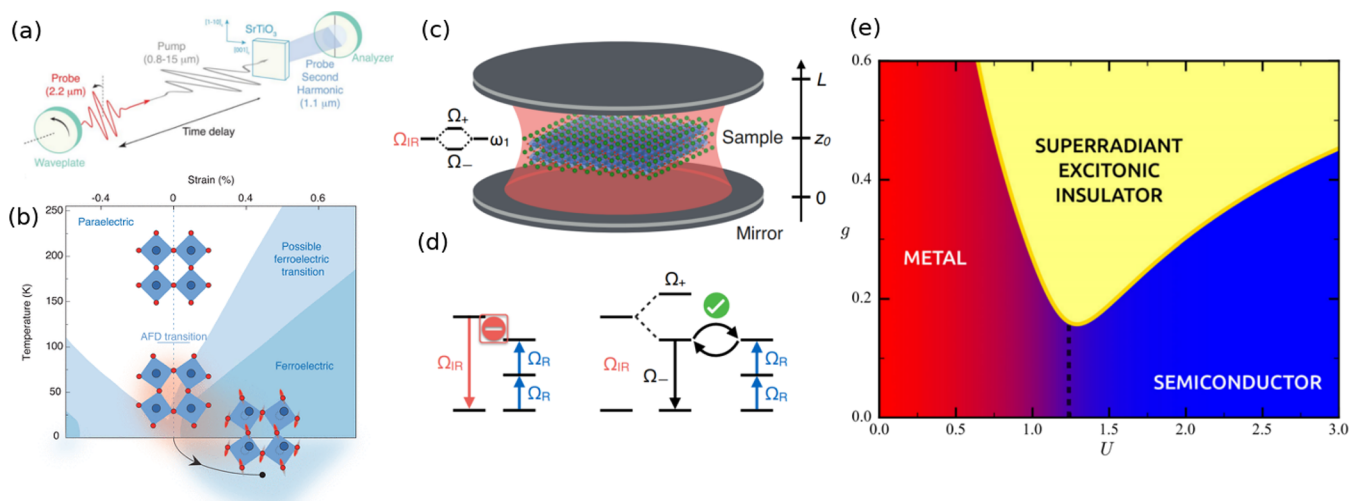


Figure 10. (a) Experimental setup for SrTiO₃ coherently excited with tunable wavelength pulses. Adapted from ref 625. Reprinted with permission from AAAS. (b) Dynamical ferroelectricity in SrTiO₃ phase diagram. While bulk SrTiO₃ is paraelectric, small amounts of strain can induce a ferroelectric transition. Alternatively, this transition can also be induced dynamically through vibrational excitation. Adapted from ref 625. Reprinted with permission from AAAS. (c) Cavity-mediated resonance in nonlinear phononics with the schematic setup of a sample material in a terahertz cavity. Adapted with permission from ref 626. (d) (left) Frequency mismatch between an IR-active and two Raman-active phonon modes hinders the transfer of energy between them and (right) formation of two phonon–polariton modes with frequencies Ω_+ and Ω_- due to the hybridization between an IR-active phonon mode leads to more efficient excitation transfer.⁶²⁶ Adapted with permission from ref 626. (e) Light–matter phase diagram as a function of the electronic interaction strength U and the light–matter coupling strength g with the novel superradiant excitonic insulator phase.⁶²⁷ Reprinted with permission from ref 627. Copyright 2019 by the American Physical Society.

external variables, $v_{\text{ext}}(\mathbf{r})$ and $j_{\text{ext}}^{(a)}$, that allows for the reformulation of expectation values as functionals of the internal variables. This density-functional theory is also called quantum-electrodynamical density-functional theory (QEDFT)^{592–595} and has been applied to electronic strong coupling in molecular systems for ground-state^{596–598} and excited-state problems,^{599,600} as well as vibrational strong coupling⁹ and cavity losses.⁶⁰¹

Following this work in QEDFT, other electronic first-principles methods were generalized to account for electron–photon interactions. Key examples include the Maxwell–Hartree–Fock wave function approach,⁶⁰² the multiconfiguration time-dependent Hartree method,⁶⁰³ the polaritonic coupled cluster approach,^{604,605} the exact factorization approach^{606,607} for electron–photon systems, a conditional approach,⁶⁰⁸ extensions of the Born–Oppenheimer approximation,^{609–611} and efficient Maxwell–Schrödinger propagation schemes.^{612,613} First-principles descriptions of electron–photon problems are still nascent. We expect that in the next few years, with joint experimental and theoretical advances, more accurate *ab initio* models will explore the realm of strong light–matter interactions for quantum chemical systems. There are still many open questions in this field, including what is the role of a realistic description of the optical cavity, including its imperfections, in an *ab initio* description, and questions about the precise change of the transition state in vibrational strong coupling experiments, the effect of solvents in these experiments, and effects beyond the dipole approximation.

New avenues to explore light–matter coupling can be expected if the rich possibilities of different electromagnetic environments are considered. More specifically, can we achieve strong coupling for regimes that are systematically different from a more simple one-mode coupling as is the case for optical cavities? These ideas can be explored by using the framework of macroscopic QED,^{614–616} which provides a consistent quantiza-

tion procedure for absorbing and dispersive media and allows at the same time for an accurate description of systems and their response if they are embedded in complex photonic structures. Using this scheme, the fundamental material variables are the microscopic charge currents in the medium and the quantized field operators, both of which have the correct commutation relations leading to Maxwell’s equations in the classical limit. In this description, the losses of the system are already intrinsically included in the field operators and do not have to be introduced as parameters. The same is true for electron–photon coupling strength and the broadening and line widths of electromagnetic modes and excitations.

Recent theoretical proposals^{617,618} and experimental demonstrations⁶¹⁹ have shown that strong light–matter coupling can be used to access ionizing transitions. Typically, transitions above the ionization threshold strongly hybridize with the continuum, leading to Fano line shapes. Strong light–matter coupling can now be used to hybridize with this transition, leading to a lower polariton state below the ionization threshold, effectively decoupling it from the continuum. In this way, new states can be made accessible. It will remain to be seen how those states can be explored for chemical applications such as novel reaction pathways in photochemistry.

One of the key open questions concerns the limit of light–matter coupling strength. Recent experimental progress has demonstrated the so-called ultra and deep strong coupling limit^{581,620} for plasmonic systems, going far beyond the early demonstrations of this limit in circuit QED,⁶²¹ thus pushing the experimental limit of accessible systems and consequently their theoretical description. Since changes in the electronic ground state have been shown to be rather small in regular strong coupling,⁶²² ultra and deep strong coupling are a very different case due to the scaling with coupling strength. In particular, probing these experimental regimes would benefit from a first-principles description.⁵⁹⁷ Recent proposals have used coupled

systems with high transition dipole moments⁶²³ to couple directly to excitations with weak transition dipole moments. It has been shown that single-molecule strong coupling can be achieved through coupling to an additional ensemble,⁵⁸⁸ which motivates engineering of the environment to effectively enhance the light–matter coupling.

Besides the use of optical cavities to control material properties, we can also expect novel applications for strong light–matter coupling in emerging quantum information science applications⁶²⁴ and in probing quantum matter. Quantum sensing of quantum matter in regimes of ultrastrong coupling is an exciting new area. There are two closely related concepts here: harnessing ultrastrong coupling (enabled by optical or superconducting circuitry) for the detection of intrinsic quantum material properties and correlations, and creating new states of quantum matter prepared via ultrastrong coupling to the cavity.

Next we turn our attention to the manipulation of quantum materials using strong light–matter interactions. This is a particularly attractive direction in engineering quantum matter for quantum technologies, as it enables the control at fundamental time scales and access to novel nonequilibrium states of matter.^{559,628,629} Ultrafast optical methods^{505,508} have been recently used as a new tuning knob to induce insulator-to-metal transitions,⁶³⁰ topological phases,^{631,632} ferroelectricity,^{625,633} and transient superconductivity in copper oxides⁶³⁴ and organic crystals.⁶³⁵ While this provides a tantalizing opportunity to explore new quantum phases, particularly in the case of transient superconductivity, key questions remain on the underlying excitation mechanisms, as well as on how to optimize and stabilize such short-lived electronic phases. Many of these studies explore the nonlinear interactions between phonon modes that govern the behavior of vibrationally highly excited quantum matter. Two of the most prominent examples of nonlinear phonon induced states include superconductivity far above the equilibrium critical temperature^{629,636} and light-induced ferroelectricity and ferroelectric switching.^{625,633} One example of how optical cavities can be used to control the redistribution of energy from a highly excited coherent infrared-active phonon state into the other vibrational degrees of freedom using nonlinear phononic interactions has been proposed theoretically in ref 626. In this work, the hybridization of the infrared-active phonon mode with the fundamental mode of the cavity induces a polaritonic splitting that can be used to tune the nonlinear interactions with other vibrational modes in and out of resonance, as demonstrated in Figure 10c. In a typical material, the IR-active phonon mode with frequency Ω_{IR} is out of resonance with two Raman-active phonon modes with frequencies Ω_{R} , preventing efficient coupling between them. By splitting the IR-active phonon mode in a terahertz-frequency cavity, one of the polariton branches is shifted into resonance with the Raman-active phonon modes, enabling efficient energy redistribution. This work broadens the range of materials in which resonant nonlinear phononic processes can be exploited to yield nonequilibrium states of matter. Concepts in cavity control of nonlinear processes enable a new pathway for quantum optical engineering of new states of matter. The analysis presented here is applicable to resonant coupling mechanisms between IR-active phonon modes and other fundamental excitations in solids and molecules.

One of the hallmarks of quantum materials is that their electronic ground state can be extremely susceptible to small perturbations. This susceptibility presents an opportunity to

engineer these quantum materials, for example, by small tweaks to their chemical composition, lattice structure, or symmetry, leading to a dramatically altered ground state and uncovering interfacially correlated quantum effects with dramatic changes to conductivity, superconductivity, and magnetism.

3.4.1. New Directions in QED Control of Correlated Quantum Materials. Research in this direction has been motivated by theoretical proposals and experimental results that suggest that placing materials in a cavity or other environment with a strong dielectric response can also substantially affect the many-body physics. This includes exciton–polariton condensates⁶³⁷ or superfluidity⁶³⁸ formed by hybrid quasiparticles composed of photons and excitons in semiconductors,⁶³⁹ driving a material through an excitonic insulator transition,^{627,640} polaritons in excitonic insulators,⁶⁴¹ the manipulation of the ferroelectric phase-transitions,⁶⁴² and nonlinear phononics.⁶²⁶ Recently, various studies have suggested an influence of strong light–matter coupling with different mechanisms on superconductivity.^{643–647} It has also been studied that an unconventional dielectric environment can enhance the transition temperature of superconductivity. The underlying idea of cavity-enhanced superconductivity is that by embedding a material in an appropriate dielectric environment, key modes may be changed in a way that is advantageous for stabilizing the superconducting phase. Further, the cavity modes can couple to carriers, serving as a new “boson pairing glue” and possibly leading to new kinds of superconducting states.⁶⁴⁵ This so-called cavity-mediated superconductivity is particularly appealing in nonequilibrium regimes, which may enable the field to attain nonthermal distributions. However, cavity-activated phenomena in superconductors remains an experimentally largely unexplored field with only very recent first experimental realizations.⁶²³ Inspired by recent developments on nonlinear phononics in optical cavities,⁶²⁶ other possible examples for light–matter altered effects can be expected not only in chemical reactivity, but also in other molecular relaxation mechanisms, such as intramolecular vibrational energy redistribution (IVR)⁶⁴⁸ in ground-state potential energy surfaces. Similar effects have been shown for excited-state relaxation processes⁶⁴⁹ and anharmonicities.⁵⁸³

3.5. Emerging Directions in Descriptions of Correlated Quantum Matter

Much like other areas in the physical sciences, ideas from machine learning and data science, in particular neural networks, are seeing more applications in capturing correlations in quantum chemistry and quantum material science. Ideas that have been already successfully realized include using neural networks as a representation for quantum states in electronic structure calculations⁶⁵⁰ for problems such as the Hubbard and Heisenberg models, and now even in chemistry for small molecules reaching chemical accuracy.⁶⁵¹ Molecular-orbital-based machine learning methods have also been applied to accurately predict post-Hartree–Fock energies in molecular systems.^{652–654} Along similar lines, deep neural networks^{655,656} have been explored as representations for quantum wave functions^{655–657} to accurately represent electronic correlations.^{652–654}

4. QUANTUM ALGORITHMS FOR QUANTUM MATTER

The focus in both wave function and density based electronic structure has been on reducing the exponential scaling of the N -body problem. While classical electronic structure theory has

many methods to address this problem as discussed in sections 2 and 3, all of these methods face the challenge of describing the intrinsically quantum mechanical nature of the problem using a classical representation, which can become impractical for highly entangled or correlated states. Because of this, many open problems are still far beyond the current classical computing capabilities. An alternative pathway toward a solution for quantum systems is the use of quantum devices, which leverage their inherently quantum-mechanical nature for computation.

The first quantum algorithms suited particularly for quantum system predictions appeared as early as the late 1990s with various attempts at simulating fermionic Hamiltonians. Recent developments and improvements of functional quantum hardware devices have re-energized the field, leading to both research and commercial interests in exploiting the inherent quantum properties of the machinery to achieve Feynman's original vision dating back to 1982.⁶⁵⁸ There has been much anticipation over the potential for quantum computers to be able to solve classically intractable chemical, physical, or combinatorial problems, increasingly so since the recent demonstration of quantum advantage using a superconducting device by colleagues at Google and NASA.¹ As they highlight and demonstrate,^{3–5} a co-design approach to the hardware and algorithms is critical to utilizing the advantages offered by small-scale noisy quantum devices. We note that there has also been compelling progress in cold-atom and ultracold Rydberg quantum “emulators”⁶⁵⁹ that are beyond the scope of this Review.

There is a considerable push in the quantum computing community to achieve algorithms with nonexponential complexity for strongly correlated systems with applications in excitonic quantum matter, many-body quantum states, large-scale entangled states, and high-temperature superconductivity. Each of these has remained a “holy grail” problem in condensed matter physics and quantum chemistry. Remarkably, despite decades of intense effort, we still lack a full theoretical understanding of the workings of high-temperature superconductors, thereby precluding rapid progress in raising the critical temperature from less than half of room temperature⁶⁶⁰ under ambient pressure. Notable recent developments under high pressure have demonstrated critical temperature up to 250 K.⁶⁶¹

This search for a theoretical description and an understanding of the phase diagram has animated large-scale research in quantum simulations of the Hubbard (or Fermi-Hubbard) model, presenting a high-reward application of quantum algorithms in correlated quantum matter. Tractable and accurate quantum algorithms to address these applications would be transformative not only for the quantum materials community but across the physical sciences.

Practical applications on current quantum devices are challenged by the susceptibility of the devices to various noise mechanisms, effectively limiting the number of operations that can be performed. To this end, research has been focused on hybrid quantum–classical algorithms that combine classical resources, which are much more established and error-tolerant, with quantum computation. For chemical systems, the resource estimates to use quantum computers to elucidate the reaction mechanism in complex chemical systems have been suggested to be within reach of near-term quantum devices.⁶⁶²

Recently, there have been several excellent reviews on the topic of quantum algorithms for quantum chemistry and materials science applications, including refs 663–666, to

which we refer the interested reader for an in-depth introduction to quantum algorithms from various perspectives. In section 4.1, we primarily focus on introducing the concepts of quantum computation for applications in quantum matter simulations. We then give an overview of recent progress on algorithm development for modeling physical systems using quantum and hybrid classical–quantum hardware suitable for the NISQ area in section 4.2. In section 4.3, we present a brief outlook on the field, including error mitigation schemes and protocols for scalable quantum networks. We recognize that this field is vast and fast-paced with important papers appearing daily; our Review captures key contributions to the field, constrained by our original motivation to highlight the potential of new quantum algorithms to discover entirely unexplored regimes of quantum matter.

4.1. Early Algorithms and Quantum Computation of Matter

Early work on quantum algorithms such as Grover's⁶⁶⁷ and Shor's⁶⁶⁸ algorithms brought to the forefront the potential for computational speed-ups due to quantum resources. A few years later the concept of quantum speed-ups was transferred over to physical and chemical systems such as approximation of partition functions for Ising spin glasses,⁶⁶⁹ calculation of thermal rate constants,⁶⁷⁰ and simulation of fermionic systems.⁶⁷¹ Around the same time, the quantum phase estimation algorithms (QPEAs) emerged.⁶⁷² However, these original algorithms faced the challenge of requiring very deep circuits. To successfully perform the necessary operations, error mitigation schemes on current quantum devices that are inherently noisy (NISQ devices) are insufficient, and fault-tolerant quantum computers would be essential.^{664,673} Despite these challenges, the advent of the QPEA triggered a plethora of algorithms applied to chemical and physical systems,⁶⁷⁴ including an algorithm for simulating many-body Fermi systems,⁶⁷⁵ followed by the first algorithm that allowed for the calculation of eigenvalues and eigenvectors of a local Hamiltonian.⁶⁷⁶ This novel approach allowed for the first calculation of static electronic structure properties of a system on a quantum simulator.⁶⁷⁶

An impressive push forward for the field of electronic structure was presented in 2005 when Aspuru-Guzik et al. proposed and validated an algorithm for calculating molecular energies on a quantum device.⁶⁷⁷ Using the FCI Hamiltonian on the quantum device and using the Hartree–Fock wave function as a reference, correlation effects were taken into account for small molecules.⁶⁷⁷ This algorithm proved to require only polynomial scaling in terms of system size, suggesting great potential for quantum speed up while treating quantum chemical systems. Further work was done by replacing the Hartree–Fock wave function with a wave function from MC-SCF to obtain an energy spectrum for molecular systems that included excited-state energies.⁶⁷⁸ These early quantum algorithms showed great potential toward more efficient modeling of electronic structure. However, their requirements of many qubits and large gate depth renders them impractical on existing NISQ devices. This obstacle inspired investigation toward hybrid quantum–classical algorithms, which can be computationally efficient by dividing the work between the robust classical devices and more noise-susceptible quantum devices. The theory, advances, and application of these algorithms are discussed in the next section.

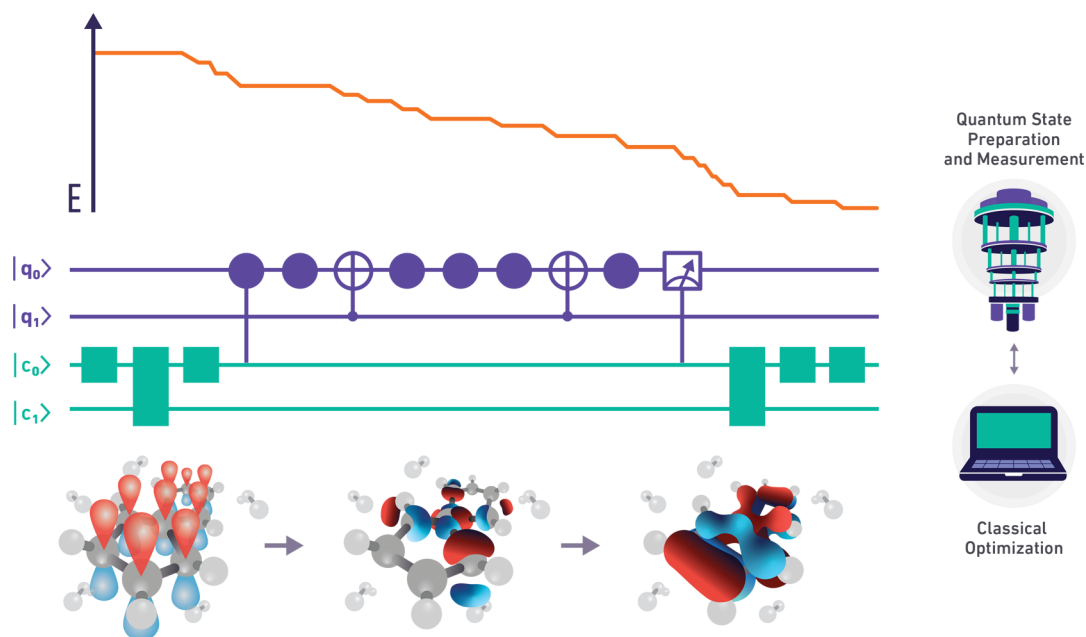


Figure 11. Generic hybrid quantum–classical algorithm where classical resources are used for optimization and quantum resources for state preparation and measurement. As the algorithm iterates, the molecular energy is decreased and the predicted molecular orbital density becomes more accurate.

4.2. Hybrid Quantum–Classical Algorithms

Currently, the majority of quantum algorithms relevant to physics and chemistry applications are hybrid algorithms. In these methods, part of the computation is performed on a classical device, typically a parameter optimization step, while the remaining part is done on a quantum device. Both parts of the calculation can interact or are iterated, when necessary. A general schematic of a generic hybrid algorithm is shown in Figure 11. In the figure, the rail diagram in the center shows a calculation using a classical device (teal squares), which generally corresponds to a classical initialization of the parameters of interest. Information is then passed to a quantum device (purple circles), which performs an additional calculation and is then measured. The classical device can read in the outcome of the quantum measurement and in the majority of cases, many such cycles are performed iteratively until a convergence threshold is obtained. Above the rail diagram, we show an energy diagram to demonstrate the iterative procedure, here the decrease of the system energy during the calculation for an arbitrary quantum mechanical system, while on the bottom of the figure an iterative improvement on molecular orbitals can be seen.

4.2.1. General Concepts of the Variational Quantum Eigensolver Algorithm. Early work in hybrid algorithms includes many-body simulation algorithms⁶⁷⁹ and calculations on the Hubbard model.⁶⁸⁰ More recently, the most widely used hybrid algorithm has been the variational quantum eigensolver (VQE), which is designed to variationally minimize the expectation value of the full molecular Hamiltonian based on the variational principle. This minimization strategy leads to solutions of eigenvalue problems by using classical resources for parameter optimization in an outer loop and quantum resources for quantum state preparation and measurement in an inner loop.^{681–684} Within this scheme, the VQE algorithm requires the definition of the system Hamiltonian and the specific parameters that can be optimized. One way to define these parameters is based on the classical unitary coupled cluster

(UCC) method^{102,103,685,686} discussed in section 2.2. The number of terms in the many-body Hamiltonian scales polynomially, and the number of possible excitations used to define the UCC wave function also scales polynomially. Since the Baker–Campbell–Hausdorff series does not terminate^{102,103} for UCC, its complexity is exponential on a classical device, and no general efficient implementation of UCC is known on classical computers. In contrast, this state can be prepared and measured efficiently on a quantum device. After initial state preparation and measurement of the expectation value on the quantum device for a specific initial guess, the classical computer can then be used via an optimization algorithm to provide a new set of parameters leading to a lower total energy. This procedure is iterated until a convergence criterion is met, resulting in the lowest eigenvalue of the Hamiltonian.^{681,682}

In practice, to map the electronic operators onto qubits, fermion-to-spin mappings,⁶⁸⁷ such as the Jordan–Wigner transformation,⁶⁷¹ parity transform,⁶⁸⁸ or Bravyi–Kitaev⁶⁸⁹ transformations, can be used. Other mappings, such as those based on ternary trees have been put forward recently.⁶⁹⁰ Once the electronic operators are mapped onto qubits, the UCC state can be constructed. To construct this state on the quantum device, the Trotter expansion is used,⁶⁹¹

$$e^{A+B} = \lim_{n \rightarrow \infty} (e^{A/n} e^{B/n})^n \quad (22)$$

where A and B are one- or two- particle operators contributing to the UCC operator. This expression is only exact if the operators A and B commute or in the limit of $n \rightarrow \infty$, and it therefore in general requires truncation. In practice it has been shown that even truncation to first order can often be sufficient to obtain accurate results, since the variational nature of the algorithm can mask the truncation error.^{692,693} However, in general first order Trotterization still requires a high gate complexity, which is one of the drawbacks of this approach. Multiple studies have been dedicated to investigating other VQE ansätze and general-

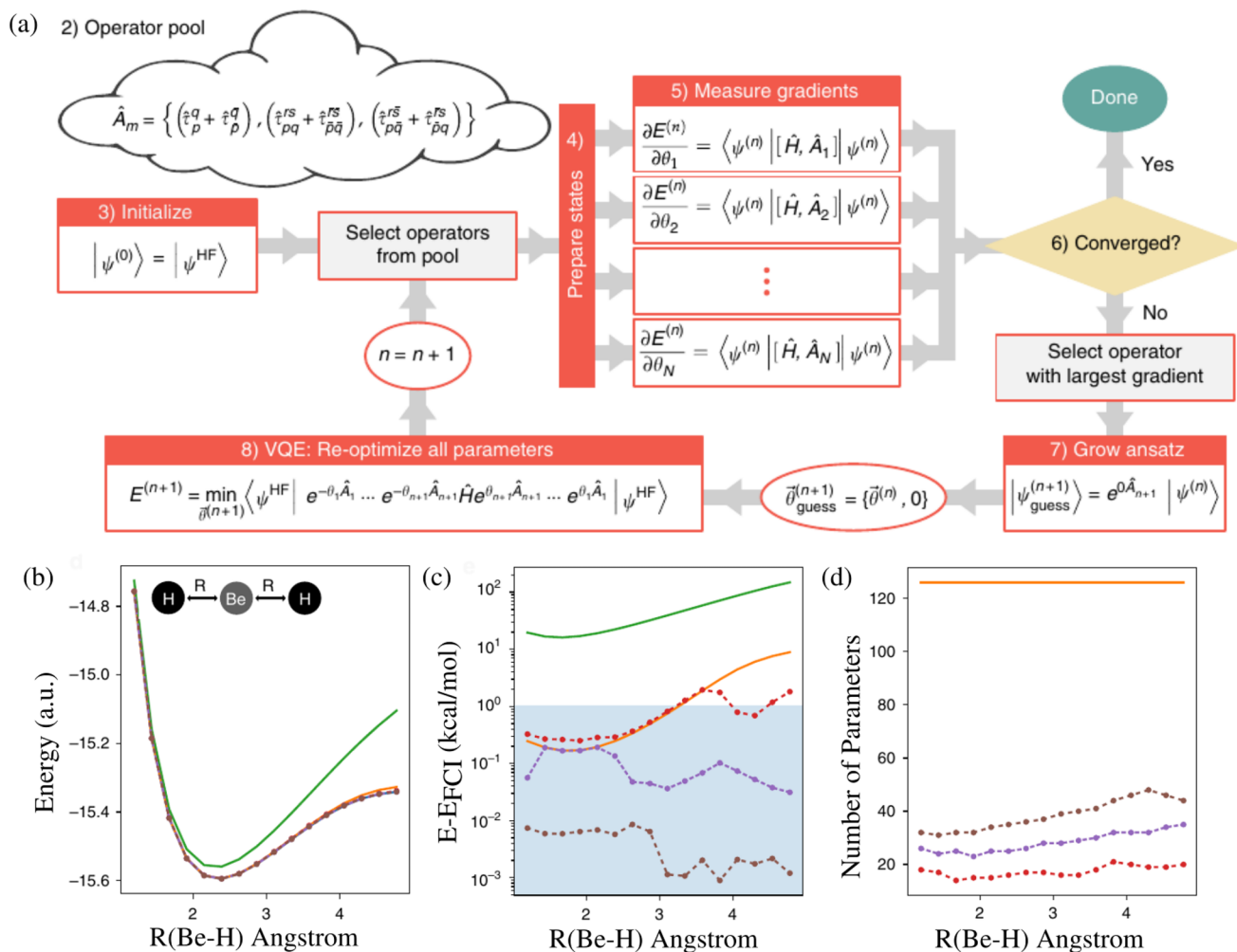


Figure 12. (a) Schematic depiction of the ADAPT-VQE algorithm where a collection of operators are defined in an “operator pool” to be used to construct the ansatz. The wave function is initialized, operators are selected from the pool, a trial state is prepared, and then the gradient is measured. If the convergence criteria is not met then the operator with the largest gradient is added to the ansatz for a new VQE calculation and the process is repeated. (b) Potential energy as a function of nuclear coordinate of BeH₂ in units of hartrees. (c) Error between the ADAPT-VQE energy and the FCI energy in kcal/mol for BeH₂. (d) Number of variational parameters required for the ansatz used in the energy calculation in panel b. Reproduced with permission from ref 693. Copyright 2019 Springer Nature.

izations,^{686,694} such as a VQE ansatz based on the particle preserving exchange gate to achieve excitations⁶⁹⁵ and constrained VQE schemes.⁶⁹⁶

In comparison with the early quantum algorithms discussed in section 4.1, a strength of the VQE algorithms lies in their use of shorter circuits with more measurements,⁶⁹³ allowing for adaptability to a wide variety of quantum hardware. Since its inception on photonic qubits, VQE has also been used on superconducting qubit^{683,697} and trapped ion devices.^{698,699}

Early experimental work on superconducting (SC) NISQ devices at IBM Research successfully produced potential energy surfaces using the VQE ansatz for small molecules, including H₂ and BeH₂.⁶⁸³ This was a major achievement for the field at the time; however, imperfections in the potential energy surfaces arose from the quantum calculations. While experimental setups and hardware can be responsible for some of these imperfections, this study inspired further theoretical method development to improve upon these methods. Many studies have focused on extending the VQE to increase accuracy, including state and ansatz preparation improvements,^{693,700,701} which will be the focus of the next section.

4.2.2. Extensions of VQE. A recent adaption of the VQE scheme has used a transcorrelated Hamiltonian that is connected to the original Hamiltonian by a similarity transformation, showing increased accuracy without the need for extra quantum resources.⁷⁰² Another such study aimed to increase the accuracy specifically for strongly correlated systems by allowing the system to determine a quasi-optimal ansatz. This method is referred to as the Adaptive Derivative-Assembled Pseudo-Trotter variation, or the ADAPT-VQE, and is outlined in Figure 12a.⁶⁹³ In this schematic, the first step is performed classically and therefore omitted from the diagram. However, it is the standard first step for VQE and involves computing the 1- and 2-electron integrals then transforming the fermionic Hamiltonian into a qubit representation. The ADAPT-VQE was demonstrated on several molecular examples, one being the BeH₂ molecule. The potential energy of dissociation, the error as compared to FCI, and the number of variational parameters required for the ansatz are shown in Figure 12b,c,d respectively. To date this method has been tested on a simulator and has shown substantial improvement toward the accuracy of the VQE algorithm for molecular dissociation energies.

VQE has also found applications beyond the established chemical systems, including strongly correlated quantum matter systems. In such systems, hybrid quantum–classical DMFT and DMET algorithms suitable for NISQ devices have been proposed and realized by using VQE as the impurity solver.^{703–706} Similar ideas have been applied using the constrained random-phase approximation approach⁷⁰² to investigate color centers with defects in wide-band gap materials, also discussed in section 3.2. While research continues to be dedicated to the improvement of the VQE method in terms of accuracy and efficiency, there also exist many extensions of the VQE algorithm to broaden the scope of applicability to different quantum system regimes including excited states, spin states, and energy derivatives.

Excited states play a fundamental role in quantum chemistry and condensed matter physics, including in predictions of reaction rates and optical spectra. Many extensions of the VQE algorithm exist to treat excited-state phenomena.^{681,682,697,707–709} One of the first such techniques was the folded spectrum method, which was proposed in the original VQE work some time ago.⁶⁸¹ While this method has the ability to successfully capture excited-state properties, it requires a quadratic increase in the number of terms in the effective Hamiltonian and consequently, a significant increase in the number of required measurements.⁷¹⁰ There are Lagrangian-based methods that require variationally minimizing the Lagrangian instead of the original Hamiltonian⁶⁸² to obtain an approximation for the excited state. The quantum subspace expansion (QSE) is yet another approach that has been popular in the last few years and is based on linear response theory.^{697,707} Essentially, after obtaining a wave function from a quantum channel (defined by a set of Kraus operators), a subspace of low-level excited states is approximated. The key drawback of the quantum subspace expansion is that the quality of the excited states (and corresponding spectra) obtained depends heavily on errors introduced by the linear-response expansions and on the chosen ansatz. However, an advantage of the QSE method is that it can be used as an error mitigation scheme, a topic that will be discussed in detail in section 4.3. Yet another excited-state extension of VQE is referred to as the witness-assisted variational eigenspectra solver,⁷¹⁰ which augments the objective function to include the energy and an approximation for the entropy. A control ancilla qubit is considered along with the trial state, with the control qubit acting as an “eigenstate witness,” where its entropy measurement nears zero if the optimized trial state is arbitrarily close to an eigenstate of the Hamiltonian. A tunable parameter is used to bias toward excited states; this parameter is set to zero for the ground state as we might expect and then is tuned for each successive iteration such that the resulting states correspond to approximate excited states of the systems. Using either an iterative phase estimation algorithm or a Hamiltonian averaging approach,⁷⁰⁷ the corresponding energies can be extracted. There are certainly other methods out there and this is a rapidly developing area at the vibrant intersection of quantum chemistry and quantum information science.

There has also been relevant work in extensions of VQE to be able to capture electronic properties of ions and different spin states as well as excitation spectra.^{696,707,708} One such example, referred to as the multistate contracted VQE, was able to successfully capture the transition energies and oscillator strengths in an 18-chromophore light-harvesting complex.⁷¹¹ Another interesting extension to the VQE algorithm is for the

treatment of nonequilibrium steady states,⁷¹² which has the potential to lead to the treatment of open quantum systems using quantum resources.

While energies are important properties for any quantum chemical or material system, the derivatives and gradients of these energies also provide valuable physical insight including optimal molecular geometries, partition functions, and vibrational frequencies.⁷¹³ By derivation of analytical formalisms and quantum circuits, the VQE algorithm has been extended to measure energy derivatives.^{714,715} A recent study has investigated thermodynamic properties of molecules by using VQE on a NISQ device to construct potential-energy surfaces.⁷¹⁶ These surfaces are used to construct a Morse potential to mitigate noise and provide vibrational energy levels on a classical computer. Using these parameters and the potential, the partition function can be computed as a function of temperature leading to thermodynamic observables of the molecule. These extensions broaden the scope of VQE by allowing access to these quantities more directly, which are critical to both electronic structure and chemical reactivity.⁷¹⁵ Moreover, these parameters can be obtained using similar quantum architecture and circuits as those used in the original variational calculation.⁷¹⁴

As previously mentioned a strength of the VQE framework is in its adaptability to a wide variety of quantum hardware. For successful adaptation across different platforms, optimization of an algorithm is crucial since parameters such as the number of qubits and circuit depth is currently limited. Moreover, the circuit structure and gate set availability need to be taken into account when implementing these algorithms on real devices. For variational quantum algorithms, quantum circuit structures often break the symmetry of the Hamiltonian.⁷¹⁷ To overcome this challenge, an adapted-variational scheme was proposed to restore the spatial symmetry through postprocessing classical application of a projection operator.⁷¹⁷ This algorithm showed increased fidelity of the ground state while adding versatility to the hardware by using the same ground-state circuit structure to approximate low-lying excited states.⁷¹⁷

One of the biggest challenges that quantum algorithms face is that increasing system size is generally associated with an increase in the required number of qubits and the circuit depth. Inspired by classical active space methods as discussed in section 2, a recent study approximated the core and virtual orbitals using a classical computer while utilizing a quantum device for the active space calculations.⁷¹⁸ Strategically chosen additional measurements make up for the accuracy lost due to the active space approximation. Through this method, the accuracy of a 20-qubit representation was matched with a 4-qubit quantum computer for the hydrogen atom.⁷¹⁸

When developing novel algorithms, validation and verification is important in part due to the high error rates and initially unknown nature of errors of NISQ hardware. This has led to interesting research questions in how to systematically benchmark results of quantum computations. Toward this goal, a two-electron ansatz was developed that uses the N -representability constraints of a two-electron system, discussed in section 3.1 to efficiently partition local and nonlocal degrees of freedom on the classical and quantum computer for a basis set of arbitrary size. The ansatz can be used for benchmarking small molecular systems and was used to evaluate 4- and 6-qubit simulations of H_2 and H_3^+ , respectively, on superconducting quantum devices.⁷¹⁹ The ease of classical simulation for the electron pair and related pair theories could serve as verifiable targets for

benchmarking molecular simulations as quantum devices continue to expand.⁷¹⁹

4.2.3. Beyond VQE: Other Hybrid Quantum–Classical Algorithms. A major drawback of the VQE algorithm is that it often requires high-dimensional optimization over a nonoptimal surface thus requiring rapidly increasing computational cost with increasing system size. While improvements continue to be made to the VQE algorithm to overcome this obstacle, a variety of alternative algorithms are emerging. One recently presented alternative approach is based on the classical anti-Hermitian contracted Schrödinger equation (ACSE), mentioned briefly in section 3.1. The ACSE is a contraction of the Schrödinger equation onto the 2-particle space and has been successfully used to capture strong correlation in atoms and molecules.^{187–197} Classically, this method is limited because it requires reconstruction of the 3-RDM; however, in the quantum analogue this dependency can be eliminated through the preparation of an appropriate state.⁷²⁰ This novel study introduces a quantum eigenvalue solver which solves a contracted eigenvalue equation for efficient, scalable molecular simulations on quantum computers that does not rely on derivative-free optimization. This method is benchmarked on IBM's quantum devices and a quantum simulator with the ground-state dissociations of H₂ and H₃, respectively. Due to its potentially short circuit depths and exponential speed-up over its classical counterpart, the quantum ACSE algorithm shows great promise for capturing strong correlation in molecules using quantum devices.⁷²⁰

The search for near-term quantum advantage has been highly focused on variational algorithms, one of the most promising being the quantum approximate optimization algorithm (QAOA). This algorithm leverages quantum computers to solve combinatorial optimization problems by encoding a cost function as an operator in the Hilbert space. QAOA uses ideas similar to VQE for classical optimization problems and has been shown to work for a variety of optimization problems, especially those in the NP-Complete regime such as the Max-Cut problem, or its extensions. The Max-Cut problem involves grouping of nodes in a graph into two subgroups by cutting their edges. These cuts are optimized in such a way that the added weights of the edges are maximized. This problem has been shown to be NP-complete and has many applications in network science and in statistical physics.⁷²¹ Some avenues of potential application in correlated matter include spin models, molecular structure problems, and other optimization frameworks relevant in condensed matter physics. The first quantum algorithm to tackle the Max-Cut problem was the QAOA algorithm.⁷²² Since the Max-Cut problem can be mapped onto a classical Ising Hamiltonian, it can also be solved on a quantum device similarly to the VQE method.^{723,724} Research on these quantum problems has in turn inspired developments of improved classical algorithms by exploiting parallelization.⁷²⁵ The variational nature of this algorithm means it includes generalized parameters that must be trained to match the problem instance, so repeated calls to a quantum device are necessary to traverse the parameter space and find global optima. Additionally, it includes an iteration variable that decides how many full applications of the operator are to be executed. This iteration variable increases with the size of the constraint problem, and thus the length of the quantum circuit does as well. Largely, research in this area has focused on a small number of iterations, mainly one or two due to the ability to find exact best parameters. Recent developments have been made when

looking at higher numbers of iterations and on how best to train parameters at given iteration levels and quantification of results versus other methods. One strategy for parameter training that shows promise is doing most or all training on a scaled-down version of the full problem in an attempt to save quantum resources while maintaining high-fidelity results.

In contrast to classical problems, defining a quantum advantage for problems in correlated quantum matter is not as straightforward and remains an open question. Many of the classical optimization problems can be mapped onto the Ising-spin Hamiltonian, which is diagonal in the underlying computational basis. One advantage that a quantum algorithm may offer over classical algorithms is the potential to avoid and escape local minima. However, we note that a quantum advantage for these problems is under heavy debate in the community.

While the primary focus of this Review is on correlated systems, since the ideas of VQE are general, that is, to solve an eigenvalue problem, the principles and similar ideas have found applications beyond electronic structure theory. A few examples include quantum algorithms solving sets of linear equations such as of the form $Ax = b$. It has been shown that quantum algorithms can solve such problems exponentially faster than classical algorithms.^{726,727} These ideas have also been extended to problems in data science with the least-squares fit⁷²⁸ and also extended to nonlinear partial differential equations.⁷²⁹

Besides the developments on universal quantum computers, there have been various efforts to realize adiabatic quantum computing,⁷³⁰ with realizations up to 1800 qubits based on annealing-based quantum processors. These devices can also be useful for quantum chemistry applications⁷³¹ in particular if other mapping schemes are used.⁷³² So far practical simulations of chemical systems remain limited for these devices.

4.2.4. Quantum Convolutional Neural Networks for Quantum Phase Classification. The emergence of NISQ devices has co-occurred with increased interest and progress in classical artificial intelligence and machine learning techniques. Neural network-based algorithms in particular have garnered considerable attention for their ability to learn complex patterns from very high dimensional data sets. Physicists have also sought out pure scientific applications of various machine learning algorithms, particularly in condensed matter physics, where algorithms have been trained to reproduce or even discover phase diagrams by probing complicated long-range patterns of entanglement and classical correlations in many-body quantum systems. Since the dimension of the Hilbert space of a quantum system grows exponentially with the number of qubits, a classical computer will be unable to perform computations on, or even store the state of a quantum system with a large ($N \gtrsim 40$) number of sites. Currently, there are NISQ devices containing more high fidelity qubits than can be simulated on a classical computer. We expect that the community will be able to extend or improve upon existing machine learning algorithms, as well as develop new algorithms, by taking advantage of these devices. This could enable learning tasks to be performed on large quantum and very large classical data sets. The quantum convolutional neural network (QCNN) is a hybrid quantum–classical algorithm with a structure similar to that of classical convolutional neural networks.⁷³³ QCNNs can learn the features of a quantum data set by performing a binary classification task on a nontrivial phase of quantum matter, and we expect such approaches to be realized on near term trapped-ion NISQ devices. An important reason to use a

trapped-ion device here is to leverage intermediate measurements, that is, to measure a fraction of the active qubits and condition subsequent operations on their measurement outcomes, needed for QCNNS to perform such classification tasks. Looking ahead, successful demonstration of a QCNN for classification on a quantum device will pave the way for development and implementation of novel hybrid quantum machine learning algorithms, which will likely take further advantage of intermediate measurement capabilities of trapped-ion devices, and other architectures.

4.3. Error Mitigation to Enable Practical, Near-Term Quantum Algorithms for Strongly Correlated Quantum Matter

One of the biggest challenges that quantum algorithms face is the transition from running on ideal quantum simulators to realization of these algorithms on actual “noisy” devices. While devices are continuously improving, they are prone to errors, decoherence, and noise. Ideally, scalable error correction techniques could be used to catch and eliminate errors; however, the computational cost of such a task is resource-intensive and currently impractical. A low-cost alternative is error mitigation or error resiliency schemes being built into algorithm design, leveraging algorithm-hardware co-design approaches. These improvements are critical toward the goal of using these devices to accomplish more complex tasks in computational quantum materials science. General error mitigation schemes include active error mitigation, where the impact of errors are artificially boosted and then the zero-error case is extrapolated.^{684,734–736} Many schemes have been proposed specifically to mitigate error while using hybrid variational algorithms to consider the properties of physical systems.

Several of these error mitigation schemes are motivated by the physical nature of the system of interest. One such method relies on the reduced density matrix approach²⁴⁷ as mentioned in section 3.1. This work recognized that the quantum computer measures the 2-RDM and can be assisted by physically motivated constraints placed on the system density matrix, referred to as the N -representability constraints as discussed in section 3.1. In this work, at every iteration of the VQE on the classical device, the occupation numbers of the density matrix are confined to obey the Borland–Dennis constraints prior to feeding an improved set of parameters back into the quantum device. The result of this procedure is a physically motivated error-mitigation scheme, and it has produced a state-of-the-art dissociation curve of the H_3 molecule, accurately predicting the Mott phase transition.²⁴⁷ A second physically motivated error mitigation scheme was presented in recent work that exploited the inherent symmetries found in physical systems.⁷³⁷ A symmetry of a system is an operator that commutes with the system Hamiltonian. Due to this commutation relation, the Hamiltonian can be block diagonalized within the eigenspaces of its symmetry. The system’s eigenstates can therefore be considered by performing the investigation within a single target eigenspace of the symmetry. Since the resulting eigenstates should remain within the target eigenspace, errors due to certain types of noise can be detected and discarded based on symmetry verification during or after the calculation. Symmetry verifications have been performed using multiple protocols and have been shown to successfully reduce the error due to noise, as benchmarked on the ground-state dissociation curve for a hydrogen molecule.⁷³⁷

A widely used error mitigation scheme is the quantum subspace expansion (QSE) technique, which was developed to explore the low energy excited subspace of a system and consequently mitigates the effects of decoherence.^{697,718,738,739} In this protocol, an estimate for the ground-state wave function is obtained from the VQE algorithm. A quantum subspace expansion is applied by measuring additional correlation operators to form an approximate matrix representation within an extended subspace. From this approximate matrix, low-lying excited-state energies and improved energies for the ground state can be obtained, while minimizing the errors that could arise due to the quantum channel.⁷⁰⁷ The QSE technique has also been used in conjunction with a superconducting-qubit-based processor to consider the ground and excited states of a hydrogen molecule.⁶⁹⁷ This protocol is outlined in Figure 13a,

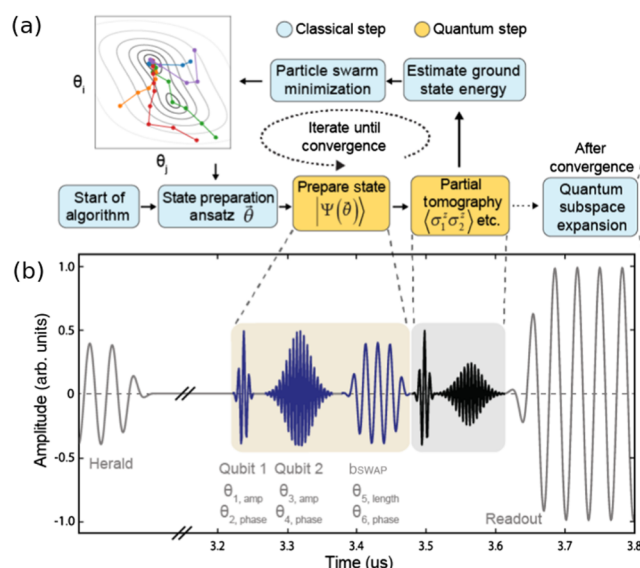


Figure 13. (a) Schematic of the QSE-VQE algorithm with classical and quantum resources shown in blue and yellow, respectively. (b) Typical qubit preparation and measurement sequence consisting of a projective heralding measurement, single-qubit and two-qubit pulses, tomography pulses, and finally a projective readout. Reproduced with permission from ref 697. Copyright 2018 American Physical Society.

where classical and quantum operations are shown in blue and yellow, respectively, and the QSE technique is used on the resulting converged state. The qubit preparation and measurement pulse sequence corresponding to the algorithm are shown in Figure 13b. This study showed successful error mitigation for incoherent errors, which further suggests potential for larger-scale quantum calculations.⁶⁹⁷

Small-scale partial quantum error correction schemes with near term applications, as well as ideas for full-scale error-correction, have been proposed. Many of these can be achieved by measuring syndromes of corresponding parity check operators and accordingly applying recovery operations, which are computed by a classical decoding algorithm. One class of examples are topological quantum codes, such as surface codes,^{740,741} which are implemented on a two-dimensional grid of qubits with local check operators. These codes offer great promise as they result in high error thresholds by introducing the concept of stabilizer qubits, yet they are currently still impractical due to their large overhead.⁷⁴²

Next we present two recent and exciting examples of practical quantum algorithms to capture quantum dynamics while leveraging error mitigation strategies. The first is predicting exciton condensates on NISQs. An interesting practical application of quantum computation in capturing correlated quantum matter was recently presented in predicting the creation and characterization of exciton condensates.⁷⁴³ Exciton condensation occurs when excitons, or particle–hole pairs, produce a superfluid single quantum state. Understanding superfluidity in exciton condensates has the potential to aid in a variety of technological advances from wire design to efficient room-temperature energy transport.^{229,744} A recent study prepares a highly entangled state on 3–53-qubit IBM quantum computers, which represent 3–53 particles, respectively.⁷⁴³ Using the largest eigenvalue of a modified particle–hole density matrix as a quantum signature of exciton condensation, the presence and the extent of exciton condensation was evaluated. These results reveal the formation of an exciton condensate of photons, illuminating a new avenue for the creation and characterization of exciton condensates. This study also highlights the potential for using different quantum computing architectures to facilitate preparation of different exciton condensates.⁷⁴³ The second example involves exploiting the natural mapping between molecular vibrations and photonic waveguides. Boson sampling was one of the first experimentally accessible systems able to challenge the computational power of classical computers with early proposals including the calculation of Franck–Condon profiles (FCPs) with quantum optical networks, using the connection between molecular vibronic spectra and boson sampling.⁷⁴⁵ As an example, refs 746 and 747 have simulated the vibrational dynamics energy transport and relaxation of small molecules including harmonic and anharmonic effects using a versatile photonic chip.

Fully leveraging quantum computers for scientific discovery presents numerous challenges due to the experimental and heterogeneous nature of quantum hardware, and the gaps in essential software abstractions and controls needed to program this hardware in the near term. Software for quantum computing is still being developed, and therefore the development of executable code for quantum hardware using current strategies is arduous. In quantum computers, efforts to realize a set of abstractions analogous to classical computing and create “layers” of the quantum software stack are underway. Many of these have been large open-source projects co-designed with quantum hardware to ensure that the approaches are scalable with larger and more complex circuits. Currently, different types of hardware have different instruction sets, therefore both the basic computer operations and the programming language are still being defined. In addition, reducing the error rates is essential for maximizing the reliability of the results produced by current hardware. To overcome these challenges, recent developments have introduced efficient schemes that allocate the quantum program, consisting of an allocation of logical qubits, and the sequence of circuits onto physical qubits, incorporating the device specific constraints.^{748–753} The traditional approach to compiling and executing quantum circuits is restricted to using a highly limited set of “native” gates and does not easily allow for the ability to optimize and generalize quantum operations at the pulse level, though some hardware providers (like IBM) have given users pulse-level access to overcome this issue. While the native gates are converted into pulse sequences designed for optimal fidelity of individual single- and two-qubit operations for execution on a

universal quantum computer, they lack diversity and flexibility for optimal performance in specific tasks. More recently, quantum hardware providers have started offering open-source access designed to enable quantum instructions at the level of individual analog pulses. Initial studies have demonstrated that such basic pulse-level optimizations can yield remarkable gate and circuit fidelity improvements. A default implementation of native quantum gates uses fixed pulse shapes and duration found through prior calibration to maximize fidelity of individual operations. This approach, while offering the advantage of simplicity in implementation, suffers from suboptimal overall performance when applied universally to all quantum circuits, particularly in the context of SC NISQ devices. Given one of the primary constraints of NISQ devices, the limited quantum circuit depth, reducing the duration of microwave pulses that implement quantum operations directly increases the number of gates that can be executed within the limited coherence time of a qubit. Unfortunately, reduced pulse duration inevitably leads to an increased level of errors that arise from higher pulse amplitudes and wider spectral components of the corresponding pulses. Using quantum gates that are always realized by pulses of fixed amplitude and duration, therefore, aims to achieve optimal balance between pulse duration and gate fidelity. We anticipate important advances from the field in improved overall fidelity of quantum computation enabled through pulse-level control, thereby enabling larger calculations of quantum materials.

The efficient control of quantum systems creates a competition between the need to couple the system to the control fields while minimizing the detrimental influence of the environment. Accounting for the environment is thus indispensable to the high-precision control demands of quantum technologies. Thus, a different approach toward improving the fidelity of qubit states and therefore the accuracy and noise-resiliency of quantum algorithms is to borrow tools from the field of open quantum systems and explicitly incorporate effects of the environment, which will be the focus of the next section in this Review.

5. DECOHERENCE AND NOISE IN QUANTUM SYSTEMS

Many electronic structure methods treat quantum systems in a vacuum as closed systems, without taking their environment into account. Realistic quantum systems interact with an environment, and in many cases, this interaction dictates both their properties and dynamics. The dynamics of the system and environment together can be treated as closed and therefore evolved under unitary transformations; however, such a treatment quickly becomes computationally intractable.^{754,755} A common approach is to trace out the bath degrees of freedom and consider the dynamics of the reduced density matrix as an open quantum system under the influence of the environment. Due to the openness induced by this framework, the dynamics can no longer be mapped to a unitary evolution, and more complex methods are required. Moreover, depending on the choice of system and environment partitioning and the relative time scales of dynamics, interesting physical phenomena, such as memory effects, can arise. Despite these complications, how quantum systems evolve under the presence of an environment is important for the study of most molecular processes. One example is the excitonic energy transfer in reaction centers such as photosynthetic light-harvesting complexes.^{756,757} It is also critical to the development and improvement of novel quantum technologies, since decoherence and noise currently strongly

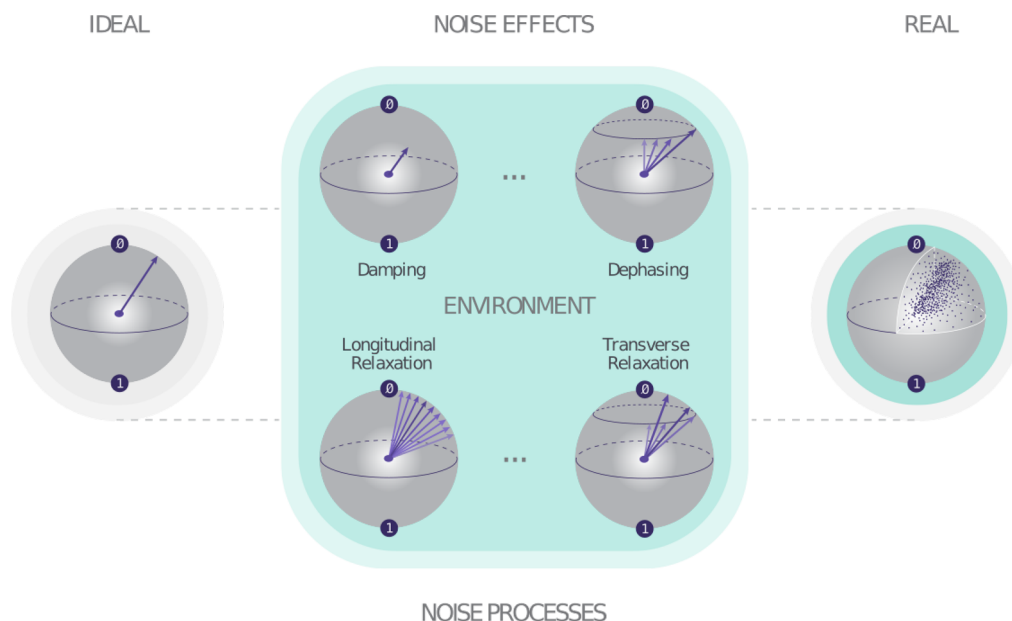


Figure 14. Effects of environmental noise on a qubit as depicted on a Bloch sphere: An ideal qubit (left) would be perfectly isolated and immune to the detrimental effects of environmental noise processes such as longitudinal and transverse relaxation and therefore unwanted effects including damping and dephasing (center), which decrease the desired state fidelity, shown by a spread of possible states (right).

impact NISQ devices, the depth of quantum circuits available for practical use, and the storage of quantum information.⁶⁶³ Quantum information technologies use the principles of quantum superposition and nonlocal entanglement for applications in computing, sensing, and communication. Applying concepts from the field of open quantum systems by explicitly simulating molecular and physical qubit candidate dynamics and their environment has the potential to improve our understanding of decoherence and noise effects. This in turn has the potential to lead to control protocols that can protect qubits from the environment, decreasing the detrimental effects of the noise and therefore increasing quantum fidelity.

A schematic of this fidelity loss to the environment can be seen in Figure 14. The left panel shows a Bloch sphere representation of an arbitrary qubit state in the ideal situation where the qubit is isolated with no unwanted interactions with its surroundings. Environmentally induced processes, including but not limited to longitudinal and transverse relaxation, lead to detrimental noise effects, such as damping and dephasing, as depicted in the center panel. These noise effects can result in the loss of critical properties of the qubit and therefore a loss in fidelity of the qubit state, as demonstrated in the right panel.

A more specific example is depicted by the general point defect in a solid-state lattice, as depicted in Figure 15. Electronic structure methods can predict the properties of a single defect as discussed in section 3.2; however, defect–defect interactions and defect–lattice interactions can be treated as system–bath interactions from a master equation or numerical open quantum system perspective at a reduced computational cost. The nuclear spins from the nuclei in the lattice behave as a spin bath, while the spins in surrounding defects also interact with the system of interest, leading to decoherence and shorter spin lifetimes. Several methods have been developed to treat the dynamics of such defect spin systems, including multiple flavors of cluster-expansion (CE) methods, which will be discussed in section 5.2.2. Looking to the future, we anticipate these methods to aid in the prediction of the behavior of a local array of defects in a

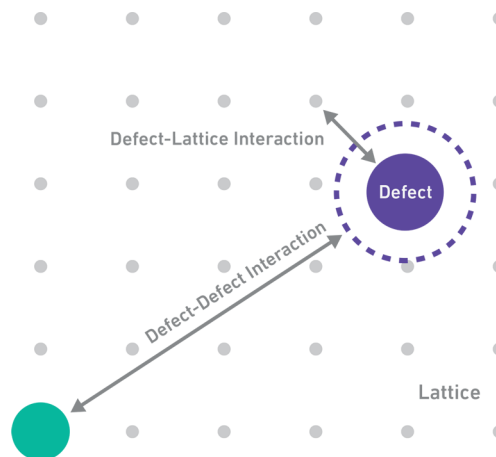


Figure 15. General defect in a lattice where the defect is an open quantum system (purple) interacting with both the lattice and other defects (teal).

quantum material, descriptions of local and long-range properties such as interdefect coherence lifetimes, minute adjustments to the spacing or arrangements of defects, and direct engineering of the structure–function relationships that govern specific quantum behaviors needed to enable scalable integration. This integration is critical, especially for the application of solid-state quantum technologies, as additional qubits in quantum repeaters will be needed for error correction, entanglement distillation, and quantum repeater multiplexing. These quantum repeaters constitute the essential nodes of a quantum network, the subject of intense current and future science and engineering endeavors across the globe.

When discussing the treatment of open quantum systems through a reduced density matrix framework, the separation of system and environmental degrees of freedom dictates the nature of the dynamics. If the whole system is partitioned such that the system is weakly coupled to the environment, then Markovian evolution will arise. In more complex cases, such as

when the system is strongly coupled to the environment, the system evolution can deviate from strict Markovianity.⁷⁵⁸ The measure of Markovianity and potential applications of the deviation from strict Markovianity are discussed in section 5.1. An overview of methods developed to treat open quantum systems in a variety of regimes is given in section 5.2, and applications of these methods, along with an outlook of this field with respect to quantum technologies are discussed in section 5.3.

5.1. Markovianity: Definition and Measures in Quantum Systems

Markovian evolution occurs when the dynamics of a system are driven by a weakly coupled reservoir with short-lived memory effects. In this limit, the Born–Markov approximation is valid and has been successfully implemented in a variety of methods for capturing accurate open system dynamics. However, depending on parameters such as coupling strength and relative relaxation and correlation time scales of the system and the environment, this approximation can breakdown. The deviation from Markovianity is often referred to as non-Markovianity and is colloquially defined by the “backflow” of energy or information from the environment into the system. The formal definition and quantification of Markovianity versus non-Markovianity of a system is an active field of research as demonstrated by recent reviews and literature.^{759–762} The importance of distinguishing between these regimes lies in this “backflow” of information; if understood and controlled correctly, it could aid in the preservation of important quantum properties such as coherences and entanglement. In this section, our aim is to summarize recent developments in the characterization of non-Markovianity and its potential applications.

While many measures of non-Markovianity have been developed,^{758,763–769} there are two leading measures that are most commonly used.⁷⁶² The first is the RHP measure based on the divisibility of dynamical maps proposed by Rivas, Huelga, and Plenio in 2010.⁷⁵⁸ A process is Markovian if the linear, trace-preserving, completely positive map, $\Lambda(t_j, t_i)$, that connects the density matrix at time t_i to its evolved state at time t_j , can be decomposed as

$$\Lambda(t_j, t_i) = \Lambda(t_j, t_k)\Lambda(t_k, t_i) \quad (23)$$

where t_i, t_j , and t_k are times such that $t_i \leq t_k \leq t_j$. Since the introduction of this measure, many related techniques have been produced either as direct extensions of the RHP measure or through similar means of derivation.^{770–772} The second leading quantifier of non-Markovianity is referred to as the BLP measure, introduced by Breuer, Laine, and Piilo. It quantifies the non-Markovianity as the maximum rate of change of the trace distance between pairs of evolving quantum states D_1 and D_2 for a given evolution time frame⁷⁶⁵

$$\mathcal{N} = \max_{\{D_1(0), D_2(0)\}} \int_0^T \frac{1}{2} \frac{d}{dt} \text{Tr}|D_1(t) - D_2(t)| dt \quad (24)$$

where $|\dots|$ is the square-root of the matrix norm, and the integral runs from 0 to the final time of the evolution, T .⁷⁶⁵ For Markovian evolution, the trace distance between two quantum states $D_1(t)$ and $D_2(t)$ monotonically decreases as a function of time.⁷⁶⁵ This implies that no matter how these two states are initialized, they will become less distinguishable as they evolve. Non-Markovian behavior is connected to intervals of increase in this trace distance. Much like the RHP measure, many novel

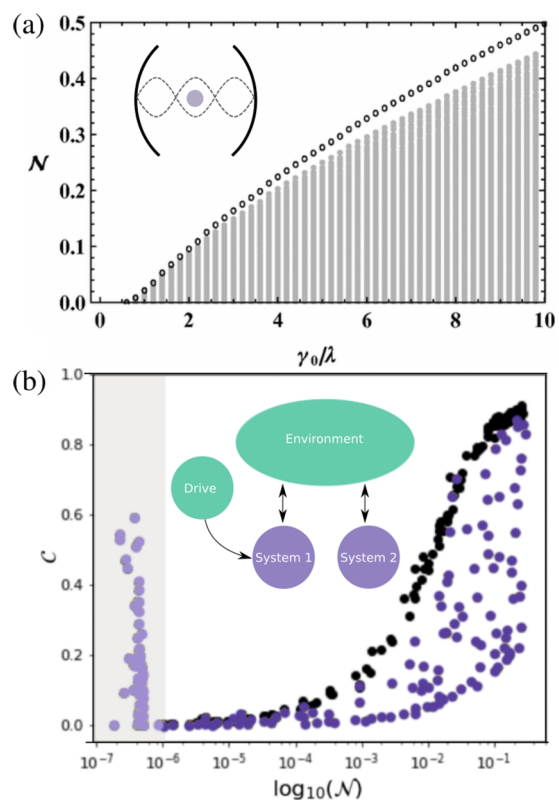


Figure 16. (a) Breuer–Laine–Piilo (BLP) measure of non-Markovianity as a function of coupling strength in the Jaynes–Cummings model, where the degree of non-Markovianity for two randomly chosen initial states (gray dots) and for two orthogonal initial states (black circles) are shown. Reproduced with permission from ref 765. Copyright 2009 by the American Physical Society. (b) Concurrence of two noninteracting subsystems interacting with a mutual environment versus the logarithm of the measure of non-Markovianity. The entanglement between the two systems is increased with the application of the control field. Adapted with permission from ref 775. Copyright 2019 by the American Physical Society.

measures have been produced either as extensions to the work of BLP or through a similar means of derivation.⁷⁷³

An example of the BLP measure is shown in Figure 16a, where the degree of non-Markovianity \mathcal{N} is shown as a function of coupling strength for the Jaynes–Cummings model. This is a commonly used benchmarking model consisting of a two-level electronic system interacting with one environmental mode, as shown schematically in the upper left corner.^{765,774} With increasing coupling between the two-level system and the environment, an increase in non-Markovianity is observed. The gray dots, which lay in lines of fixed coupling strengths, represent the BLP measure of non-Markovianity resulting from tracking the distinguishability of two randomly chosen initial density matrix states for a fixed interval of time. The black circles represent the BLP measure resulting from tracking the distinguishability of initially orthogonal density matrix states, which produces the maximum amount of non-Markovianity.

Due to their physically motivated derivations and mathematical ease of use, the above two measures have been widely used for the distinguishability between Markovianity and non-Markovianity. This is a rich and active field of research with a variety of other measures being developed, including recent works that use the covariance matrix,⁷⁷⁶ relative entropies,⁷⁷⁷ optimal state pairs,⁷⁷⁸ and semiempirical methods.^{779,780}

While the formal definition and quantification of non-Markovianity is still an active topic of research, the established measures are being used to design and analyze both theoretical and experimental set ups. One recent example is shown in Figure 16b, where several driving schemes were investigated as protocols for entanglement between two subsystems that are not directly coupled but have the potential to interact through a mutual environment.^{775,781} While three different driving schemes are considered in these works, Figure 16b shows the entanglement in terms of concurrence, C , as a function of non-Markovianity, \mathcal{N} , for the case in which only one subsystem is being driven. It should be noted that in this case, the concurrence depends on two elements of the density matrix and can range from 0 for completely separable states to 1 for maximally entangled states. Entanglement is shown to increase with increasing non-Markovianity, with purple and black circles representing the non-Markovianity measure given from randomly and optimally chosen initial density matrix states, respectively. This study demonstrates that entanglement can be generated by exploiting the non-Markovianity in these systems through invoking different driving schemes.⁷⁸¹ This entanglement generation protocol demonstrates how the measure of non-Markovianity can be a guiding parameter when designing optimal properties of open quantum systems for use in quantum technologies including connected quantum sensors and scalable quantum networks.

A critical component of the entanglement protocol scheme presented above is how to model the dynamics of the open quantum system. In the case of small systems, the dynamics can be solved exactly; however, for the majority of systems of interest this is rarely the case. This has spurred the development and improvement of many methods to treat open system dynamics, which will be discussed in the next section.

5.2. Methods in Non-Markovian Dynamics of Quantum Systems

As demonstrated by the comprehensive review of non-Markovian methods for open quantum systems in ref 782 and the recent perspective on the definitions, measures, and quantifiers of non-Markovianity in ref 762, handling non-Markovian effects in open quantum systems is an active field of research spanning mathematics, physics, chemistry, and quantum engineering. While it has been a topic of interest for many years, it has gained recent attention due to the development of hybrid quantum technologies, including transduction schemes between different realizations of qubits and large-scale quantum network architectures. Since these technologies often depend on optimal information transfer fidelity and preserving coherence, the ability to treat quantum systems in terms of their interactions with their surroundings is critical. Here, we discuss the most commonly used methods of treating open quantum systems in both the Markovian and non-Markovian regimes. It should be noted that this section is meant to serve as an overview of methodologies, highlighting the variety of options and progress in the field. The references within this section and the recent review articles⁷⁸² are recommended for the reader looking for more in-depth detail on the methods presented.

5.2.1. Perturbative Approaches to Open Quantum Systems. One of the most common methods of treating open quantum systems is through the use of master equations, which can be solved exactly in some cases and perturbatively in others.⁷⁵⁴ This involves integrating out the environmental

degrees of freedom from the full density matrix to consider the dynamics of the system through the reduced density matrix.⁷⁸³ In the Born–Markov approximation, the Gorini–Kossakowski–Sudarshan–Lindblad formalism is a commonly used master equation method for calculating dynamics, as it guarantees the positivity of the system’s density matrix.^{784,785} Derived from Kraus operators with a perturbative expansion to second-order, the Lindblad equation is a first-order differential equation and is given by

$$\frac{dD_s(t)}{dt} = -i[H, D_s] + \sum_k \gamma_k \left(C_k D_s C_k^\dagger - \frac{1}{2} \{ C_k^\dagger C_k, D_s \} \right) \quad (25)$$

where D_s is the system density matrix, H is the system Hamiltonian, C_k are the k Lindbladian matrices defining different dissipation or decoherence channels, γ_k are the positive decay rates, and $\{, \}$ is the anticommutator.^{754,784,785} Due to its computational simplicity and guaranteed positivity, this has been a widely used method of treating open quantum systems weakly coupled to their environments. It should be noted that the Lindbladian matrices generally come from physical intuition, experimental evidence, or theories such as Marcus theory. In recent years, extensions to this approach such as the inclusion of accurate fermionic statistics^{786,787} and non-Markovian effects have been made.^{788,789} One example extension invoked a systematic Keldysh diagrammatic perturbation theory technique to derive Lindblad-like operators from higher order perturbative terms to investigate a broader variety of dissipative processes.⁷⁹⁰ By including fourth-order diagrams that generated correlated dissipation, this method was able to explain experimental gains and losses in driven double quantum dot resonator systems.⁷⁹⁰

A second popular master equation approach under the Born–Markov approximation is Redfield theory.^{791,792} While this master equation does not inherently preserve the positivity of the density matrix, work has been dedicated to making adjustment to include positivity such as a coarse-grained averaging technique.⁷⁹³ Similar to Lindblad’s theory, the Redfield theory has also been modified, extended, and widely used in applications such as energy transfer in photosynthetic light-harvesting complexes.^{794–796}

These two methods and their extensions are common and straightforward choices for considering Markovian dynamics. However, considering system–environment interactions beyond the Markovian regime leads to a plethora of other options.^{754,797} For non-Markovian dynamics, there are several master equation approaches that are extensions of the methods used to treat Markovian dynamics.^{788,789,798–806} Among these extensions are methods referred to as post-Markovian master equations^{807–809} and semi-Markov methods,⁸¹⁰ which are computationally inexpensive but restricted to a somewhat narrow range of interaction regimes.

More generally, non-Markovian master equations tend to be divided into two main categories. There are time nonlocal master equations, which involve the calculation of a memory kernel, and time local equations, which do not explicitly treat the system memory.⁸¹¹ Neglecting the inhomogeneity term and assuming an initially factorized state of the density matrix, $D_{S+E}(0) = D_S(0) \otimes D_E(0)$, the simplified Nakajima–Zwanzig equation, or generalized master equation, is a starting point for many time nonlocal methods and is given by^{754,797,812–814}

$$\frac{dD(t)}{dt} = \int_0^t d\tau \mathcal{K}(t, \tau) D(\tau) \quad (26)$$

where $\mathcal{K}(t, \tau)$ is the memory kernel. With few exceptions, this method is computationally intractable due to the complexity of the kernel. Often for calculational purposes, the memory kernel needs to be approximated through physical intuition or perturbative expansion.⁸¹⁵ Approximations of the memory kernel lead to a risk of violating the positivity of the system density matrix. An example of this violation can be seen when the generalized master equation was perturbatively expanded to second order and negative occupation numbers were observed in a simple two-level system.⁷⁵⁴ Several methods have been developed to work around this obstacle through careful mathematical construction of the memory kernel.^{814,816} Other methods have bypassed the perturbative approach entirely and opted for numerical methods for computing the memory kernel,^{817–823} including the use of surface hopping and Ehrenfest dynamics⁸²⁴ and Mori theory.^{825–827}

The Nakajima–Zwanzig method is often compared to a time-local projection operator technique referred to as the time-convolutionless or TCL method.^{754,828,829} The TCL master equation is written as,

$$\frac{d\mathcal{P}D(t)}{dt} = \mathcal{K}(t)\mathcal{P}D(t) + I(t)QD(0) \quad (27)$$

where \mathcal{K} is the time local generator, I is the inhomogeneity, and \mathcal{P} and Q are projection operators that act on the full density matrix to obtain the relevant (system) and irrelevant (environment) components, respectively.⁸²⁸ While this equation is exact, the memory kernel and the inhomogeneity are computationally challenging and eq 27 in its general form is impractical. To overcome this computational challenge, this equation is often solved by perturbatively expanding the time local kernel then truncating at some order. However, the cost of truncating the kernel is that the positivity of the density matrix is no longer guaranteed, similar to the nonlocal form. Despite the risk of losing positivity,⁸³⁰ the time-convolutionless form has been successfully applied to many systems and processes of interest including both linear and nonlinear spectroscopic predictions.⁸³¹ Similar to the Nakajima–Zwanzig equation, numerical approaches have been invoked to solve for the memory kernel in this framework.⁸³²

5.2.2. Numerical Approaches to Open Quantum Systems. While perturbative approaches offer sets of equations for calculating the density matrix, numerically exact methods can be implemented when an algebraic solution is not required. A variety of methods have been developed that rely on systematic convergence of numerical simulation, including methods based on path integrals^{754,782,833} such as the quasi-adiabatic path integral (QUAPI),^{834–836} path integral Monte Carlo (PIMC),^{837,838} and noninteracting blip approximation.^{839,840} The QUAPI method employs the adiabatic reference to determine the short-term system evolution operator and integrate out the degrees of freedom from the bath. By incorporation of nonadiabatic corrections through an influence functional, the exact dynamics of a system along a given adiabatic path can be described. While the method was originally developed to describe low-dimensional systems coupled to a bath of harmonic oscillators, it has been generalized and employed extensively to treat open quantum system dynamics,^{841,842} including those of charge qubits in complex environments.^{843–845} These path integral approaches have also been combined to exploit their respective strengths to further progress numerical simulation of open system dynamics.⁸⁴⁶

A complementary method that stems from Feynman's path integral approach is the hierarchical equations of motion (HEOM) method.^{847–850} Due to its ability to calculate the exact dynamics of a system linearly coupled to its environment, HEOM has been successfully applied to a variety of systems of chemical and physical interest. However, this method is hindered by its requirement that the environment possess a continuous spectral density. In recent years, many improvements and extensions of the HEOM method have been developed and successfully applied to a variety of systems,^{851–857,857} including photosynthetic light-harvesting complexes.^{757,858–861} It should be noted that when the hierarchy is truncated at low order, the HEOM method reduces to the perturbative Nakajima–Zwanzig or time-convolutionless master equation forms presented in the previous section.⁸⁶²

Monte Carlo wave function methods have been an effective alternative to density matrix approaches for numerically simulating the dynamics of Markovian open quantum systems.^{863–865} These methods evolve Monte Carlo wave functions of the system using a non-Hermitian Hamiltonian while incorporating stochastic quantum jumps. In its dissipative form, this method has been widely applied in quantum optics.⁸⁶⁶ The biggest challenge in generalizing this method to treat non-Markovian dynamics is the emergence of negative quantum jump probabilities.⁷⁸² Using a combination of forward and backward jumps enables capturing the backflow of energy or information that is associated with non-Markovian behavior.^{867,868} The positivity of the density matrix in the non-Markovian quantum jump method has also been assessed, noting that violations of positivity are associated with singularities in the jump probabilities and therefore unphysical results are prevented.⁸⁶⁹ This non-Markovian extension has been successfully applied to observe population beatings in a room temperature dimer system and excitonic energy transfer in photosynthetic complexes.^{870,871}

Some numerical methods for open system modeling have been developed with specific systems in mind. One such example is the cluster-expansion (CE) method, which has a close relationship with Feynman diagrams and acts as a systematic truncation of the Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy for interacting systems. Due to its origins being rooted in the numerical treatment of interacting systems, the cluster-expansion method in a variety of forms has been applied to the treatment of open systems interacting with spin baths, including pure dephasing and the qubit decoherence problem.⁸⁷² Different flavors of the CE method have been developed including the density matrix cluster-expansion method,^{873–875} the linked cluster-expansion method,⁸⁷⁶ the pair-correlation cluster-expansion method,^{877–879} and the cluster-correlation expansion method.^{872,880,881} The cluster-correlation expansion (CCE) method factorizes the bath spin evolutions into cluster correlations and has been proven to bear accurate results when converged.^{872,880}

A very different alternative approach for the treatment of open quantum systems is to use machine learning methods,^{882,883} including the use of restricted Boltzmann machines.^{650,884,885} Work in this field has focused on Markovian dynamics of open quantum systems,^{886–889} with a recent extension that uses parametrized quantum circuits to produce an open quantum system algorithm based on Lindbladian dynamics.⁸⁹⁰ Along these same lines, there has been some progress toward capturing the dynamics of open quantum systems through adapting master equation approaches to be amenable to run on quantum

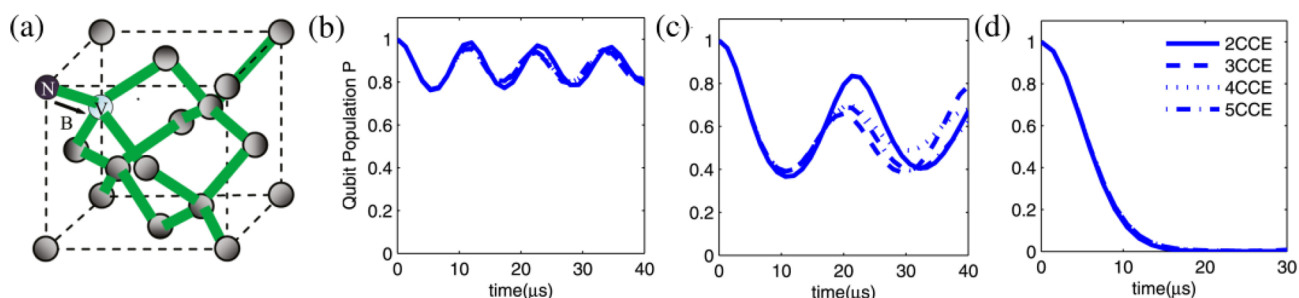


Figure 17. (a) Structure of a NV center diamond. The longitudinal relaxation process of the NV center is shown in terms of the survival probability of the initial state of electron spin using different orders of CCE with a bath size of 50 under the magnetic field intensity (b) $B_z = 1025.01$ G, (c) $B_z = 1024.99$ G, or (d) $B_z = 1024.97$ G. Adapted with permission from ref 881. Copyright 2020 Elsevier.

devices.^{891–894} The major challenge that these methods face is capturing nonunitary evolution of the system while relying on unitary gates. Dilation methods must be used to incorporate the important environmental degrees of freedom into a new effective system such that the evolution remains unitary. While early work could perform such dilations through use of the Stinespring dilation theory,^{892,895} the computational scaling was not favorable. Recent work used the Sz.-Nagy dilation theorem, which reduces the scaling of the mapping from the dissipative Lindbladian dynamics into a unitary form.^{896–899} Unitary operations can be decomposed into a sequence of quantum gates,⁹⁰⁰ which allowed for a two qubit calculation of a two-level system in an amplitude damping channel.⁸⁹⁹ This work has recently been extended to treat non-Markovian dynamics.⁹⁰¹ While quantum algorithms for the treatment of open quantum systems is still in its infancy, it shows promise for capturing accurate dynamics in a variety of coupling regimes at a reduced cost.

5.3. Emerging Directions in Environmentally Coupled Quantum System Dynamics

Many of the recently developed open quantum systems methods have proven to be useful in studying a variety of hybrid quantum systems. While the above two sections classified methods as either perturbative or numerical, many methods have been developed at the intersection of these two categories to better treat given systems of interest.^{902,903} In this section, we highlight a few key recent examples.

As previously mentioned, NV centers in diamond or artificial atom qubits in general exhibit complex environmental interactions, and therefore, sources of decoherence are an inherent and critical component of the system. The nitrogen atom and corresponding vacancy together introduce a net electronic spin, which interacts with an environment made up of nitrogen nuclear spins and ^{13}C spins as shown in Figure 17a.⁸⁸¹ The CCE method mentioned in section 5.2 was generalized and has been applied to treat a NV center in a diamond crystal. Figure 17b,c,d depict different intensities of magnetic fields ranging from having a large energy gap between the electron and nuclear spins as compared to their hyperfine interaction to the nearly resonant case, respectively.⁸⁸¹ The orders of CCE from 2CCE to 5CCE are also compared, where 2CCE represents including clusters with one bath spin and the NV center while 5CCE represents including clusters with four bath spins and the NV center. Through these three figures, it was shown that the 5CCE provides little advantage over the 4CCE, and therefore the 4CCE is sufficient for accurate calculations. It should be noted in these methods that the spins outside of the cluster of interest are considered to be frozen when considering the cluster

contribution. In the cases where the bath spins are as strongly coupled to one another as they are to the system spin, the CCE method is challenging to implement.⁹⁰⁴ However, this recent work shows that the CCE method provides a numerically tractable method of treating open quantum system dynamics in the presence of spin baths, a useful tool for improving the coherence lifetimes in NV centers, which show promise as spin qubit candidates. Moreover, many experimental studies have been committed to utilizing non-Markovian effects for the control of spin qubits such as NV centers.^{905–907} One experimental study showed that preparing different initial superposition states for the nuclear spins allows control of the electron spin dephasing and decoherence dynamics.⁹⁰⁵

Another important framework is the study of transport through molecular junctions since it is an important step toward the improvement of molecular electronics.^{908,909} Recent literature has used a variety of open quantum system methods, including master equations and Monte Carlo, to model both thermal and charge transport in molecular junctions.^{803,910–912} Using these improved methods to capture dynamics, a more accurate depiction of transport through molecular junction can be found, facilitating the path toward improved efficiency. Similar methods have also been used to model energy transfer in molecular or biological systems,⁹¹³ such as photosynthetic light-harvesting complexes,^{822,914–917} as well as manufactured devices such as molecular batteries.⁹¹⁸ Figure 18a shows the 7 site Fenna–Matthews–Olsen complex,⁹¹⁷ a commonly studied photosynthetic light-harvesting complex,^{919,920} while the dynamics of sites 3, 5, and 6 are shown in panel b.⁸²² Here, two methods are compared to the exact solution obtained from the HEOM approach.⁹¹⁴ The first is Ehrenfest mean field theory

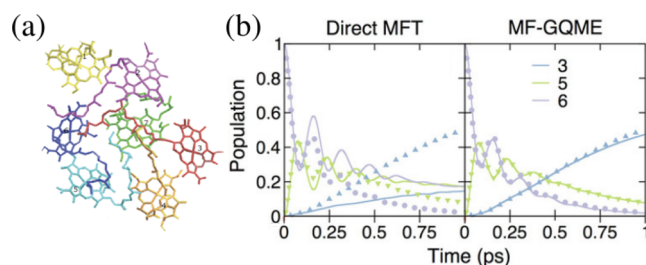


Figure 18. (a) Seven site Fenna–Matthews–Olsen complex. Reproduced with permission from ref 917. Copyright 2014 AIP Publishing. (b) Populations of sites 3, 5, and 6 with an initial excitation in the sixth site as it decays using HEOM (dots) and direct mean field theory shown on the left and mean field generalized quantum master equation shown on the right (lines). Adapted with permission from ref 822. Copyright 2019 American Institute of Physics.

(MFT), which shows poor agreement with the exact dynamics. The second is mean field generalized quantum master equation (MF-GQME), which involves combining mean field theory with the generalized master equation and iteratively optimizing the memory kernel. This method is an example of utilizing many different open quantum system techniques, from perturbative to numerical, to obtain an efficient and accurate model of an important system.

A third area of application is in NISQ-based quantum information processing, where controlling the system evolution to minimize the detrimental effect of noise is critical for optimal information communication. While dissipative dynamics exclusively decreases quantum properties such as coherence, the presence of non-Markovian effects can create recurrences of coherences and other quantum properties. With the increased interest in developing methods to treat non-Markovian dynamics, there has also been interest in the exploitation of non-Markovian dynamics for quantum control,^{921–925} entanglement creation,^{775,781,926} and other quantum information tasks.^{927,928} Similarly, work has been dedicated toward controlling the degree of non-Markovianity of a qubit,⁹²⁹ considering the NV center in diamond as a sample system.⁹⁰⁵ Recent work considered a general weakly anharmonic ladder as the system and partitioned the infinite set of oscillators into primary and secondary baths. The primary bath is a set of two-level systems that are strongly coupled to the system and could be the source of quantum backflow, while the secondary bath is weakly coupled and responsible for relaxation and dephasing. The isolated system allows only for operations in the Lie algebra group, $SO(4)$, while system control through non-Markovian effects enables the realization of all quantum operations in $SU(4)$. The error after optimization of one element in $SU(4)$ in terms of the spin–lattice, or T_1 , relaxation time is shown in Figure 19a considering both a two-level system and a qudit. Figure 19b in the top panel shows the optimized control amplitudes through use of a ramping scheme shown in blue and a fast oscillating control shown in red. The bottom panel shows the amount of non-Markovianity using the determinant of the volume of reachable system states as the measure. As discussed in section 5.1, non-Markovianity is associated with an increase in this volume. This work shows that the environment can act as a resource for near-unitary quantum control of open quantum systems.⁹²³

The above example highlights how the environment can be used as a resource for controlling an arbitrary open quantum system. More generally, the control and application of non-Markovian effects are emerging as promising avenues for quantum information purposes including the development of engineered reservoirs and the improvement of quantum algorithms and protocols. A recent example is the consideration of the fidelity of generalized Pauli channels, which engineered nonlocal noise to maintain prolonged entanglement in the system.⁹³⁰ There also exists the potential to improve physical quantum systems or quantum hardware. Methods such as neural networks or the stochastic estimation of dynamical variables can be used to parametrize experimental noise.^{931,932} Through use of the perturbative methods discussed in previous sections, improved noise models can be integrated into these parameter estimation schemes to provide more realistic models and improved parameters.

Various approaches for using the dissipative dynamics as a computational resource have been explored under the umbrella of “reservoir engineering”. During the early years of quantum

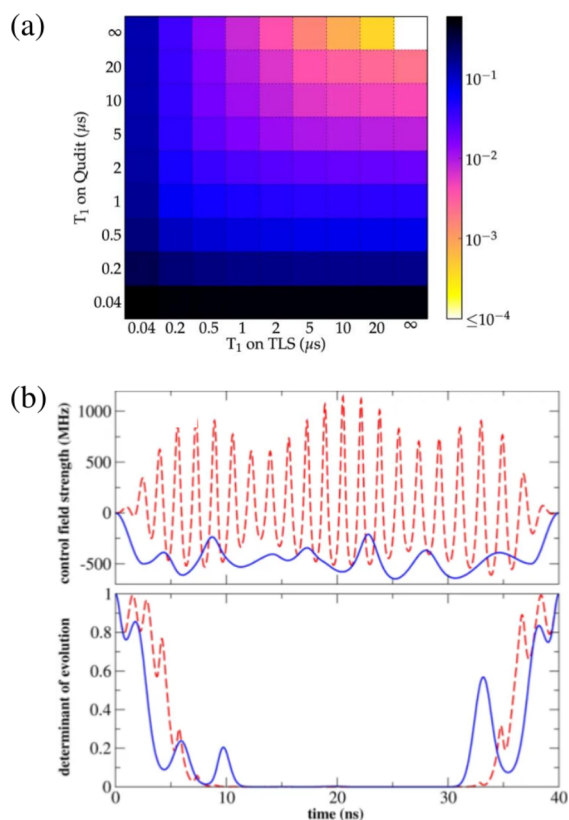


Figure 19. (a) Error from the realization of an element of $SU(4)$ on a qudit and on a two-level system. (b) Optimized amplitudes with the control with no ramp (red) and following a fixed ramp of ± 500 MHz over 2.5 ns at the beginning and end (blue) with the Liouville space determinant of the system evolution. Reproduced with permission from ref 923. Copyright 2015 Springer Nature.

information, a common argument against the feasibility of achieving quantum computational advantage was the notion that noise processes would always conspire to decohere the computational hardware. Reservoir engineering turns that idea around by controlling the coupling between the computational subspace and the dissipative reservoir. The basic approach closely resembles the setting behind adiabatic quantum computing: ensuring that the ground state of a given slowly changing Hamiltonian is gapped from the first excited state prevents noise processes from being able to excite, and hence decohere, the system during a computation. Thus, adiabatic quantum computing enables both computation and passive error protection. Similarly, one can consider the eigenstates of the dissipative superoperator. The “ground” steady-state subspace toward which the nonunitary superoperator forces the evolution of the computational system is naturally “protected”. The goal of reservoir engineering is to find a way to make this, usually trivial, subspace into something computationally useful.^{784,785,933–939} For instance, the dissipation superoperator can be engineered such that the ground space is of dimensionality higher than one. In such a subspace the dissipation can protect coherent superpositions. The stronger the engineered dissipation is, the more resilient the memory is against other dissipative effects; thus the engineered bath becomes a passive error correcting mechanism. Moreover, computation can be performed by adiabatically modifying the form of the dissipative operators.

Non-Markovian memory effects have been exploited to improve quantum algorithms and protocols.⁹²⁸ One recent algorithmic development used non-Markovian memory effects to improve the success probability of the refined Deutsch–Jozsa algorithm implemented on NV center spin qubits.⁹⁴⁰ The Deutsch–Jozsa algorithm is a quantum algorithm that aims to determine if a function is constant or balanced.⁹⁴¹ More colloquially, this algorithm is used to determine whether a coin is fake, implying the coin will produce either only heads or only tails, or fair, implying there is an equal probability of it landing on heads or tails. Combining non-Markovian memory effects with the dynamical decoupling protection method⁹⁴² results in a substantial improvement in the algorithms' success rate.⁹⁴⁰ These results demonstrated the ability for non-Markovian memory effects to assist in quantum algorithm improvement. Similar adaptations have been made to utilize non-Markovian effects in quantum protocols, as mentioned briefly in the entanglement generation protocol^{775,781} from section 5.1. Another example is in superdense coding, where a sender can transmit two bits of classical information to a receiver through a single qubit by initially sharing an entangled state.^{674,943} Noise and decoherence decrease the initial entanglement between the sender and receiver, which in turn reduces the effects of the protocol. The experimental application of nonlocal memory effects through the use of non-Markovian noise has allowed improvements to be made in both the efficiency and security of quantum communication.^{926,944}

The measures, methods, and applications discussed here are a small sample of the vast field of open quantum systems. We anticipate that the integration of the field of open quantum systems with quantum chemistry, materials science, and quantum information will aid in improved modeling of correlated quantum matter.

6. CONCLUSIONS, OUTLOOK, AND FUTURE DIRECTIONS

In this Review, we have assembled a comprehensive foundation for those interested in the intersection of correlated quantum matter and quantum information science. In sections 2 and 3, we highlighted the strides that have been made in electronic structure theory, using both wave function and density based methods. Approaches, applications, and opportunities for algorithmic advances to capture the correlated electronic behavior in a variety of systems were discussed with a particular emphasis on molecular and color center qubits and quantum electrodynamical methods. Switching from classical approaches to quantum, in section 4, we highlighted developments in quantum algorithms as an alternative approach for reducing the scaling of the N -body problem, with a focus on hybrid algorithms. In section 5, we discussed the treatment of open quantum systems and how invoking these methodologies with respect to systems such as molecular and color center qubits has the potential to improve their performance for use in quantum technologies. Our Review highlights the interplay between electronic structure, quantum electrodynamics, quantum algorithms, open quantum systems, and novel quantum technologies. Combining breakthroughs from these fields with ideas from quantum computing has led to physical realizations and improvements of a wide range of quantum technologies and materials.

6.1. Outlook on Correlated Quantum Matter for Quantum Information Science

Currently the discovery and development of materials and molecules for quantum information science relies largely on intuition-guided trial and error. Even in the limit of atomic defects in semiconductors, conventional theoretical methods cannot always capture quantum electronic properties and dynamics at finite temperature. In the next few years, we anticipate that the field will overcome this key hurdle in solid-state quantum technologies for quantum networks and quantum sensors by developing theoretical methods to model and predict the properties of quantum defects quantitatively, identifying new protocols to characterize complex and coherently coupled solid-state quantum systems, and deploying them in practical quantum repeater nodes to translate materials-level properties into quantum devices. A success-story would be in transforming the way coherent quantum emitters are identified, developed, and engineered, to one in which numerical modeling and computational screening precede complex and costly intuition-guided experiments. Computational advantages of these methods, tested against precision quantum spectroscopy of emitters, could then be translated to broad classes of materials for other quantum devices and quantum networks. The tight discovery loop availed by the approach would allow the community to, for instance, generate a local array of emitters in a material, predict local and long-range properties such as interemitter coherence lifetimes, make minute adjustments to the spacing or arrangements of emitters, and engineer directly the structure–function relationships that govern specific quantum behaviors needed to enable scalable integration of quantum emitters. Such integration is critical for solid-state quantum technologies as additional qubits in quantum repeaters will be needed for error correction, entanglement distillation, and quantum repeater multiplexing. Further, by driving such many-body systems out of equilibrium, new states of matter can be created as recent results across nanophotonics and condensed matter physics have shown. Nominally prohibited in equilibrium, such novel states of matter feature unexpected properties, including surprisingly long coherence times, allowing for specific tailoring of quantum material and emitter properties. We envision other intersections between predictions of new quantum emitters, understanding their couplings and many-body dynamics, and theoretical control schemes of impurity arrays driven out of equilibrium via strain and phonons with the goal of optimizing them for producing new quantum optical states for quantum sensing, metrology, and quantum networking related applications.

A related promising direction is in theory-guided design of molecules with ideal ground and excited state electronic structure to create optically addressable qubits. The optical addressability in solid-state defect-based spins is dependent on a number of key factors, including an excited state manifold that allows for selective relaxation to a specific spin sublevel, an optically addressable excitation, and the capacity for fluorescence. To create molecules with comparable properties to these defect-based systems, the target molecules need to be designed to have similar attributes. In spin 1 systems, generating the optical excited state manifold requires consideration of the relative energies of the excited state triplet and the excited state singlet. Optical selection rules dictate that allowed optical excitations from a triplet ground state will be to a triplet excited state, which can then relax to a singlet state via intersystem crossings mediated by spin–orbit coupling. Designing molec-

ular qubits with the requisite excited state manifold is achievable and, indeed, well worked out for octahedral and tetrahedral systems in which the Tanabe–Sugano diagrams determine the relationship between ligand field strength and optical excitation energy. Identifying generalizable concepts for arbitrary correlated molecular quantum matter to create modular molecular qubits, such as macrocyclic ligands with varying conjugation and axial ligands, is a rapidly growing area with close feedback between theoretical predictions and experimental investigations.

From a theory perspective, these molecular qubit candidates present an exciting challenge. Popular molecular candidates considered consist of transition metal centers with large ligands, as demonstrated by the examples shown in Figure 5. These molecules tend to exhibit strong correlation, necessitating the use of large active spaces. Systems such as these are what continue to drive electronic structure theory development toward the goal of accurate prediction of strong correlation at a tractable computational cost. For instance, using the reduced density matrix framework discussed in section 3.1, active spaces as large as 42 electron in 40 orbitals⁷ or 120 electrons in 120 orbitals in the seniority zero space²⁴³ have successfully captured strong correlation. Further development of both these and other methods mentioned in sections 2 and 3 will allow for more accurate treatment and therefore prediction of electronic properties of nontrivial molecular complexes, which can in turn be used toward the improvement of quantum technologies.

Theoretical predictions have revealed pathways toward control of microscopic parameters in complex materials, as we have discussed extensively in section 3.4. This includes mode-selective enhancement, control of the amplitude and phase of order parameters, and Floquet-driven symmetry protected topological edge states. Utilizing such electromagnetically engineered nonequilibrium phases necessitates a concerted effort spanning theory and computation. Various groups are constructing variational wave functions that extend Gaussian states by including generalized canonical transformations between the matter and light degrees of freedom. The key advantage of such states compared to simple Gaussian states is the presence of nonfactorizable correlations and the possibility of describing states with strong entanglement between electrons and phonons. These wave functions are different from the commonly used canonical transformations, such as the polaron or Lang–Firsov transformations, in that parameters of the transformations are time dependent, which extends their regions of applicability. The main questions that are being addressed from these methods are enhancement of transient superconducting and charge density wave orders by parametric driving of phonons. Further, we envision exciting new work from the community in identifying new states of quantum matter under optical excitation, with a quantitative understanding of microscopic quantum dynamics and collective excitations. This is crucial to realize solid-state quantum information platforms based on nonequilibrium phenomena and has so far been a roadblock to technological exploitation of quantum matter.

6.2. Predicting Correlated Quantum Matter with New Quantum Algorithms

For problems in QED and in particular in the field of strong light–matter coupling, we foresee a wide range of applications for computational quantum algorithms. As the simulation of the Rabi model in strong coupling has demonstrated,^{945,946} such quantum simulations are now within reach. By going beyond the two-level limitation of the Rabi model, some of the still open

questions for chemical systems in optical cavities can be targeted. Questions such as the changes in transition state of chemical reactions under strong light–matter coupling and cavity-induced superconductivity are still unsolved. These light–matter correlated systems, which include electronic, nuclear, and photonic degrees of freedom, necessitate algorithmic advances on how to efficiently describe the complex interplay of these interactions. Ideas from the electron–phonon mapping⁹⁴⁷ can also be used to map electron–photon problems to NISQ devices.

The last two decades have seen dramatic computational advances in electronic structure theory driven by software development that has exploited massive-parallelization available today on large supercomputers. Most of these highly sophisticated software packages in material science and quantum chemistry still remain poorly interfaced with the frameworks used to access NISQ devices. On the forefront of these developments are highly flexible python-based quantum chemistry packages such as PSI4⁹⁴⁸ and PySCF²⁰ that have already led to successful implementations of hybrid quantum–classical algorithms for molecular systems using VQE. Overcoming the barriers between the optimized and powerful general software packages in material science and general quantum programming languages will drive the development of more advanced hybrid quantum–classical algorithms for applications of extended systems.

We highlight that developing quantum algorithms and useful implementations thereof, which maximize the impact of quantum and classical computing capabilities, requires a diverse set of tools. One such tool is scalable *ab initio* codes that compute the parameters for second-quantized quantum algorithms. Another is quantum compilers that can translate algorithms for different physical realizations of quantum computers. A third tool is quantum device simulators, which can be used to simulate the behavior of algorithms on quantum computers, to complement a physical quantum device, or to simulate the noise sensitivity of a quantum computing technology or algorithm.

So far, the wide-range of nonequilibrium dynamics of quantum systems on quantum devices remains largely unexplored. As has been discussed in this Review, general methods to accurately describe nonequilibrium many-body systems remain limited. While there exists a variety of methods that are in principle capable of describing larger systems, such as TDDFT, in practice these methods often use the adiabatic approximation, and therefore are limited to states close to the ground state. On the other hand, methods based on many-body perturbation theory, such as nonequilibrium GW, are intrinsically computationally complex, and efficient approaches for modeling larger systems have only recently been developed. This wide gap opens many possibilities for quantum devices, due to their scalability and capability to accurately describe the electronic structure. Among the exotic effects that nonequilibrium dynamics of quantum systems promises to reveal is the recently demonstrated light-induced superconductivity. To properly describe these systems, not only is the scaling of current architectures in terms of qubit size and noise reduction necessary, but also ideas of hybrid quantum–classical algorithms have to be transferred to the time domain.

6.3. Open Quantum Systems and Quantum Transport on NISQ Devices

Modeling excitonic energy transport is another example where we anticipate that quantum algorithmic development will make rapid progress toward efficiently using quantum resources. Here, quantum transport, as seen in molecular complexes and correlated condensed matter, can arise from intricate, multibody interactions on partially ordered landscapes. In these cases, energetic disorder tends to localize particles and to inhibit coherent transport, while noise destroys coherence and enhances transport. However, too much noise and decoherence drives the system to a regime in which transport is suppressed resulting in an “optimal spot”, where the interplay between static and dynamic disorder optimizes energy transport. One of the current key obstacles in understanding this many-body energy transport dynamics is the difficulty of simulating quantum systems with more than a few dozen particles or sites. NISQ information processors hold the promise of being able to simulate energy transport in quantum systems with 50–100 particles or sites, which should allow the direct simulation of quantum energy transport in catalytic systems. While variational methods are crucial to characterizing the individual energy eigenstates of complex quantum systems in the vicinity of the ground state, simulating quantum energy transport, by definition, requires an approach that goes beyond variational quantum eigensolvers, as one must take into account dynamic processes involving multiple energy eigenstates. In addition, we expect that methods of quantum simulation of complex many-body systems on NISQs will require special attention to the modeling of noise and decoherence. Though environmental noise from the thermal vibrational background can in principle be simulated using conventional open quantum system simulation methods, the NISQ processor will add its own sources of noise, which in general will not match up with the actual effects of noise from the physical environment. Carefully designing the quantum simulation could allow at least part of the hardware noise in the quantum simulator to mimic the effects of environmental noise. This could extend the applicability of noisy quantum simulators to simulating noisy quantum systems for sufficiently long time periods that they can encompass crucial and currently poorly understood aspects of quantum energy transport in multiparticle molecular complexes.

The trend toward increased interest in novel techniques for quantum simulation of open quantum systems in order to better understand and tune the effects of noise and errors is likely to continue. One direction is to directly adapt classical techniques, such as propagation schemes,⁹⁴⁹ to superconducting quantum processors with pulse-level control.⁹⁵⁰ Current NISQ superconducting quantum information processors consist of qubits coupled via local couplings and via superconducting cavities. The Hamiltonian of the information processor can be controlled by on-chip static fields, and its dynamics is controlled by the application of time-dependent microwave pulses. The conventional method for performing quantum simulations using such devices is to divide up the action of the Hamiltonian to be simulated into small time steps and to simulate each small time step using finite quantum logic operations. We anticipate that the quantum simulation can in principle be made significantly more efficient by using Hamiltonian mapping techniques, in which a carefully designed time-dependent Hamiltonian is used to simulate the quantum dynamics.

Catalyzed by recent discoveries in quantum computation, research has focused on using quantum resources to describe


open quantum systems.^{890,894,899,901} A new quantum algorithm for such open systems, one that scales favorably on quantum devices, would have far reaching impact beyond the quantum computing community. Recently presented approaches invoke the Sz.-Nagy dilation theorem for either a single Lindbladian trajectory⁸⁹⁹ or an ensemble of trajectories⁹⁰¹ to treat open quantum systems in a wide variety of complex environments. With these resulting methods, the time evolution can be simulated on a quantum device with the potential for exponential improvements in simulation time and storage over classical algorithms, offering a more efficient alternative especially with large, correlated systems. We anticipate further algorithmic advances in the treatment of both Markovian and non-Markovian dynamics on quantum computers, as well as extensive application to systems of chemical and material interest.


We hope our timely presentation of breakthroughs, advances, and developments in the direction of quantum information and algorithms for correlated quantum matter resonate with readers interested in this intersection. From our perspective, the field is rapidly approaching algorithms with nonexponential complexity to address the grand challenge of the strongly correlated problem. Looking ahead at the vibrant intersection of quantum information science and algorithms for correlated quantum matter, we envision seminal advances in predicting many-body quantum states, describing excitonic quantum matter and large-scale entangled states, a better understanding of high-temperature superconductivity, and quantifying open quantum system dynamics.

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Notes

The authors declare no competing financial interest.

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Johannes Flick is an associate research scientist at the Center of Quantum Physics (CCQ) of the Flatiron Institute in New York, NY, and earned his Ph.D. in theoretical physics from the Fritz Haber Institute and the Humboldt University in Berlin, Germany. Before joining CCQ, Johannes was a postdoctoral researcher at the Max Planck Institute for the Structure and Dynamics of Matter in Hamburg, Germany, and a DFG Postdoctoral Research Fellow in the Narang Lab at Harvard University, Cambridge, MA. His research is focused on the development of new computational methods for light–matter interactions on a microscopic level, as well as their applications in catalysis, spectroscopy, strong light–matter coupling, and quantum-information processing.

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Prineha Narang is an Assistant Professor at the John A. Paulson School of Engineering and Applied Sciences at Harvard University. Prior to joining the faculty, Prineha came to Harvard as a Ziff Fellow and worked as a Research Scholar in Condensed Matter Theory at the MIT Department of Physics. She received an M.S. and Ph.D. in Applied Physics from the California Institute of Technology (Caltech). Prineha's work has been recognized by many awards and special designations, including an NSF CAREER Award in 2020, being named a Moore Inventor Fellow by the Gordon and Betty Moore Foundation for pioneering innovations in quantum science and technology, CIFAR Azrieli Global Scholar by the Canadian Institute for Advanced Research, a Top Innovator by MIT Tech Review (MIT TR35), and a Young Scientist by the World Economic Forum in 2018. In 2017, she was named by Forbes Magazine on their "30under30" list for her work in atom-by-atom quantum engineering. Narang Lab's research focuses on how quantum systems behave, particularly away from equilibrium, and how we can harness these effects. By creating predictive theoretical and computational approaches to study dynamics, decoherence, and correlations in molecules and matter, her work would in future enable technologies that are inherently more powerful than their classical counterparts ranging from scalable quantum information processing to ultrahigh efficiency optoelectronic and energy conversion systems. Prineha is also the CTO and cofounder of a Boston-based startup, Aliro Quantum, towards the commercialization of quantum information processing. Outside of science, she is an avid triathlete and runner.

ACKNOWLEDGMENTS

The authors thank Dr. Stefan Krastanov, Dr. Tomáš Neuman, Gregory D. Cunningham (Harvard University), Scott E. Smart, Dr. Alexandra E. Raeber, Prof. David A. Mazziotti (University of Chicago), Olivia Werba (University of Pennsylvania), and Dr. Anthony Schlimgen (Los Alamos National Lab) for the reading of and helpful suggestions on the manuscript. The authors acknowledge support from the Army Research Office MURI (Ab-Initio Solid-State Quantum Materials) grant number W911NF-18-1-0431 (for supporting work on algorithms for correlated quantum materials), the U.S. Department of Energy "Photonics at Thermodynamic Limits" Energy Frontier Research Center under grant number DE-SC0019140 (for

supporting work on algorithms and methods for excited-state quantum materials), and DOE Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division under FWP ERKCK47 "Understanding and Controlling Entangled and Correlated Quantum States in Confined Solid-state Systems Created via Atomic Scale Manipulation" (for supporting algorithms and computational approaches in entangled states and open quantum systems). P.N. is a Moore Inventor Fellow and gratefully acknowledges generous support through Grant GBMF8048 from the Gordon and Betty Moore Foundation. K.H.-M. also acknowledges support from the Harvard Quantum Initiative Seed Grant. The Flatiron Institute is a division of the Simons Foundation.

GLOSSARY

C_k	Lindbladian operator corresponding to k th channel
E	energy
E_{HF}	Hartree–Fock energy
E_{corr}	correlation energy
E_{exact}	exact energy
GW	Expansion of electron self-energy in terms of the Coulomb operator W and single particle Green's function G
N_e	number of electrons
N_{orb}	number of orbitals
SO	special orthogonal group
SU	special unitary group
T_2	partial 3-body N -representability condition
ΔSCF	delta self-consistent field
Λ	dynamical map
Ψ	N -body wave function
Σ	electron self-energy
$\chi_{\text{R}}^{(1)}$	response function
γ_k	decay rate corresponding to Lindbladian channel C_k
\hat{H}	Hamiltonian
\hat{T}	excitation operator
\hat{a}	annihilation operator
\hat{a}^\dagger	creation operator
\mathbf{D}	electric displacement
\mathbf{R}	electronic dipole operator
\mathbf{r}	position vector
C	concurrence
$I(t)$	inhomogeneity term
\mathcal{K}	memory kernel
\mathcal{N}	measure of non-Markovianity
\mathcal{P} and \mathcal{Q}	projection operators
τ	time lag
1D	1-electron reduced density matrix
2D	2-electron reduced density matrix
2G	particle-hole reduced density matrix
2K	2-body Hamiltonian
2Q	2-hole reduced density matrix
${}^N D$	N -electron reduced density matrix
i	imaginary number $\sqrt{-1}$
n	electronic density
n_i	occupation number of i th orbital
$v_o(\mathbf{r})$	static external potential
$v_{\text{xc}}(\mathbf{r})$	exchange-correlation potential
ACBN0	Agapito Curtarolo and Buongiorno Nardelli pseudohybrid Hubbard density functional

ACSE	Antihermitian contracted Schrödinger equation	RDM	reduced density matrix
B3LYP	Becke, 3-parameter, Lee–Yang–Parr hybrid functional	RDMFT	reduced density matrix functional theory
BCH	Baker–Campbell–Hausdorff	RHP	Rivas, Huelga, Plenio measure of non-Markovianity
BLP	Breuer–Laine–Piilo measure of non-Markovianity	RI	resolution of identity
CAS	complete active space	RPA	random-phase approximation
CASPT2	complete active space perturbation theory to second order	SC	superconducting
CASPT	complete active space perturbation theory	SCAN	strongly constrained and appropriately normed semilocal density functional
CASSCF	complete active space self-consistent field	SDP	semidefinite programming
CC	coupled cluster	SiC	silicon carbide
CCE	cluster correlation expansion	SiV	silicon vacancy
CCS	coupled cluster singles	STO-6G	Pople Slater-type orbital 6-Gaussian basis set
CCSD	coupled cluster singles doubles	TCL	time convolutionless master equation
CCSDT	coupled cluster singles doubles triples	TDDFT	time-dependent density functional theory
CDW	charge density wave	TDRDMFT	time-dependent reduced density matrix functional theory
CE	cluster expansion	UCC	unitary coupled cluster
CI	configuration interaction	v2RDM	variational 2-electron reduced density matrix method
CIS	configuration interaction singles	VQE	variational quantum eigensolver
CISD	configuration interaction singles doubles	YAG	yttrium ion garnet
CISDT	configuration interaction singles doubles triples	ZPL	zero-phonon line
DFT	density functional theory		
DMET	density matrix embedding theory		
DMFT	dynamical mean field theory		
DOC1	doubly occupied configuration interaction		
FCI	full configuration interaction		
FCP	Franck–Condon profile		
GAS	generalized active space		
GGA	generalized-gradient approximation		
GME	generalized master equation		
GPC	generalized Pauli constraints		
hBN	hexagonal boron nitride		
HEOM	hierarchical equations of motion		
HF	Hartree–Fock		
HOMO	highest-occupied molecular orbital		
HSE	Heyd–Scuseria–Ernzerhof functional		
LAS	localized active space		
LDA	local density approximation		
LED	light-emitting diode		
LR	linear response		
LUMO	lowest-unoccupied molecular orbital		
MC-SCF	multiconfigurational self-consistent field		
MFT	mean field theory		
MFT-GQME	mean field theory generalized quantum master equation		
MP2	Møller–Plesset perturbation theory to second order		
MPT	Møller–Plesset perturbation theory		
NISQ	noisy intermediate-scale quantum		
NO	natural orbital		
NV	nitrogen-vacancy		
OQS	open quantum systems		
PBE	Perdew, Burke, and Ernzerhof functional		
PIMC	path integral Monte Carlo		
QCNN	quantum convolutional neural networks		
QEDFT	quantum electrodynamic density-functional theory		
QPEA	quantum phase estimation algorithms		
QUAPI	quasi-adiabatic path integral		
RAS	restricted active space		
RASPT2	restricted active space perturbation theory to second order		

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