Real-time density-matrix coupled-cluster approach for closed and open systems at finite temperature F

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Philip Shushkov , and Thomas F. Miller

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Philip Shushkov^{a)} and Thomas F. Miller III

AFFILIATIONS

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

^{a)}shushkov@caltech.edu

ABSTRACT

We extend the coupled-cluster method to correlated quantum dynamics of both closed and open systems at finite temperatures using the thermofield formalism. The approach expresses the time-dependent density matrix in an exponential ansatz and describes time-evolution along the Keldysh path contour. A distinct advantage of the approach is exact trace-preservation as a function of time, ensuring conservation of probability and particle number. Furthermore, the method avoids the computation of correlated bra-states, simplifying the computational implementation. We develop the method in a thermal quasiparticle representation, which allows seamless connection to the projection method and diagrammatic techniques of the traditional coupled-cluster formalism. For comparison, we also apply the thermofield framework to the density-matrix renormalization-group method to obtain reference results for closed and open systems at finite temperature. We test the singles and doubles approximation to the density-matrix coupled-cluster method on the correlated electronic dynamics of the single-impurity Anderson model, demonstrating that the new method successfully captures the correlated dynamics of both closed systems at finite temperature and driven-dissipative open systems. This encouraging performance motivates future applications to nonequilibrium quantum many-body dynamics in realistic systems.

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I. INTRODUCTION

The simulation of nonequilibrium quantum many-body dynamics is an outstanding challenge in chemical physics. The theoretical description of nonequilibrium phenomena is essential for the understanding of many processes, including chemical dynamics of molecules,^{1,2} defects in extended systems,^{3–5} quantum transport in molecular junctions,^{6,7} and chemical reactions at surfaces and interfaces,^{8–10} as well as the description of novel driven-dissipative phenomena in open systems, such as discrete time crystals.^{11,12} These open questions motivate the extension of well-established wavefunction approaches of quantum chemistry to the correlated quantum dynamics of closed and open systems at finite temperature.

Among the methods of quantum chemistry, the coupled-cluster approach has become the gold standard for incorporation of correlation effects in weakly correlated molecular systems.^{13,14} The approach relies on an exponential ansatz for the wavefunction of the system, which is parameterized by connected cluster

amplitudes. The singles and doubles approximation to the cluster operator together with a perturbative triples correction has set the accuracy standard for the ground state properties of molecules, and excited state properties have been targeted via linear response theory.^{15–17} Furthermore, time-dependent coupled-cluster wavefunction methods have been recently applied to the nonequilibrium electronic dynamics of molecules,^{18–20} and beyond the single-reference framework, the coupled-cluster approach has been extended to more challenging, multireference systems.^{21,63}

Thermal effects have recently been included in the coupled-cluster formalism^{22–24} using the method of thermal cumulants^{25–27} and thermofield theory. Furthermore, thermofield theory has been combined with the method of configuration interaction to simulate finite-temperature molecular properties.²⁸ The thermofield method^{29,30} was developed to incorporate thermal mixed states in quantum field theory, and the approach was later extended to open systems.^{31–34} Besides thermal effects, the method has allowed direct application of both coupled-cluster and configuration interaction

theory to nonequilibrium stationary states,^{35–39} and it has also been combined with renormalization-group methods^{40–44} to simulate the real-time finite-temperature dynamics of closed systems, including impurity-bath models and coupled electron-nuclear dynamics.

Our goal is to extend the coupled-cluster approach to the real-time correlated quantum dynamics of closed and open systems at finite temperatures, bridging the gap between recent finite-temperature and real-time coupled-cluster extensions. We provide a unified framework to describe both equilibrium and nonequilibrium stationary states and nonequilibrium quantum dynamics. We use the thermofield theory to represent the mixed quantum states of closed and open systems in a wavefunction form, and we express this wavefunction in an exponential ansatz. We test the singles and doubles approximation to the new density-matrix coupled-cluster (DMCC) method on the correlated electronic dynamics of the single-impurity Anderson model (SIAM)^{45–47} and compare the results with the renormalization-group method.

This paper is organized as follows: We summarize thermofield theory and present the real-time finite-temperature density-matrix coupled-cluster method for closed and open systems in Sec. II. We present the results for the quantum dynamics of the single-impurity Anderson model at a range of interaction strengths and temperatures in Sec. III, including also dynamics with driving and dissipation. We conclude in Sec. IV with remarks on the future directions for method development.

II. THEORY

We start this section by reviewing the thermofield formalism and the thermal Bogoliubov transformation, which we use to define temperature-dependent quasiparticles. We then present the main result of this paper, the extension of the real-time coupled-cluster method to closed and open systems at finite temperatures using the thermal quasiparticle representation. We focus next on the test system for our quantum dynamics approximations, the single-impurity Anderson model, and the extension of renormalization group approaches to closed and open systems, which we compare with the coupled-cluster approximation.

A. Thermo field theory

Thermofield theory^{29,31,34,48} expresses the mixed states of quantum systems in the form of pure state wavefunctions. Let us define a basis in the Hilbert space $\mathcal{H}$ of a system by the ket-states $|\mathbf{n}\rangle$, generated via the action of the creation operators $a_i^\dagger$ on the vacuum ket $|0\rangle$, $|\mathbf{n}\rangle = \prod_i a_i^\dagger |0\rangle$, where $\mathbf{n}$ is the set of occupation numbers and the index i enumerates the states of the single-particle basis. The creation operators $a_i^\dagger$ and their Hermitian conjugate annihilation operators a_i obey the commutation relations

$$[a_i, a_j^\dagger]_\sigma = \delta_{ij}, [a_i^\dagger, a_j^\dagger]_\sigma = [a_i, a_j]_\sigma = 0, \quad (1)$$

where the commutator is $[A, B]_\sigma = AB - \sigma BA$ with $\sigma = 1$ for bosons and $\sigma = -1$ for fermions. Using the basis $|\mathbf{n}\rangle$ of $\mathcal{H}$, the density matrix ρ is given by

$$\rho = \sum_{\mathbf{n}, \mathbf{m}} \rho_{\mathbf{n}\mathbf{m}} |\mathbf{n}\rangle \langle \mathbf{m}| \quad (2)$$

with the ket-bra couples $|\mathbf{n}\rangle \langle \mathbf{m}|$ forming an orthonormal basis. To write Eq. (2) in the form of a wavefunction, thermofield theory uses a second replica $\tilde{\mathcal{H}}$ of the original Hilbert space $\mathcal{H}$ to express the ket-bra couples $|\mathbf{n}\rangle \langle \mathbf{m}|$ as ket-basis states $|\mathbf{n}, \tilde{\mathbf{m}}\rangle$, effectively doubling the number of degrees of freedom of the system. We define tilde creation $\tilde{a}_i^\dagger$ and annihilation $\tilde{a}_i$ operators in the tilde Hilbert space $\tilde{\mathcal{H}}$ via the relations

$$\begin{aligned} \tilde{a}_i |\mathbf{n}\rangle \langle \mathbf{m}| &= \sigma^{\mu+1} |\mathbf{n}\rangle \langle \mathbf{m}| a_i^\dagger, \\ \tilde{a}_i^\dagger |\mathbf{n}\rangle \langle \mathbf{m}| &= \sigma^\mu |\mathbf{n}\rangle \langle \mathbf{m}| a_i, \end{aligned} \quad (3)$$

with $\mu = \sum_i (n_i - m_i)$, the difference of ket- and bra-state occupation numbers. From Eqs. (1) and (3), the nontilde and tilde operators satisfy the commutation relations

$$\begin{aligned} [\tilde{a}_i, \tilde{a}_j^\dagger]_\sigma &= \delta_{ij}, [\tilde{a}_i^\dagger, \tilde{a}_j^\dagger]_\sigma = [\tilde{a}_i, \tilde{a}_j]_\sigma = 0, \\ [\tilde{a}_i^\dagger, a_j^\dagger]_\sigma &= [\tilde{a}_i, a_j]_\sigma = 0, \end{aligned} \quad (4)$$

which show that the nontilde and tilde operators represent independent fermionic or bosonic degrees of freedom. Given that the tilde Hilbert space is the Hermitian conjugate to the original Hilbert space, thermofield theory relates operators acting on the two subspaces via the antilinear tilde conjugation operation with the properties

$$\begin{aligned} (AB)^\sim &= \tilde{A}\tilde{B}, \\ (c_a A + c_b B)^\sim &= c_a^* \tilde{A} + c_b^* \tilde{B}, \end{aligned} \quad (5)$$

with c_a and c_b being complex numbers and $*$ denoting complex conjugation. The double tilde conjugation rules $\tilde{\tilde{a}}_i = \sigma a_i$ and $\tilde{\tilde{a}}_i^\dagger = \sigma a_i^\dagger$ supplement Eq. (5).

In the doubled Hilbert space $\mathcal{H} \times \tilde{\mathcal{H}}$ of nontilde (physical) and tilde (hidden) degrees of freedom, the density matrix, Eq. (2), takes the form of a pure state wavefunction,

$$\rho = \sum_{\mathbf{n}, \mathbf{m}} \rho_{\mathbf{n}\mathbf{m}} |\mathbf{n}, \tilde{\mathbf{m}}\rangle. \quad (6)$$

The thermal density matrix $|\rho_0\rangle$ of a noninteracting system, for instance, can be written in the exponential form,

$$|\rho_0\rangle = \frac{1}{Q_0} \sum_{\mathbf{n}} e^{-\beta \sum_i n_i \varepsilon_i} |\mathbf{n}, \tilde{\mathbf{n}}\rangle = \frac{1}{Q_0} \exp \left(\sum_i e^{-\beta \varepsilon_i} a_i^\dagger \tilde{a}_i^\dagger \right) |0\rangle, \quad (7)$$

where β is the reciprocal temperature, $\beta = (k_B T)^{-1}$, with T being the temperature, Q_0 is the partition function, ε_i are the single-particle energy levels, and $|0\rangle = |0, \tilde{0}\rangle$ is the vacuum ket-state in the doubled Hilbert space. Similarly, the resolution of identity, the unit ket-state $|1\rangle$, also has an exponential form,

$$|1\rangle = \sum_{\mathbf{n}} |\mathbf{n}, \tilde{\mathbf{n}}\rangle = \exp \left(\sum_i a_i^\dagger \tilde{a}_i^\dagger \right) |0\rangle. \quad (8)$$

The average value of an operator O , given by the trace with the density matrix ρ , becomes an expectation value with the ket-state $|\rho\rangle$, Eq. (6), in thermofield theory. Specifically,

$$\text{tr}[\rho O] = \langle 1 | O | \rho \rangle, \quad (9)$$

where the density matrix is normalized $\langle 1 | \rho \rangle = 1$. The bra-state and ket-state in Eq. (9) are different due to the choice of the path contour in the complex time plane as shown in Sec. II C. This choice

is most suitable for extending the coupled-cluster approach to finite temperatures because it circumvents the need to compute a correlated bra-state. We provide further details in Sec. II C devoted to the coupled-cluster formalism.

The Liouville-von Neumann equation for the time-evolving density matrix, $i\dot{\rho} = [H, \rho]$, becomes the Schrödinger equation for the pure ket-state $|\rho\rangle$,

$$i|\dot{\rho}_t\rangle = \hat{H}|\rho_t\rangle, \quad (10)$$

where the super-Hamiltonian operator $\hat{H}$ is the difference of the original Hamiltonian H and its tilde conjugate,

$$\hat{H} = H - \tilde{H}. \quad (11)$$

The super-Hamiltonian in Eq. (11) does not mix the nontilde and tilde degrees of freedom for a closed system, resulting in a unitary evolution. For open, dissipative systems, the super-Hamiltonian entangles the nontilde and tilde degrees of freedom by terms that resemble pairing of opposite spin electrons in the theory of superconductivity. We will give an example of such a super-Hamiltonian in Sec. II D.

Formal integration of Eq. (10) gives the time-dependent density matrix $|\rho_t\rangle$ as

$$|\rho_t\rangle = e^{-i\hat{H}t}|\rho_{t_0}\rangle, \quad (12)$$

with $|\rho_{t_0}\rangle$ being the initial density matrix. In quantum-quench simulations, we initiate the quantum dynamics from an uncorrelated state and take into account the effects of interactions by the subsequent time evolution. In Sec. III, we present results of such simulations where most of the system, the bath, is initially at thermal equilibrium with a density matrix given by Eq. (7). Nonequilibrium states relax to stationary states, such as equilibrium states, with time-independent density matrices $|\rho_s\rangle$, which are annihilated by the super-Hamiltonian $\hat{H}|\rho_s\rangle = 0$.

B. Thermal quasiparticles

The creation $a_i^\dagger$ and $\tilde{a}_i^\dagger$ and annihilation a_i and $\tilde{a}_i$ operators have a complementary action on the unit bra-state,

$$\begin{aligned} \langle 1|a_i^\dagger &= \langle 1|\tilde{a}_i, \\ \langle 1|\tilde{a}_i^\dagger &= \sigma\langle 1|a_i. \end{aligned} \quad (13)$$

Because the super-Hamiltonian, Eq. (11), conserves the number of particles and contains equal numbers of nontilde and tilde operators, Eq. (13) gives

$$\langle 1|\hat{H} = 0. \quad (14)$$

This bra-state condition ensures the conservation of probability and the normalization of the time-dependent density matrix, Eq. (12), at all times, and it allows us to express the expectation value, Eq. (9), in the Heisenberg picture

$$\langle 1|O|\rho_t\rangle = \langle 1|O_t|\rho_{t_0}\rangle \quad (15)$$

with $O_t = e^{i\hat{H}t}Oe^{-i\hat{H}t}$ —the Heisenberg-evolved operator O .

The action of the a_i and $\tilde{a}_i$ operators on the noninteracting thermal density matrix is similarly complementary

$$\begin{aligned} a_i|\rho_0\rangle &= e^{-\beta\epsilon_i}\tilde{a}_i^\dagger|\rho_0\rangle, \\ \tilde{a}_i|\rho_0\rangle &= \sigma e^{-\beta\epsilon_i}a_i^\dagger|\rho_0\rangle. \end{aligned} \quad (16)$$

Because a_i annihilates an electron, the thermal ket-state condition, Eq. (16), shows that $\tilde{a}_i^\dagger$ creates a hole and vice versa because $a_i^\dagger$ creates an electron, $\tilde{a}_i$ annihilates a hole.

Equations (13) and (16) imply that we can transform the creation $a_i^\dagger$ and $\tilde{a}_i^\dagger$ and annihilation a_i and $\tilde{a}_i$ operators into a new set of creation $b_i^\dagger$ and $\tilde{b}_i^\dagger$ and annihilation b_i and $\tilde{b}_i$ operators, which, respectively, annihilate the unit bra-state and noninteracting thermal ket-state

$$\begin{aligned} \langle 1|b_i^\dagger &= \langle 1|\tilde{b}_i^\dagger = 0, \\ b_i|\rho_0\rangle &= \tilde{b}_i|\rho_0\rangle = 0. \end{aligned} \quad (17)$$

The transformation that satisfies Eq. (17) and preserves the commutation relations, Eqs. (1) and (4), is given by

$$\begin{aligned} b_i^\dagger &= a_i^\dagger - \tilde{a}_i, \quad \tilde{b}_i^\dagger = \tilde{a}_i^\dagger - \sigma a_i, \\ b_i &= u_i a_i - v_i \tilde{a}_i^\dagger, \quad \tilde{b}_i = u_i \tilde{a}_i - \sigma v_i a_i^\dagger, \end{aligned} \quad (18)$$

where $v_i = (e^{\beta\epsilon_i} - \sigma)^{-1}$ is the Bose-Einstein or the Fermi-Dirac distribution and $u_i = 1 + \sigma v_i$. Equation (18) preserves the commutation relations among the new set of creation and annihilation operators but does not preserve the Hermitian conjugation relation between creation and annihilation operators. Such canonical, nonunitary transformations are known in the theory of superconductivity as Bogoliubov transformations.⁴⁹ The thermal Bogoliubov transformation, Eq. (18), defines new thermal quasiparticles $b_i^\dagger$ and b_i and thermal quasiholes $\tilde{b}_i^\dagger$ and $\tilde{b}_i$ with respect to the unit bra-state and noninteracting thermal ket-state, Eq. (17), which we refer to as the new left $\langle 0|$ and right $|0\rangle$ vacuum states, respectively. We use the thermal quasiparticle representation to introduce correlated dynamics via coupled-cluster theory at finite temperatures in closed and open systems in Sec. II C.

C. Density-matrix coupled-cluster approach

In our coupled-cluster approach, we express the time-dependent density matrix of the system in the exponential form

$$|\rho_t\rangle = e^{T_t}|\rho_{t_0}\rangle, \quad (19)$$

where $|\rho_{t_0}\rangle = |\rho_0\rangle$ is the noninteracting thermal density matrix in Eq. (7) and T_t is the time-dependent cluster operator, which we expand in the number of excited thermal quasiparticle-hole pairs n as

$$T_t = \sum_{n=1}^N T_n, \quad (20)$$

where N is the highest excitation level. We express the cluster operators T_n via the quasiparticle $b_i^\dagger$ and quasihole $\tilde{b}_i^\dagger$ creation operators from Sec. II B as

$$T_n = \frac{1}{n!} \sum_{ij,\dots,kl,\dots} t_{ij,\dots,kl,\dots}^{ik,\dots} b_i^\dagger b_j^\dagger \dots \tilde{b}_i^\dagger \tilde{b}_j^\dagger, \quad (21)$$

where $t_{ij,\dots,kl,\dots}^{ik,\dots}$ are the time-dependent cluster amplitudes and the indices i, j, k , and l run over the entire single-particle basis. We test the performance of the density-matrix coupled-cluster (DMCC) method keeping terms with up to two quasiparticle-hole pairs in

Eq. (20). The explicit form of the cluster operator for this singles and doubles approximation is

$$T_t = \sum_{ij} t_{ij}^i b_i^\dagger \tilde{b}_j^\dagger + \frac{1}{4} \sum_{ijkl} t_{ijkl}^{ik} b_i^\dagger b_k^\dagger \tilde{b}_l^\dagger \tilde{b}_j^\dagger. \quad (22)$$

Equation (19) together with Eqs. (20) and (21) parameterizes a class of trace-preserving transformations that include the subset of dynamical completely positive transformations of open systems and the narrower subset of unitary transformations of closed systems. The trace-preservation directly follows from the definition of the $b^\dagger$ and $\tilde{b}^\dagger$ creation operators, Eq. (17), $\langle 1|\rho_t\rangle = \langle 1|e^{T_t}|\rho_0\rangle = \langle 1|\rho_0\rangle$. The time evolution governed by the Schrödinger equation, Eq. (10), imposes further constraints on the density matrix in addition to trace-preservation, such as the Hermiticity and positivity of the density matrix. These constraints translate to relations among the cluster amplitudes. The Hermiticity of the density matrix, for instance, gives invariance upon tilde conjugation in thermofield theory, $|\tilde{\rho}_t\rangle = |\rho_t\rangle$, resulting in a tilde invariant cluster operator $\tilde{T}_t = T_t$. For a singles-only approximation, this leads to the Hermiticity of the singles amplitude matrix $t_{ij}^i = t_{ji}^{i*}$ and similar relations hold for the higher rank cluster amplitudes. The dynamical constraints determined by the Schrödinger equation need not be incorporated in the parameterization of the cluster amplitudes; rather, their satisfaction may be used as diagnostics for the solutions to the Schrödinger equation.

The trace-preservation property of the coupled-cluster density matrix allows us to express quantum-statistical averages of time-dependent operators in a simple way.⁵⁰ Thermal averages of Heisenberg-evolved operators $O(t)$ are given in general by the ratio

$$G = \frac{\text{tr}[e^{-\beta H} O(t_N) \cdots O(t_1)]}{\text{tr}[e^{-\beta H}]} = \frac{\langle T_c U_c O_N \cdots O_1 \rangle}{\langle T_c U_c \rangle}. \quad (23)$$

In diagrammatic terms, the denominator in Eq. (23) cancels the disconnected vacuum diagrams in the numerator such that only connected diagrams contribute to the thermal average. In Eq. (23), we have also introduced a more succinct expression for the average that involves a time-ordered propagation with T_c the chronological operator and U_c the full quantum propagator along a contour in the complex time plane, which initiates at time t_i before time t_1 , evolves along the real time axis to t_f past the time t_N , comes back along the real time axis to t_i , and propagates downwards along the imaginary time axis to time $t_i - i\beta$. We can take, respectively, the initial t_i and final t_f times to the infinite past, $t_i \rightarrow -\infty$, and infinite future, $t_f \rightarrow \infty$, where the interaction is turned off, resulting in cancellation of the correlated contribution to the imaginary axis propagation. Such a contour in the complex time plane underlies nonequilibrium Keldysh diagrammatic theory^{51,52} and the density-matrix coupled-cluster theory presented here.

Using the definition of expectation value Eq. (9) and the super-Hamiltonian Eq. (11), we cast Eq. (23) in thermofield theory as

$$G = \frac{\langle 1|T e^{-i\hat{H}t} O_N \cdots O_1 |\rho_0\rangle}{\langle 1|e^{-i\hat{H}t} |\rho_0\rangle} = \langle 1|O(t_N) \cdots O(t_1) |\rho_0\rangle, \quad (24)$$

where the imaginary axis propagation is represented by the non-interacting thermal state $|\rho_0\rangle$ and the contour runs only along the real time axis from t_i to t_f . The second equality in Eq. (24) follows from the trace-preservation of the super-Hamiltonian,

allowing us to express the thermal average in an explicitly connected form. In our density-matrix coupled-cluster method, we rigorously impose the trace-preservation of the time-evolved density matrix, resulting in explicit cancellation of the disconnected contributions to the thermal average, which avoids the construction of a correlated bra-state.

Other choices for the path contour in the complex time plane are also possible because of the analytic property of thermal averages. These choices lead to equivalent formulations of thermal averages in thermofield theory but may not lead to equivalent coupled-cluster approximations. One other choice, for instance, is to place the backward portion of the real-time propagation at imaginary time $-i\beta/2$ rather than immediately below the real time axis.⁵⁰ This contour gives unitary formulation of thermal averages that has the bra-state Hermitian conjugate to the ket-state. If we express the time-dependent density matrix in this unitary formulation in an exponential form, then we also need to compute the correlated bra-state to evaluate the thermal average, unless we use a unitary form for the cluster operator.

We derive the equation of motion for the cluster amplitudes by using Eq. (19) in the Schrödinger equation (10) for the density matrix ket-state.¹⁴ Following multiplication from the left with e^{-T_t} , we obtain

$$ie^{-T_t} \partial_t e^{T_t} |\rho_0\rangle = e^{-T_t} \hat{H} e^{T_t} |\rho_0\rangle, \quad (25)$$

where $\hat{H}$ is the super-Hamiltonian of the system expressed in the thermal quasiparticle representation. Because ∂_t is a single-particle operator and the creation quasiparticle operators are time-independent, the Baker-Campbell-Hausdorff identity gives

$$e^{-T_t} \partial_t e^{T_t} = \partial_t + \dot{T}_t, \quad (26)$$

where the dot stands for the time derivative. Because the super-Hamiltonian has a finite number of creation and annihilation quasiparticle operators and the cluster operators, Eqs. (20) and (21) commute, the application of the Baker-Campbell-Hausdorff identity shows that the expansion of the similarity-transformed super-Hamiltonian $e^{-T_t} \hat{H} e^{T_t}$ contains a finite number of nested commutator terms. For the standard electronic structure super-Hamiltonian, which has terms with at most four annihilation quasiparticle operators, the commutator series exactly truncates at fourth order. Thus, the equation of motion for the cluster operators, Eq. (25), simplifies to

$$i\dot{T}_t |\rho_0\rangle = \left(\hat{H} \sum_{n=0}^{n=N} \frac{1}{n!} T_t^n \right)_c |\rho_0\rangle, \quad (27)$$

where N stands for the largest order nonvanishing term in the series and we used the time-independence of the ket-state $\partial_t |\rho_0\rangle = 0$. The subscript “c” in Eq. (27) denotes that only the connected part of the expression in the brackets has to be considered as a result of the cancellation of the disconnected part by the nested commutators. To derive differential equations for the cluster amplitudes, we project Eq. (27) onto states with a finite number of quasiparticle excitations, $\langle 0|\tilde{b}_j \cdots b_i$,

$$i\langle 0|\tilde{b}_j \cdots b_i \dot{T}_t |\rho_0\rangle = \langle 0|\tilde{b}_j \cdots b_i \left(\hat{H} \sum_{n=0}^{n=N} \frac{1}{n!} T_t^n \right)_c |\rho_0\rangle. \quad (28)$$

In our singles and doubles approximation to the DMCC method, Eq. (22), we project onto bra-states that have only single and double quasiparticle excitations. These equations contain vacuum expectation values of strings of creation and annihilation operators, which when evaluated give a set of coupled nonlinear ordinary differential equations for the cluster amplitudes that we solve using the Runge-Kutta method.⁵³

The DMCC cluster amplitude equations can also be derived from a time-dependent variational principle that parallels the time-dependent coupled cluster formalism.^{20,54} In thermofield theory, the action functional for expectation values of observables of Balian and Vénéroni⁵⁵ can be written as

$$I = i \int_{t_0}^{t_1} dt \langle A_t | i \partial_t - \hat{H} | \rho_t \rangle + \langle A | \rho_{t_1} \rangle, \quad (29)$$

where $|\rho_t\rangle$ is the density matrix in the coupled cluster form, Eq. (19), and $\langle A_t |$ is the bra-vector of an observable A , which we represent as $\langle A_t | = \langle 0 | \Omega_t e^{-T_t}$, with Ω_t being an operator in the space of single and double quasiparticle de-excitations. Unconstrained variation of this functional with respect to the amplitudes in Ω_t leads to the cluster amplitude equations, Eq. (28), whereas variation of the functional with respect to the T_t amplitudes gives a set of equations for the Ω_t amplitudes. To evaluate the expectation value of A , however, we need to integrate only the cluster amplitude equations, avoiding the propagation of the bra-vector. This confirms that the cluster amplitudes satisfying Eq. (28) are optimal for the computation of time-dependent expectation values of observables, which can be expressed in the single and double quasiparticle space.

A distinct advantage of the thermal quasiparticle representation is the existence of traditional normal ordering of operators and the applicability of Wick's theorem for evaluation of expectation values of strings of creation and annihilation operators.⁴⁹ We define normal-ordering as the string of operators, which has all creation operators to the left of all annihilation operators. Contractions of quasiparticle operators, the difference of any operator ordering from the normal order, are straightforward to evaluate because the quasiparticle operators satisfy the usual commutation relations. Given that the creation operators $b_i^\dagger$ and $\tilde{b}_i^\dagger$ annihilate the left vacuum $\langle 1 |$, vacuum expectation values of normal-ordered strings of operators are identically zero. Using Wick's theorem, we can thus show that the vacuum expectation value of any string of creation and annihilation quasiparticle operators is equal to the sum of all possible pairwise contractions. If substrings are already in normal-ordered form, then contractions need to be considered only among the normal-ordered substrings. The number of contractions, however, grows quickly with the complexity of the operator products, and diagrammatic representations, which express the contributions to the coupled-cluster equations in a graphical form, become useful. The same set of rules for drawing zero-temperature time-independent coupled-cluster diagrams^{13,14} applies to the density-matrix coupled-cluster method with upward going lines representing nontilde particles and downward going lines—tilde particles according to the interpretation of nontilde particles as thermal quasiparticles and tilde particles as thermal quasiholes. Summation over “internal” lines runs over the entire single-particle basis, and the sign of diagrams is computed by $(-1)^l$, where l is the number of loops determined in the usual way. This correspondence

allows us to estimate the computational scaling of the singles and doubles DMCC method for a general electronic structure Hamiltonian with two-body interactions to be proportional to $\mathcal{O}(M^6)$, where M is the size of single-particle basis, similarly to the conventional zero-temperature coupled-cluster method. The direct applicability of the diagrammatic techniques provides powerful methods for evaluating real-time finite-temperature coupled-cluster approximations.

D. Single-impurity Anderson model

We apply the DMCC method with single and double quasiparticle excitations to the single-impurity Anderson model (SIAM), which is a well-established system to understand the role of electron correlation in dynamical processes at surfaces. SIAM consists of a localized impurity with a repulsive interaction between opposite spin electrons that is coupled to a noninteracting electronic bath.^{45–47} The SIAM Hamiltonian $H = H_0 + W$ has a noninteracting part H_0 given by

$$H_0 = \sum_{i=0,s} \epsilon_i a_{is}^\dagger a_{is} + \sum_{i=1,s} \left(V_i a_{0s}^\dagger a_{is} + a_{is}^\dagger a_{0s} \right), \quad (30)$$

where ϵ_i are the single-particle energy levels, V_i are the impurity-bath coupling elements, $i = 0, \dots, N_b$ enumerates the single-particle basis, where $i = 0$ corresponds to the impurity, N_b is the number of bath levels, and s sums over the spins of the electrons. The interaction W is given by

$$W = U a_{0\alpha}^\dagger a_{0\alpha} a_{0\beta}^\dagger a_{0\beta}, \quad (31)$$

with U being the Hubbard parameter, a measure of the interaction strength. Equations (30) and (31) represent a closed system with a super-Hamiltonian that is the difference of H and its tilde conjugate, $\hat{H} = H - \tilde{H} = H_0 - \tilde{H}_0 + W - \tilde{W}$. Dissipative coupling of the bath levels to a continuum can be incorporated in the SIAM super-Hamiltonian via terms that mix nontilde and tilde operators,³¹ such as

$$\begin{aligned} \hat{D} = & -i \sum_{i=1,s} \left[\left(\gamma_i^{(1)} - \gamma_i^{(2)} \right) \left(a_{is}^\dagger a_{is} + \tilde{a}_{is}^\dagger \tilde{a}_{is} \right) \right. \\ & \left. - 2\gamma_i^{(1)} \tilde{a}_{is} a_{is} + 2\gamma_i^{(2)} \tilde{a}_{is}^\dagger a_{is}^\dagger + 2\gamma_i^{(2)} \right], \end{aligned} \quad (32)$$

with $\gamma_i^{(1)} = \gamma(1 - \nu_i)$, $\gamma_i^{(2)} = \gamma\nu_i$, and γ being the dissipation strength. The relation among $\gamma_i^{(1)}$, $\gamma_i^{(2)}$ and γ follows from the detailed balance condition, and $\hat{D}$ conforms with the dissipative part of a Lindblad operator⁵⁶ that represents open systems with Markovian dynamics. Non-Markovian effects of the impurity dynamics are captured by explicitly incorporating a finite electronic bath. Together with dissipation, we include driving in SIAM via a time-dependent modulation of the electronic level of the impurity, $H_t = \epsilon_0 + \delta\epsilon \sin(\Omega t)$. We use logarithmic discretization of the electronic bath in our calculations as suggested by Wilson for the Kondo model⁴⁷ with a discretization parameter $\Lambda = 1.1$ and $N_b = 100$. We also consider the more challenging asymmetric case of SIAM with $\epsilon_0 = -0.08$ eV, impurity-bath coupling strength $V = 0.04$ eV, and a range of interaction strengths U and temperatures T .

Using the thermal Bogoliubov transformation, Eq. (18), the SIAM super-Hamiltonian $\hat{H} = \hat{H}_0 + \hat{W} + \hat{D}$ becomes $\hat{H}' = \hat{H}'_0 + \hat{W}'$,

where the noninteracting super-Hamiltonian $\hat{H}'_0$ is given by

$$\hat{H}'_0 = \sum_{i,j,s} h_{ij} b_{is}^\dagger b_{js} - h_{ij}^* \tilde{b}_{is}^\dagger \tilde{b}_{js} + \Delta_{ij} (b_{is}^\dagger \tilde{b}_{js}^\dagger - b_{js}^\dagger \tilde{b}_{is}^\dagger), \quad (33)$$

with the single-particle Hamiltonian matrix h_{ijs} ,

$$h_{ij} = (\epsilon + v_0 U) \delta_{ij=0} + \epsilon'_i \delta_{ij>0} + V_i \delta_{i>0,j=0} + V_j \delta_{i=0,j>0}, \quad (34)$$

and the pairing matrix Δ_{ijs} ,

$$\Delta_{ij} = V_i (u_i v_0 - u_0 v_i) \delta_{i>0,j=0} + V_j (u_j v_0 - u_0 v_j) \delta_{i=0,j>0}, \quad (35)$$

and the interaction $\hat{W}'$ is written as

$$\begin{aligned} \hat{W}' = & U(u_0 - v_0) b_\alpha^\dagger b_\beta^\dagger b_\beta + U b_\alpha^\dagger b_\alpha \tilde{b}_\beta b_\beta + U \tilde{b}_\alpha b_\alpha b_\beta^\dagger b_\beta \\ & + U u_0 v_0 b_\alpha^\dagger b_\beta^\dagger \tilde{b}_\beta + U u_0 v_0 \tilde{b}_\alpha^\dagger \tilde{b}_\beta^\dagger b_\beta - \text{t.c.}, \end{aligned} \quad (36)$$

with t.c. standing for tilde conjugation. In Eq. (34), $\epsilon'_i = \epsilon_i - i\gamma$ are the broadened levels of the electronic bath due to dissipation and the single-particle energy of the impurity is modified by a thermal mean-field term $v_0 U$. The Hubbard interaction in Eq. (36) also incorporates thermal effects as the interaction strength depends on the thermal population of the impurity. Because $\hat{W}'$ includes contributions with up to three annihilation operators, the series in the equation of motion for the cluster operator, Eq. (27), truncates at third order, simplifying the differential equations for the cluster amplitudes.

In our quantum quench simulations, the impurity is initially decoupled from the bath, $V = 0$, and the interaction strength is set to zero, $U = 0$. Thus, the thermal quasiparticles are defined with respect to the exact noninteracting thermal state of the decoupled system at temperature T . At time $t = 0$, both the coupling to the electronic bath and the interaction are turned on, and we compute the nonequilibrium electronic dynamics of the impurity. Other quantum quench protocols are also feasible within the current formulation of DMCC. We could first switch the interaction on the impurity followed by the coupling to the electronic bath, allowing sufficient time for the impurity to thermalize to its interacting thermal state. The thermalization can be further aided by a weakly coupled bath using our open quantum system approach. Such a protocol is applicable to single-molecule quantum transport experiments, where a molecule that is initially in a thermal state is coupled to two leads at different chemical potentials, and we will explore both the thermalization to the interacting thermal state and the relaxation to the nonequilibrium stationary state in further studies.

E. Finite-temperature density-matrix renormalization-group approach for open systems

The quasiparticle representation of thermofield theory is a suitable framework to extend the time-dependent density-matrix renormalization-group (DMRG) method^{57–60} to closed and open systems at finite temperature. Our approach resembles the thermofield density-matrix renormalization group method of Refs. 40 and 41, except that we use the nonunitary thermal Bogoliubov transformation together with the physical super-Hamiltonian. We apply the time-evolving block-decimation approach^{57,58} to SIAM and compare the results to DMCC in Sec. III. We represent the time-evolving density-matrix ket-state as a matrix product state, for which we arrange the electronic sites in a linear array, starting with the α impurity site, followed by N_b α bath sites, the β impurity site, and

N_b β bath sites. Each electronic site carries both nontilde and tilde degrees of freedom. The terms of the SIAM super-Hamiltonian $\hat{H}'$ act on two sites at a time with the interaction $\hat{W}'$, Eq. (36), coupling the impurity sites and the noninteracting super-Hamiltonian $\hat{H}'_0$, Eq. (33), acting between the impurity site and each of the bath sites. The super-Hamiltonian terms, however, are nonlocal as they couple distant sites of the linear array, and we use fermionic swap operators $\hat{S}$ to rearrange sites given by

$$\hat{S}_{i+1,i} = S_{i+1,i,\alpha} S_{i+1,i,\beta} - \tilde{S}_{i+1,i,\alpha} \tilde{S}_{i+1,i,\beta}, \quad (37)$$

where

$$s_{pq\sigma} = 1 + a_{p,\sigma}^\dagger a_{q,\sigma} + a_{q,\sigma}^\dagger a_{p,\sigma} - a_{p,\sigma}^\dagger a_{p,\sigma} - a_{q,\sigma}^\dagger a_{q,\sigma}. \quad (38)$$

We apply the second-order Suzuki-Trotter decomposition⁶¹ to the super-Hamiltonian terms in the time-evolution operator, which together with the swap operators results in the following sequence of two-site gates for a half time step δt ,

$$e^{-i\hat{H}'\frac{\delta t}{2}} = \prod_{i \in \alpha} \left[e^{-i(\hat{H}'_0)_{0i}\frac{\delta t}{2}} \hat{S}_{i,i+1} \right] e^{-i\hat{W}'\frac{\delta t}{2}} \prod_{j \in \beta} \left[e^{-i(\hat{H}'_0)_{0j}\frac{\delta t}{2}} \hat{S}_{j,j+1} \right], \quad (39)$$

where i runs over the sequence of α sites and j over the sequence of β sites, respectively.

The full evolution operator is the product of Eq. (39) and its transpose. The application of each of the two-site gates in Eq. (39) requires the singular value decomposition of the resultant tensor to obtain the time-evolved matrix product state. Only singular values above a certain threshold are kept in the matrix product state, which represents the decimation step of the DMRG algorithm. At zero temperature, the doubled set of tilde and nontilde degrees of freedom is not necessary because we can evolve only the wavefunction of the system. We apply the same Suzuki-Trotter decomposition using the SIAM Hamiltonian, instead of the super-Hamiltonian, in this case. We implemented our DMRG method using the ITensor library⁶² and carried out the simulations with a singular-value truncation error of 10^{-9} according to the ITensor definition, except for the closed-system finite-temperature calculations where the truncation error was set at 5×10^{-9} , resulting in a bond dimension of around 300 in these calculations. We used an integration time step of 0.005 V^{-1} throughout.

III. RESULTS

We present the DMCC results for the electronic dynamics of SIAM in the weak-coupling regime, $U/V < 4$, and compare them with the DMRG approach, which we regard as numerically exact. We carry out quantum quench simulations where the impurity is initially decoupled from the bath and is occupied by a single electron, a state with unit total population and unit spin polarization. We turn the coupling to the bath on at $t = 0$ and monitor the electronic population dynamics of the impurity.

Figure 1 shows the time evolution of the total population (a) and spin polarization (b) of the impurity for three values of the interaction strength U at zero temperature $T = 0$. The DMCC singles (DMCC-S) approximation is exact for the noninteracting SIAM $U = 0$ as demonstrated by the correspondence to the reference data. With increasing interaction strength, the DMCC-S approximation overestimates the total population and spin polarization

FIG. 1. Nonequilibrium dynamics of the single-impurity Anderson model at $T = 0$ eV and three values of the Hubbard parameter. Long dashed lines depict the noninteracting $U = 0.0$ eV case, short dashed lines – the $U = 0.05$ eV case, and full lines – the $U = 0.1$ eV case. The density-matrix renormalization group (Exact) results are plotted in black, the density-matrix coupled-cluster singles (DMCC-S) results are in blue, and the density-matrix coupled-cluster singles and doubles (DMCC-SD) results are in red. (a) Time-dependent total impurity population and (b) time-dependent impurity spin polarization. Other parameters of the impurity model include $\varepsilon_0 = -0.08$ eV, $V = 0.04$ eV, $N_b = 100$, and $\Lambda = 1.1$. For the noninteracting case, the DMCC-S results coincide with the exact results, and for both interacting cases, DMCC-SD is graphically indistinguishable from the exact results.

of the impurity with larger deviations at higher Hubbard parameter values, revealing the importance of correlation effects. Inclusion of double quasiparticle excitations via the DMCC singles and doubles (DMCC-SD) approximation improves the electronic population dynamics of the impurity. Both the total population and spin polarization of the impurity decrease as a result of correlated dynamics, which brings the coupled-cluster performance in close correspondence to the exact DMRG results.

Figure 2 depicts the time evolution of the total population (a) and spin polarization (b) of the interacting impurity ($U = 0.1$ eV) at three values of temperature T . Whereas the zero-temperature SIAM can also be simulated via the time-dependent coupled-cluster

FIG. 2. Nonequilibrium dynamics of the single-impurity Anderson model at three values of the temperature and $U = 0.1$ eV. Long dashed lines depict high temperature $T = 0.08$ eV case, short dashed lines depict the intermediate $T = 0.04$ eV case, and full lines depict the $T = 0.0$ eV case. The color code of the curves is the same as in Fig. 1, as well as the values of the rest of SIAM parameters. (a) Time-dependent total impurity population and (b) time-dependent impurity spin polarization. The DMCC-S, DMCC-SD, and exact results coincide in the high temperature case $T = 0.08$ eV.

wavefunction method, the finite temperature cases require a density-matrix treatment. Both the total population and spin polarization of the impurity decrease with increasing temperature. Similarly, the correlation contribution to the electronic dynamics of the impurity decreases with temperature as measured by the DMCC-S deviation from the reference results. Thus, the DMCC-S approximation, which is equivalent to the time-dependent finite-temperature mean-field method, accurately describes the population dynamics of the impurity at high temperatures. Correlation effects, however, are significant in the low and intermediate temperature regimes, and the close correspondence of DMCC-SD with the exact results demonstrates that the method successfully captures the correlation contribution at finite temperatures, as well.

The models considered so far represent closed quantum systems with dynamics characterized by relaxation to the equilibrium

state of the interacting system. The DMCC method also allows us to investigate the electronic dynamics of driven-dissipative open quantum systems. In particular, we carry out quantum quench simulations of the driven-dissipative SIAM with a super-Hamiltonian that includes a dissipative contribution, Eq. (32), and a harmonic driving contribution, $H_t = \varepsilon_0 + \delta\varepsilon \sin(\Omega t)$ with $\delta\varepsilon = 0.08$ eV. Figure 3 shows the total population dynamics of the interacting impurity ($U = 0.1$ eV) at temperature $T = 0.04$ eV and two values of the modulation frequency, $\Omega = \pi V$ and $\Omega = 4\pi V$. Figure 3(a) also includes dissipation with strength $\gamma = 0.04$ eV, and Fig. 3(b) includes dissipation with strength $\gamma = 0.2$ eV. Figure 3(a) reveals that the amplitude of impurity population oscillations decreases with increasing modulation frequency. This nonadiabatic effect results from the inefficient

FIG. 3. Nonequilibrium dynamics of the single-impurity Anderson model at $T = 0.04$ eV and $U = 0.1$ eV, including driving and dissipation. We consider two values of the frequency of impurity level modulation, Ω , and dissipation strength, γ . Full lines depict the high frequency $\Omega = 4\pi V$ case, and long dashed lines depict the low frequency $\Omega = \pi V$ case. (a) Time-dependent total impurity population at $\gamma = 0.04$ eV and (b) time-dependent total impurity population at $\gamma = 0.2$ eV. The DMCC-S and the DMCC-SD results without driving and dissipation are also shown in short dashed lines for reference. The color code of the curves is the same as in Fig. 1, as well as the rest of the SIAM parameters. In (b), the DMCC-S results are indistinguishable from both the DMCC-SD and exact data when dissipation is present.

FIG. 4. Demonstration of total electron number conservation during the DMCC-SD dynamics of the single-impurity Anderson model. Three cases are considered: zero-temperature closed system ($T = 0.0$ eV and $\gamma = 0.0$ eV) in black, finite-temperature closed system ($T = 0.04$ eV and $\gamma = 0.0$ eV) in blue, and finite-temperature open system ($T = 0.04$ eV and $\gamma = 0.04$ eV) in red. The closed system results (black and blue lines) are graphically indistinguishable.

equilibration of the impurity with the electronic bath and is reproduced by both DMCC approximations. The DMCC-S results, however, show asymmetric deviations from the reference data, especially in the low-frequency case where the DMCC-S deviations are larger near the peaks of the population oscillations. This time-evolving correlation effect is captured by DMCC-SD and results from the decrease in the correlation contribution as the impurity depopulates. Comparison of the results in Figs. 3(a) and 3(b) further shows that both the amplitude of oscillations and average value of impurity population decrease with increasing dissipation strength. The coincidence of DMCC-S, DMCC-SD, and exact results demonstrates that dissipation depresses correlation effects, similarly to increasing temperature. Overall, the DMCC-SD approximation reproduces well the rich nonequilibrium behavior of the model, underscoring the promise of the approach to study systems far from equilibrium.

Finally, Fig. 4 demonstrates the particle number conservation during the coupled-cluster time evolution. The number of electrons is conserved within numerical convergence thresholds for the closed system at zero and finite temperature and shows characteristic oscillations for the driven-dissipative, open quantum system. Taken together, the DMCC-SD method successfully captures the nonequilibrium many-body dynamics of SIAM in close correspondence with the renormalization-group method.

IV. CONCLUSIONS

The current work presents an extension of coupled-cluster theory to real-time finite-temperature correlated quantum dynamics. The method uses the Keldysh path contour in the complex time plane, which incorporates thermal correlation effects via thermalization from a noninteracting thermal state. The density matrix is expressed in an exponential ansatz, and the equation of motion for the cluster amplitudes is obtained via projection from

the Schrödinger equation for the cluster operator. The thermal quasiparticle presentation of thermofield theory is applied to the cluster operator, ensuring the trace-preservation of the density matrix. In addition, the diagrammatic techniques of the traditional coupled-cluster approach are directly transferable, which facilitates the computational implementation of the method.

Investigation of the single-impurity Anderson model in the weak-coupling regime demonstrates the accuracy of the approach in reproducing the electronic dynamics of the impurity compared to the density-matrix renormalization-group method. The coupled-cluster time evolution captures the balance of correlation effects with increasing interaction strength and temperature in closed systems, and also efficiently includes driving and dissipation effects in open systems. The encouraging performance of the approach on the SIAM motivates the extension of the method within a unified framework for both closed and open systems at finite temperature to the nonequilibrium many-body dynamics of realistic molecular systems, many of which fall within the weak to moderate correlation regime.

This work presents a study of a coupled-cluster formalism with many avenues for further developments. One possibility is the more general definition of the thermal Bogoliubov transformation that incorporates explicit time dependence. Furthermore, the time-dependent approach can serve as a basis for more approximate treatments that explicitly include thermal and dissipative effects, and possibly more general single-particle density matrices can also be accommodated. Finally, the approach is well-suited for the investigation of the process of thermalization in disordered quantum systems with both short-range and long-range interactions, including the influence of external perturbations.

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REFERENCES

- 1 F. Krausz and M. Ivanov, *Rev. Mod. Phys.* **81**, 163 (2009).
- 2 W. Domcke and D. R. Yarkony, *Annu. Rev. Phys. Chem.* **63**, 325 (2012).
- 3 M. W. Doherty, N. B. Manson, P. Delaney, F. Jelezko, J. Wrachtrup, and L. C. Hollenberg, *Phys. Rep.* **528**, 1 (2013).
- 4 A. L. Falk, P. V. Klimov, V. Ivády, K. Szász, D. J. Christle, W. F. Koehl, Á. Gali, and D. D. Awschalom, *Phys. Rev. Lett.* **114**, 247603 (2015).
- 5 C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, *Rev. Mod. Phys.* **86**, 253 (2014).
- 6 M. Thoss and F. Evers, *J. Chem. Phys.* **148**, 030901 (2018).
- 7 L. Cui, R. Miao, C. Jiang, E. Meyhofer, and P. Reddy, *J. Chem. Phys.* **146**, 092201 (2017).
- 8 Y. Zhang, S. He, W. Guo, Y. Hu, J. Huang, J. R. Mulcahy, and W. D. Wei, *Chem. Rev.* **118**, 2927 (2017).
- 9 B. Jiang and H. Guo, *J. Chem. Phys.* **150**, 180901 (2019).
- 10 R. J. Maurer, W. Liu, I. Poltavsky, T. Stecher, H. Oberhofer, K. Reuter, and A. Tkatchenko, *Phys. Rev. Lett.* **116**, 146101 (2016).
- 11 S. Choi, J. Choi, R. Landig, G. Kucsko, H. Zhou, J. Isoya, F. Jelezko, S. Onoda, H. Sumiya, V. Khemani *et al.*, *Nature* **543**, 221 (2017).
- 12 D. V. Else, C. Monroe, C. Nayak, and N. Y. Yao, preprint [arXiv:1905.13232](https://arxiv.org/abs/1905.13232) (2019).
- 13 R. J. Bartlett and M. Musiał, *Rev. Mod. Phys.* **79**, 291 (2007).
- 14 T. D. Crawford and H. F. Schaefer, *Rev. Comput. Chem.* **14**, 33 (2000).
- 15 R. J. Bartlett, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 126 (2012).
- 16 M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **106**, 6441 (1997).
- 17 A. I. Krylov, *Annu. Rev. Phys. Chem.* **59**, 433 (2008).
- 18 C. Huber and T. Klamroth, *J. Chem. Phys.* **134**, 054113 (2011).
- 19 T. Sato, H. Pathak, Y. Orimo, and K. L. Ishikawa, *J. Chem. Phys.* **148**, 051101 (2018).
- 20 S. Kvaal, *J. Chem. Phys.* **136**, 194109 (2012).
- 21 D. I. Lyakh, M. Musiał, V. F. Lotrich, and R. J. Bartlett, *Chem. Rev.* **112**, 182 (2011).
- 22 A. F. White and G. K.-L. Chan, *J. Chem. Theory Comput.* **14**, 5690 (2018).
- 23 F. Hummel, *J. Chem. Theory Comput.* **14**, 6505 (2018).
- 24 G. Harsha, T. M. Henderson, and G. E. Scuseria, "Thermofield theory for finite-temperature coupled cluster," *J. Chem. Theory Comput.* (to be published).
- 25 G. Sanyal, S. H. Mandal, and D. Mukherjee, *Chem. Phys. Lett.* **192**, 55 (1992).
- 26 G. Sanyal, S. H. Mandal, S. Guha, and D. Mukherjee, *Phys. Rev. E* **48**, 3373 (1993).
- 27 S. H. Mandal, R. Ghosh, G. Sanyal, and D. Mukherjee, *Int. J. Mod. Phys. B* **17**, 5367 (2003).
- 28 G. Harsha, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **150**, 154109 (2019).
- 29 Y. Takahashi and H. Umezawa, *Int. J. Mod. Phys. B* **10**, 1755 (1996).
- 30 H. Chu and H. Umezawa, *Int. J. Mod. Phys. A* **9**, 2363 (1994).
- 31 T. Arimitsu and H. Umezawa, *Prog. Theor. Phys.* **74**, 429 (1985).
- 32 T. Arimitsu and H. Umezawa, *Prog. Theor. Phys.* **77**, 32 (1987).
- 33 T. Arimitsu, M. Guida, and H. Umezawa, *Physica A* **148**, 1 (1988).
- 34 T. Arimitsu and H. Umezawa, *Prog. Theor. Phys.* **77**, 53 (1987).
- 35 A. A. Dzhioev and D. S. Kosov, *J. Chem. Phys.* **134**, 044121 (2011).
- 36 A. A. Dzhioev and D. Kosov, *J. Phys.: Condens. Matter* **24**, 225304 (2012).
- 37 A. A. Dzhioev and D. Kosov, *J. Chem. Phys.* **134**, 154107 (2011).
- 38 A. A. Dzhioev and D. Kosov, *J. Phys. A* **47**, 095002 (2014).
- 39 A. A. Dzhioev and D. Kosov, *J. Phys. A* **48**, 015004 (2014).
- 40 I. de Vega and M.-C. Bañuls, *Phys. Rev. A* **92**, 052116 (2015).
- 41 F. Schwarz, I. Weymann, J. von Delft, and A. Weichselbaum, *Phys. Rev. Lett.* **121**, 137702 (2018).
- 42 R. Borrelli, *J. Chem. Phys.* **150**, 234102 (2019).
- 43 R. Borrelli and M. F. Gelin, *J. Chem. Phys.* **145**, 224101 (2016).
- 44 R. Borrelli and M. F. Gelin, *Sci. Rep.* **7**, 9127 (2017).
- 45 D. Newns, *Phys. Rev.* **178**, 1123 (1969).
- 46 P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).
- 47 K. G. Wilson, *Rev. Mod. Phys.* **47**, 773 (1975).
- 48 M. Schmutz, *Z. Phys. B: Condens. Matter Quanta* **30**, 97 (1978).
- 49 J.-P. Blaizot and G. Ripka, *Quantum Theory of Finite Systems* (MIT Press, Cambridge, MA, 1986), Vol. 3.
- 50 H. Matsumoto, Y. Nakano, and H. Umezawa, *J. Math. Phys.* **25**, 3076 (1984).
- 51 L. V. Keldysh, *Sov. Phys. JETP* **20**, 1018 (1965).
- 52 A. Altland and B. D. Simons, *Condensed Matter Field Theory* (Cambridge University Press, 2010).
- 53 W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes, The Art of Scientific Computing*, 3rd ed. (Cambridge University Press, 2007).
- 54 J. Arponen, *Ann. Phys.* **151**, 311 (1983).
- 55 R. Balian and M. Vénéroni, *Phys. Rev. Lett.* **47**, 1353 (1981).
- 56 G. Lindblad, *Commun. Math. Phys.* **48**, 119 (1976).
- 57 G. Vidal, *Phys. Rev. Lett.* **91**, 147902 (2003).
- 58 G. Vidal, *Phys. Rev. Lett.* **93**, 040502 (2004).
- 59 S. R. White and A. E. Feiguin, *Phys. Rev. Lett.* **93**, 076401 (2004).
- 60 U. Schollwöck, *Ann. Phys.* **326**, 96 (2011).
- 61 M. Suzuki, *J. Math. Phys.* **26**, 601 (1985).
- 62 See <http://itensor.org> for ITensor Library (version 2.0.11).
- 63 F. A. Evangelista, *J. Chem. Phys.* **149**, 030901 (2018).