Thermofield theory for finite-temperature coupled cluster

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We present a coupled cluster and linear response theory to compute properties of many-electron systems at non-zero temperatures. For this purpose, we make use of the thermofield dynamics, which allows for a compact wavefunction representation of the thermal density matrix, and extend our recently developed framework [J. Chem. Phys. 150, 154109 (2019)] to parameterize the so-called thermal state using an exponential ansatz with cluster operators that create thermal quasi-particle excitations on a mean-field reference. As benchmark examples, we apply this method to both model (one-dimensional Hubbard and Pairing) as well as ab-initio (atomic Beryllium and molecular Hydrogen) systems, while comparing with exact results.

I. INTRODUCTION

Temperature is an import parameter of physical systems. For many problems, the temperature scale of interest is far below the optical gap (or the excitation energies). For example, typical electronic excitation energies in molecules are of the order of a few electron volts (or eV), which is much larger than room temperature (~ 25meV). In such problems where we are interested only in electronic degrees of freedom, it suffices to know the ground electronic state and perhaps a few low-lying excited states. To access these states, we solve the time-independent Schrödinger equation. As is well known, this is a very complicated problem and one generally relies on a series of approximate methods such as Hartree-Fock, perturbation theory, configuration interaction (CI), coupled cluster theory (CC), Monte Carlo methods among many more.

There are, however, many interesting problems and applications where one may be interested in temperature scales that are comparable or even larger than the excitation gap. Examples include metallic compounds with small gap that host an unconventional superconductivity persisting at relatively high temperatures, ultra-cold chemistry, geophysical processes which generally involve very high temperatures and pressure, and many more. In these problems, we can no longer make do with a few electronic states and must evaluate properties as thermal averages weighted over an appropriate ensemble of states. For a system in thermal equilibrium at inverse temperature \( \beta \), the ensemble of choice is generally canonical or grand-canonical and the expectation value of an observable \( \hat{A} \) is defined by

\[
\langle \hat{A} \rangle_\beta = \frac{1}{Z} \text{Tr}(\hat{A} \hat{\rho}),
\]

where \( \hat{\rho} \) is the thermal density matrix, and \( Z \) is the partition function, given by

\[
\hat{\rho} = e^{-\beta \hat{H}'} \quad Z = \text{Tr}(\hat{\rho}),
\]

with \( \hat{H}' = H \) for the canonical ensemble and \( \hat{H}' = H - \mu \hat{N} \) for the grand canonical ensemble, where \( \mu \) is the chemical potential. In this paper, we shall work explicitly with the grand canonical ensemble.

Exactly computing \( \hat{\rho} \) (or equivalently \( Z \)) requires information about the entire spectrum of the Hamiltonian, which is far from feasible. Accordingly, just as for zero temperature, a series of approximate methods are needed. Several methods have been proposed over the years to evaluate thermal averages of operators. Most of these methods can be broadly categorized into deterministic methods such as diagrammatic perturbation theory based on the Matsubara formalism and stochastic quantum Monte Carlo methods. Wavefunction methods are particularly convenient in the study of zero-temperature ground-state properties of finite sized systems and clearly, their thermal equivalents are highly desirable. However, the development of such thermal wavefunctions methods has been rather challenging, primarily because the thermal density matrix cannot be expressed in terms of a single wavefunction in the original Hilbert space. Nevertheless, several such methods have been introduced over the years such as the Ancilla density matrix renormalization group and finite-temperature perturbation theories among many more.

Given its features, especially size-extensivity and success with weakly correlated systems, the coupled cluster ansatz is an ideal candidate to study finite-temperature properties. A thermal analogue of the CC method was proposed by Mukherjee et al. and has been further elaborated recently in independent works by White et al. and Hummel. This formulation uses a thermal Wick’s theorem to compactly represent the imaginary time evolution operator as a thermal normal ordered exponential of some cluster operator and a number.

In this paper, we present an alternative approach to thermal coupled cluster based on the thermofield dynamics (TFD) using a framework we recently explored in Ref. 38. Thermofield dynamics provides a convenient way to represent the thermal density matrix via
a wavefunction which evolves in temperature according to the imaginary-time evolution Schrödinger equation. Undoubtedly, TFD has the potential to study many-electron systems in quantum chemistry and condensed-matter physics. Here, we parametrize this so-called thermal wavefunction as an exponential ansatz to integrate the evolution equation.

II. COUPLED CLUSTER THEORY

The coupled cluster method is one of the most widely used methods in quantum chemistry. Introduced first in nuclear physics by Coester and Kümmer, and later reformulated for electronic structure theory by Čižek and Paldus, it is considered as the gold standard for weakly correlated many-electron systems. In CC theory, one uses an exponential wavefunction ansatz

|Ψ⟩ = e^T|Φ0⟩, (3)

where |Φ0⟩ is some Hartree-Fock (HF) Slater determinant reference and T contains particle-hole excitations defined on this reference state,

\[ T = \hat{T}_1 + \hat{T}_2 + \ldots, \]

\[ \hat{T}_1 = \sum_{i,a} t_{i,a} c_{a}^\dagger c_i, \]

\[ \hat{T}_2 = \frac{1}{4} \sum_{i,j,a,b} t_{ij,a} c_{a}^\dagger c_b c_j c_i, \ldots \]

where we have followed the standard notation for labeling orbital indices, i.e., occupied orbitals are denoted by indices i, j, k, ..., while unoccupied orbitals are denoted by a, b, c, ... The CC equations for the ground state energy and the unknown t-amplitudes can be obtained by left-projecting the Schrödinger equation

\[ \hat{H}|\Phi_0⟩ = E|\Phi_0⟩, \quad \hat{H} = e^{-T} \hat{H} e^T \]

with various Slater determinants. For example, if the cluster operator T is truncated to single and double excitations only (CCSD), the energy and amplitude equations are obtained by solving the following equations

\[ E = \langle \Phi | \hat{H} | \Phi \rangle, \]

\[ 0 = \langle \Phi | t_{i,a} | \hat{H} | \Phi \rangle, \]

\[ 0 = \langle \Phi_{ij,a}^b | \hat{H} | \Phi \rangle, \]

where \( \Phi_{i,a}^b \) and \( \Phi_{ij,a}^b \) are singly- and doubly-excited Slater determinants.

As introduced so far, CC describes a correlated ansatz for the ket wavefunction. In order to compute expectation values other than that of the Hamiltonian, one also needs a correlated bra state. A linear response wavefunction is generally employed for this purpose, i.e. one makes the energy functional

\[ E = \langle \Phi | (1 + \hat{Z}) e^{-T} \hat{H} e^T | \Phi \rangle \]

stationary with respect to \( \hat{T} \) and \( \hat{Z} \), where

\[ \hat{Z} = \hat{Z}_1 + \hat{Z}_2 + \ldots, \]

\[ \hat{Z}_1 = \sum_{i,a} z_{i,a} c_{a}^\dagger c_i, \]

\[ \hat{Z}_2 = \frac{1}{4} \sum_{i,j,a,b} z_{ij,a} c_{a}^\dagger c_b c_j c_i. \]

By realizing that the cluster operator T and CI operator \( \hat{Z} \) are composed of particle-hole excitation and de-excitation operators respectively, the bra state can be re-written as an explicit CI wavefunction

\[ \langle \Psi | = \langle \Phi | (1 + \hat{Z}) e^{-T} = \langle 0 | (1 + \hat{W}) e^{w_0}, \]

where \( w_0 \) is a constant and \( \hat{W} \) has the same operator form as \( Z \).

A similar formulation known as equation of motion CCSD (EOM-CC) can be used for excited states. Coupled cluster gives highly accurate results for weakly correlated systems and its success can be attributed to the polynomial computational scaling (\( O(N^6) \) for CCSD) as well as to the fact that the computed properties are size-extensive (scale linearly with the particle number) in the thermodynamic limit.

III. THERMOFIELD DYNAMICS

Thermofield dynamics is a real-time thermal field theory that treats both time and temperature on equal footing, and was proposed as an alternative to the Keldysh approach in the Matsubara imaginary time formalism. It provides a prescription for purification of the thermal density matrix, allowing us to construct a wavefunction \( |\Psi(\alpha, \beta)\rangle \), with \( \alpha = \beta \mu \), generally known as the thermal vacuum, thermofield double state or simply as the thermal state, so that the trace over an ensemble of states in Eq. [4] can be replaced by an expectation value over this wavefunction, i.e.

\[ \langle \hat{A} \rangle = \frac{\langle \Psi(\alpha, \beta) | \hat{A} | \Psi(\alpha, \beta) \rangle}{\langle \Psi(\alpha, \beta) | \Psi(\alpha, \beta) \rangle}. \]

That the thermal state \( |\Psi(\alpha, \beta)\rangle \) cannot be a pure state in the physical Hilbert space \( \mathcal{H} \) is easily established since the density matrix \( \hat{\rho} \) represents mixed states to begin with. In TFD, one therefore introduces a fictitious, conjugate copy of the original Hilbert space, known as the tilde-conjugate space or \( \tilde{\mathcal{H}} \), and the thermal state is then defined in the doubled space \( \mathcal{H} \otimes \tilde{\mathcal{H}} \) as

\[ |\Psi(\alpha, \beta)\rangle = e^{(\alpha N - \beta H)/2} |\tilde{\mathcal{I}}\rangle, \quad |\tilde{\mathcal{I}}\rangle = \sum_m |m, \tilde{m}\rangle, \]

where \( H \) is the Hamiltonian, \( \{ |m\rangle \} \) is some orthonormal basis in the Hilbert space \( \mathcal{H} \) and \( |\tilde{m}\rangle \) is the tildé-state corresponding to \( |m\rangle \), while we have used the shorthand.
notation $|m, \tilde{m}\rangle = |m\rangle \otimes |\tilde{m}\rangle$. The state $|[1]\rangle$ is the state with maximal entanglement between $\mathcal{H}$ and $\tilde{\mathcal{H}}$ and is the exact thermal state at infinite temperature i.e. $\beta = 0$ and $\alpha = 0$. Moreover, it is invariant under any transformation of the basis. Further details about the TFD formalism and the structure of the tilted-conjugate space $\mathcal{H}$ can be found in Ref. [33] and the references therein.

By construction, the thermal state satisfies the following imaginary time evolution equations,

$$\frac{\partial}{\partial \beta} |\Psi(\alpha, \beta)\rangle = -\frac{1}{2} H |\Psi(\alpha, \beta)\rangle,$$  
(14a)

$$\frac{\partial}{\partial \alpha} |\Psi(\alpha, \beta)\rangle = \frac{1}{2} N |\Psi(\alpha, \beta)\rangle.$$  
(14b)

One can solve for $|\Psi(\alpha, \beta)\rangle$ by integrating Eq. 14 generally starting from $(\alpha, \beta) = (0, 0)$, where the initial thermal state is known exactly. Exactly evolving the thermal state satisfies the following imaginary time evolution equations,

$$\frac{\partial}{\partial \beta} |\Psi(\alpha, \beta)\rangle = -\frac{1}{2} H |\Psi(\alpha, \beta)\rangle,$$  
(14a)

$$\frac{\partial}{\partial \alpha} |\Psi(\alpha, \beta)\rangle = \frac{1}{2} N |\Psi(\alpha, \beta)\rangle.$$  
(14b)

IV. THERMAL COUPLED CLUSTER

As explained in Eq. 3 the CC expectation value of any operator $\hat{A}$ can be evaluated as an asymmetric expectation value,

$$\langle \hat{A} \rangle_{CC} = \frac{\langle \Psi' | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle},$$  
(19)

where both the ket $|\Psi\rangle$ and the bra $\langle \Psi'|$ states are approximations to the same thermal state, and consequently evolve according to Eq. 14 and its adjoint respectively.

Given that the Bogoliubov transformation in Eq. 18 is BCS-like, we parametrize the ket state as an exponential of quasiparticle creation operators acting on an $\alpha$- and $\beta$-dependent mean-field thermal reference, $|0(\alpha, \beta)\rangle$, defined in Eq. 16,

$$|\Psi\rangle = e^{S(\alpha, \beta)} |0(\alpha, \beta)\rangle,$$  
(20a)

$$\langle \Psi' | = \langle 0(\alpha, \beta) | (1 + \hat{W}) e^{-S} \rangle,$$  
(21)

and as explained in Eq. 11 it can be expressed as an effective CI wavefunction

$$\langle \Psi' | = \langle 0 | (1 + \hat{W}) e^{-S} \rangle,$$  
(22a)

$$\hat{W} = \sum_{p,q} w_{pq} \hat{a}_p \hat{a}_q + \frac{1}{4} \sum_{p,q,r,s} w_{pqrs} \hat{a}_r \hat{a}_s \hat{a}_q \hat{a}_p + \ldots$$  
(22b)

For both the bra and the ket states, the reference $|0(\alpha, \beta)\rangle$ evolves continuously as we evolve the Schrödinger Eq. 14 (hence the name ‘covariant’). Accordingly, both the amplitudes $(w_{pq}, w_{pq}, \ldots)$ and the quasiparticle operators $\hat{a}^\dagger, \hat{a}^\dagger$ carry $\alpha$- and $\beta$-dependence. The $\alpha$- and $\beta$-evolution of $\langle \Psi' |$, a thermal CI wavefunction, is governed
by
\[
(0) \left( \frac{\partial W}{\partial \alpha} + (1 + W) \frac{\partial v_0}{\partial \alpha} \right) = \frac{1}{2} \langle 0 | N_{CI}, \tag{23a} \right.
\]
\[
(0) \left( \frac{\partial W}{\partial \beta} + (1 + W) \frac{\partial v_0}{\partial \beta} \right) = -\frac{1}{2} \langle 0 | H_{CI}. \tag{23b} \right.
\]
where \( H_{CI} \) and \( N_{CI} \) are effective CI Hamiltonian and Number operators respectively, and are given by
\[
H_{CI} = (1 + W) H - H_0 (1 + W),
\]
\[
N_{CI} = W N - N W.
\]

A detailed discussion on thermal CI and the derivation of these equations can be found in Ref. [38].

For the evolution of \(|\Psi\rangle\), substituting the CC ansatz from Eq. 20a into the Schrödinger Eq. 14 gives
\[
e^{-S} \left( \frac{\partial}{\partial \alpha} e^S \right) |0\rangle = \frac{1}{2} \left( e^{-S} N e^S - N \right) |0\rangle, \tag{24a} \right.
\]
\[
e^{-S} \left( \frac{\partial}{\partial \beta} e^S \right) |0\rangle = -\frac{1}{2} \left( e^{-S} H e^S - H_0 \right) |0\rangle. \tag{24b} \right.
\]

The evolution equations for the amplitudes can be obtained by left projecting Eq. 24 with the respective determinants.

1. Wilcox identity

The process of reducing Eq. 24 to evolution equations for the amplitudes is complicated by the fact that the derivative of the cluster operator does not commute with the operator itself, i.e.
\[
\left[ \frac{\partial S}{\partial x}, S \right] \neq 0,
\]
where \( x = \alpha, \beta \). The derivative of the exponential cluster operator is appropriately performed by making use of the Wilcox identity [39] which states that the derivative of the exponential of an operator \( M \) with respect to some parameter \( \lambda \) can be evaluated as
\[
\frac{\partial e^{M(\lambda)}}{\partial \lambda} |_{\lambda=0} = \int_0^1 dy \ e^{(1-y)M} \left( \frac{\partial M}{\partial \lambda} \right) e^{yM}. \tag{25} \]

With this, the left-hand side of Eq. 24 becomes
\[
e^{-S} \left( \frac{\partial}{\partial \alpha} e^S \right) = \int_0^1 dy e^{-yS} \left( \frac{\partial}{\partial \alpha} \right) e^{yS}, \tag{26a} \right.
\]
\[
e^{-S} \left( \frac{\partial}{\partial \beta} e^S \right) = \int_0^1 dy e^{-yS} \left( \frac{\partial}{\partial \beta} \right) e^{yS}, \tag{26b} \right.
\]
where we have used the shorthand \( \partial_x \) for \( \partial/\partial x \), and made use of the Baker-Campbell-Hausdorff expansion in going from Eq. 26a to 26b. Finally, breaking the derivative \( \partial_x e^S \) into the amplitude (\( \partial_{\text{amp}} S \)) and operator (\( \partial_{\text{op}} S \)) derivatives,
\[
\partial_x e^S = \partial_{\text{amp}} S + \partial_{\text{op}} S,
\]
and realizing that the former commutes with \( S \), we can compactly write the left-hand side of Eq. 24 as
\[
e^{-S} \left( \frac{\partial}{\partial x} e^S \right) = \partial_{\text{amp}} S + S_x, \quad S_x = e^{-S} \partial_{\text{op}} S e^S. \tag{27} \]

With these details, Eq. 24 can be further simplified as
\[
\frac{\partial_{\text{amp}} S}{\partial \alpha} |0\rangle = \left[ \frac{1}{2} \left( e^{-S} N e^S - N \right) - S_{\alpha} \right] |0\rangle, \tag{28a} \right.
\]
\[
\frac{\partial_{\text{amp}} S}{\partial \beta} |0\rangle = -\left[ \frac{1}{2} \left( e^{-S} H e^S - H_0 \right) + S_{\beta} \right] |0\rangle, \tag{28b} \right.
\]

which can then be left-projected with various thermal quasiparticle states to yield a set of differential equations governing the evolution of the \( s \)-amplitudes in the chemical potential - temperature or \( \alpha-\beta \) space. Complete expressions for the CCSD evolution equations are included in Appendix A.

V. RESULTS

Armed with the working equations, we now proceed to present results for the application of the thermal CC in the covariant formalism, truncated at singles and doubles (CCSD), to various many-electron systems, viz. the one-dimensional Hubbard model, the pairing or the reduced BCS model, as well as chemical systems (atomic Beryllium and molecular \( H_2 \)). In order to make correspondence with the canonical ground state limit, we present results for all of these systems with a fixed number of particles on average - at each \( \beta \) grid-point, we evolve the thermal states in \( \alpha \) to fix the average number of particles before evolving again in \( \beta \). We compare our results with full configuration interaction (FCI) results.

In our implementation, we split the Hamiltonian into a diagonal one-body \( H_0 \) and a two-body part \( V \), such that these components do not have any dependence on the chemical potential \( \alpha \) and the temperature \( \beta \). The benefits of such partitioning are two-fold: (i) with \( H_0 \) being diagonal, the thermal Bogoliubov takes a simple form as shown in Eq. 15 (ii) the fixed partitioning removes any implicit imaginary-time dependence from \( H_0 \) and \( V \), allowing us to write clean, analytical forms for the \( \alpha \)- and \( \beta \)-derivatives of the mean-field thermal state \(|0(\alpha, \beta)\rangle \). However, we note that this is not the usual approach in, for instance, standard thermal HF theory [35,36].

We first apply the CCSD methods to the one-dimensional Hubbard model with periodic boundary conditions. Having already presented results for thermal CI truncated to singles and doubles (CISD) in Ref. [38], this
model system seems to be the right place to start comparing thermal CC with thermal HF and CI. The Hamiltonian is given by

\[
H = -t \sum_{\langle p,q \rangle, \sigma} \langle p,q \rangle \sigma \left( c_{p,\sigma}^\dagger c_{q,\sigma} + \text{h.c.} \right) + U \sum_p \hat{n}_{p,\uparrow} \hat{n}_{p,\downarrow},
\]

where \( \langle \rangle \) denotes that the sum is carried over sites connected in the lattice, \( t \) denotes the strength of the kinetic energy term, \( U \) denotes the strength of the on-site Coulomb repulsion, and \( \hat{n}_{p,\sigma} = c_{p,\sigma}^\dagger c_{p,\sigma} \) is the number operator for lattice site \( p \) and spin \( \sigma \). The ratio \( U/t \) characterizes the correlation strength.

Figure 1a shows the temperature dependence of the error in internal energy for a two-site Hubbard model at half-filling on average with \( U/t = 1 \) as computed by thermal HF, covariant CISD, thermal CCSD as well its fixed-reference formulation. Figure 1b presents the same for a six-site Hubbard model with \( U/t = 2 \). Thermal CCSD clearly outperforms CISD, especially for larger systems where CI is a less accurate wavefunction ansatz. Moreover, the covariant thermal CCSD goes to the appropriate ground-state restricted CCSD in the limit \( \beta \to \infty \) (or \( \theta \to 0 \), where \( \theta = 1/\beta \) is the temperature). We note that while CCSD and CISD are exact in describing the ground state of the two-site Hubbard model, they are not
exact at finite temperatures since we are working in the grand canonical ensemble. The fixed-reference CCSD, on the other hand, performs poorly except for a small window around $\beta = 0$. Such a behaviour can be anticipated since this method uses the thermal reference corresponding to $\beta = 0$ as its starting point. Accordingly, for all other results that follow, we present only the covariant methods.

Next, we consider the reduced BCS or the pairing model, the Hamiltonian for which is given by

$$ H = \sum_p \epsilon_p N_p - G \sum_{p,q} P_p^\dagger P_q $$  \hspace{1cm} (30)

where $N_p$ counts the number of electrons, $\epsilon_p$ denotes the energy, and $P_p^\dagger/P_p$ respectively creates/annihilates a pair of electrons in the $p^{th}$-level, while $G$ quantifies the attractive pair-hopping interaction. Here we choose the energy levels with a uniform spacing of 1 unit, i.e., $\Delta \epsilon = \epsilon_{p+1} - \epsilon_p = 1$. Figure 2a describes the temperature dependence of the error in internal energy for a six-level pairing model with $G = 0.2$ (weakly correlated) at average half-filling. Figure 2b shows the same for $G = 0.5$ (near critical regime). Once again, we see that the covariant thermal CCSD improves significantly over both the HF and CISD. We also recover the zero-temperature ground-state limit for thermal CCSD. Figures 3 and 4 show similar trends for atomic Beryllium and molecular $\text{H}_2$ at bond length 0.74 Å in STO-3G basis sets.

In addition to the internal energy, we can also compute other physical properties and correlation functions at any temperature / chemical potential. In Figure 5, we show the $z$-component spin-spin correlation function

$$ \chi(i,j) = \langle \hat{S}^z(i) \hat{S}^z(j) \rangle $$  \hspace{1cm} (31)

for the ten-site Hubbard model with $U/t = 2$. Here, the expectation values are computed using linear-response density matrices and orbital relaxation effects have not been considered. As one would expect, at very high temperature $\theta$, there is no-correlation between adjacent spins. As $\theta$ is reduced, the correlation appears and becomes maximal in the zero-temperature limit. Again, as with the internal energies, we see that the correlation function approaches the ground state CC in the limit $\beta \to \infty$.

VI. CONCLUSIONS

We have demonstrated that the framework of thermofield dynamics can be exploited to formulate a finite-
temperature coupled cluster theory. We use the CCSD approximation to benchmark our method on various many-electron Hamiltonians and find that it performs substantially better than the thermal Hartree-Fock and thermal CI, just as one would expect for their ground-state counterparts. This improved accuracy comes with the same asymptotic $O(N^3)$ scaling ($N$ being the number of spin-orbitals or basis functions) as does standard quasiparticle CCSD, with a modestly larger pre-factor, though note that we must solve these equations at each grid point in the imaginary-time evolution. We also observe that in the zero-temperature limit, thermal HF approaches ground-state RHF and accordingly, thermal CC also diverges eventually. This issue can be avoided if we evolve the thermal reference to approach UHF in the large-$\beta$ limit, or by using a more sophisticated wavefunction ansatz. Both of these directions will be explored in future work.

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Appendix A: Thermal CCSD Equations

When the cluster operator $S$ is truncated to singles and double excitation operators only, i.e.,

$$ S = s_0 + \sum_{pq} s_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} s_{pqrs} a_p^\dagger a_q^\dagger a_r^\dagger a_s^\dagger, $$

the evolution equations (c.f. Eq. 24) for the CC amplitudes take the following form for the $\alpha$-evolution,

$$ \frac{\partial s_0}{\partial \alpha} = \frac{1}{2} R_N^0 - S_\alpha^0, \quad (A1) $$
$$ \frac{\partial s_{pq}}{\partial \alpha} = \frac{1}{2} R_N^{pq} - S_{\alpha}^{pq}, \quad (A2) $$
$$ \frac{\partial s_{pqrs}}{\partial \alpha} = \frac{1}{2} R_N^{pqrs} - S_{\alpha}^{pqrs}, \quad (A3) $$

where $R_N^0$ denotes the various CC residuals for the $\alpha$-evolution,

$$ R_N^0 = \langle 0 | (e^{-S} N e^S - N) | 0 \rangle, $$
$$ = \sum_a x_a y_a s_{aa} \quad (A4a) $$

$$ R_N^{pq} = \langle 0 | \tilde{a}_q a_p (e^{-S} N e^S - N) | 0 \rangle, $$
$$ = (x_p^2 - y_p^2) s_{pq} + \sum_a x_a y_a (s_{apaq} - s_{paqa}) \quad (A4b) $$

$$ R_N^{pqrs} = \langle 0 | \tilde{a}_r \tilde{a}_s a_q a_p (e^{-S} N e^S - N) | 0 \rangle, $$
$$ = (x_p^2 + x_r^2 - y_p^2 - y_r^2) s_{pqrs} $$
$$ + \frac{1}{2} P(pq) P(rs) \sum_a x_a y_a (s_{aspqar} - s_{paqras}) \quad (A4c) $$

and the operator-derivative terms are given by

$$ S_\alpha^0 = -\frac{1}{2} \sum_a x_a y_a s_{aa} \quad (A5a) $$
$$ S_{\alpha}^{pq} = \frac{1}{2} \sum_a x_a y_a (s_{paqa} + s_{apaq}) \quad (A5b) $$
$$ S_{\alpha}^{pqrs} = \frac{1}{4} P(pq) P(rs) \sum_a x_a y_a (s_{aspqar} - s_{paqras}), \quad (A5c) $$

where $x$ and $y$ are the thermal Bogoliubov parameters and the dummy indices $a, b, \ldots$ are summed over all the spin-orbitals. Equations for the $\beta$-evolution can be obtained in a similar way,
where \( h_0, h^{(11)} \), etc. are effective matrix elements of the general quasiparticle Hamiltonian, given by

\[
h_0 = \sum_a y_a^2 \epsilon_a + \frac{1}{2} \sum_{ab} y_a y_b u_{ab} \tag{A10}
\]

\[
h^{(11)}_{ab} = x_a y_b f_{ab}, \quad h^{(20)}_{ab} = x_a x_b f_{ab}, \quad h^{(02)}_{ab} = -y_a y_b f_{ab}, \quad \text{with } f_{ab} = \delta_{ab} \epsilon_a + \sum_c y_c^2 u_{abc}
\tag{A11}
\]

The residuals can then be expressed compactly in terms of the effective Hamiltonian matrix elements,

\[
R^0_H = \langle 0 | (e^{-S} H e^S - H_0) | 0 \rangle,
\]

\[
= h_0 + \sum_{ab} h^{(11)}_{ab} s_{ab} + \sum_{abcd} (2s_{ac}s_{bd} + s_{abcd}) h^{(221)}_{abcd}
\tag{A13a}
\]

\[
R^p_H = \langle 0 | a_q a_p (e^{-S} H e^S - H_0) | 0 \rangle,
\]

\[
= h^{(11)}_{pq} + \sum_a \left( h^{(02)}_{a} s_{pa} + h^{(20)}_{a} p_{sa} - \sum_{ab} \left( h^{(11)}_{ab} (s_{aq}s_{pb} + s_{pab}) - h^{(221)}_{ab} q_{abs}b \right) + \sum_{abc} \left( h^{(13)}_{abcp} (2s_{ab}s_{pc} + s_{apbc}) - h^{(31)}_{abcp} (2s_{ac}s_{ba} + s_{abc}) - 2 \sum_{abcd} h^{(221)}_{abcd} (2s_{ac}(s_{bd}s_{pa} + s_{pbd}) - s_{aq}s_{pcb} - s_{pc}s_{abq}) \right) \right)
\tag{A13b}
\]

\[
R^{pqr}_{H} = \langle 0 | a_r a_q a_p (e^{-S} H e^S - H_0) | 0 \rangle,
\]

\[
= \mathcal{P}(pq) \mathcal{P}(rs) \left[ h^{(221)}_{pqr} + \sum_a \left( \frac{1}{2} \left( h^{(02)}_{ar} s_{pa} + h^{(20)}_{ar} p_{sa} \right) + h^{(13)}_{prsa} s_{qa} + h^{(31)}_{pqs} s_{ar} \right) + \frac{1}{2} \sum_{ab} \left( h^{(04)}_{abrs} (2s_{pa}s_{qb} + s_{pqab}) + h^{(40)}_{abpq} (2s_{ar}s_{bs} + s_{sbr}) - h^{(11)}_{ab} (s_{aq}s_{pb} + s_{pab}) - h^{(222)}_{ab} (s_{qa}s_{bs} + s_{as}s_{qb}) \right) + \sum_{abc} \left( h^{(13)}_{abcr} (s_{ab}s_{pqc} + \frac{1}{2} s_{as}(2s_{pb}s_{qc} + s_{spc}) - 2s_{pb}s_{qca}) + h^{(31)}_{abcr} (s_{ac}s_{brs} + \frac{1}{2} s_{pc}(2s_{ar}s_{bs} + s_{sbr}) - s_{ar}s_{bpc}) \right) + \sum_{abcd} h^{(221)}_{abcd} (2s_{ac}(s_{br}s_{pqds} + s_{pd}s_{bqr}) - \frac{1}{2} s_{ar}s_{bs} (2s_{pc}s_{qd} + s_{pqcd}) + 4s_{ar}s_{pc}s_{qds} - \frac{1}{4} s_{acs}(2s_{pc}s_{qd} + s_{pqcd}) + (s_{abcr}s_{pqds} + s_{apcd}s_{bpc}) + 2s_{bcqs}s_{apcs}) \right] \right)
\tag{A13c}
\]

The operator-derivative terms in the \( \beta \)-evolution are given by

\[
S^0_{\beta} = \frac{1}{2} \sum_a \epsilon_a x_a y_a s_{aa}
\tag{A14a}
\]

\[
S^{pq}_{\beta} = -\frac{1}{2} \sum_a \epsilon_a x_a y_a (s_{pa}s_{aq} + s_{paaq})
\tag{A14b}
\]

\[
S^{pqr}_{\beta} = \frac{1}{4} \mathcal{P}(pq) \mathcal{P}(rs) \sum_a \epsilon_a x_a y_a (s_{as}s_{pqr} - s_{qa}s_{aprs})
\tag{A14c}
\]

\[
\langle \psi(\alpha, \beta) | e^{\alpha N - \beta H} | \alpha \rangle = e^{\alpha N - \beta H} | \alpha \rangle,
\tag{B1}
\]
so that the thermal expectation value of any physical quantity $A$ becomes

$$\langle \hat{A} \rangle = \frac{\langle \hat{A}_1 e^{-\beta H} \hat{A}_2 \rangle}{\langle \hat{A}_1 e^{-\beta H} \hat{A}_2 \rangle},$$  \hspace{1cm} \text{(B2a)}

and a better bra is no longer required. Correspondingly, the governing imaginary time Schrödinger equations become

\begin{align*}
\frac{\partial}{\partial \beta} \psi(\alpha, \beta) &= -H\psi(\alpha, \beta), \quad \text{(B3a)} \\
\frac{\partial}{\partial \alpha} \psi(\alpha, \beta) &= N\psi(\alpha, \beta). \quad \text{(B3b)}
\end{align*}

The thermal state for a given chemical potential $\alpha$ at inverse temperature $\beta$ can then be written as an exponential coupled cluster wavefunction

$$|\Psi(\alpha, \beta)\rangle = e^{\hat{T}(\alpha, \beta)} |\rangle,$$  \hspace{1cm} \text{(B4)}

where the cluster operator $\hat{T}(\alpha, \beta)$ builds correlation atop $|\rangle$. With this CC wavefunction ansatz, the finite-temperature expectation value of any physical quantity $\hat{A}$ becomes

$$\langle \hat{A} \rangle = \langle \hat{A}_1 \hat{A}_2 \rangle e^{-\beta_0} = \langle \hat{A}_1 \hat{A}_2 \rangle e^{-\beta_0} \hat{T} \hat{T} \rangle.$$

The state $|\rangle$ is annihilated by thermal quasiparticle operators $a_p$ and $\tilde{a}_p$ corresponding to $x_p = y_p = 1/\sqrt{2}$ in the Bogoliubov transformation in Eq. 18. We will refer these field operators as

$$d_p, \ t^\dagger_p, \ \tilde{d}_p, \ \tilde{t}^\dagger_p.$$ 

Therefore, the cluster operator $\hat{T}$ can be expressed as

$$T = t_0 + \sum_{p,q} t_{pq} d_p^\dagger d_q + \frac{1}{(2l)!^2} \sum_{p,q,r,s} t_{pqrs} d_p^\dagger d_q^\dagger d_r^\dagger d_s^\dagger + \ldots,$$  \hspace{1cm} \text{(B6)}

where the $\alpha$- and $\beta$-dependence is carried by the cluster amplitudes. These cluster amplitudes are found by integrating the imaginary time Schrödinger Eq. [33], which, upon substituting the wavefunction ansatz of Eq. 6 gives the following working equation

\begin{align*}
\frac{\partial T}{\partial \alpha} &= e^{-T} Ne^{-T}, \quad \text{(B7a)} \\
\frac{\partial T}{\partial \beta} &= -e^{-T} He^{-T}, \quad \text{(B7b)}
\end{align*}

Like conventional ground-state CC, Eq. 7 can be left-projected with the ground and excited slater determinants to yield the evolution equations for the amplitudes,

\begin{align*}
\frac{\partial t_0}{\partial \beta} &= -\frac{1}{Z_t} \langle \hat{A}_1 \hat{A}_2 \rangle e^{-T} \hat{T} \hat{T} \rangle, \quad \text{(B8a)} \\
\frac{\partial t_{pq}}{\partial \beta} &= -\frac{1}{Z_t} \langle \hat{A}_1 \hat{A}_2 \rangle \hat{T} \hat{T} \rangle, \quad \text{(B8b)} \\
\frac{\partial t_{pqrs}}{\partial \beta} &= -\frac{1}{Z_t} \langle \hat{A}_1 \hat{A}_2 \rangle \hat{T} \hat{T} \rangle, \quad \text{(B8c)}
\end{align*}

and so on, where $Z_t = \langle \hat{A}_1 \hat{A}_2 \rangle$. Similar equations can be derived for evolution along $\alpha$. These equations can be integrated starting from $\beta = 0$ (or any other value) where the initial values of the amplitudes is known. Here, since $\langle \hat{A}_1 \hat{A}_2 \rangle$ is exact at $\alpha, \beta = 0$, we have the initial conditions,

$$t_0 = 0, \ t_{pq} = 0, \ t_{pqrs} = 0, \ldots,$$

to the required inverse temperature and chemical potential.