Thermofield Theory for Finite-Temperature Quantum Chemistry

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Thermofield dynamics has proven to be a very useful theory in high-energy physics, particularly since it permits the treatment of both time- and temperature-dependence on an equal footing. We here show that it also has an excellent potential for studying thermal properties of electronic systems in physics and chemistry. We describe a general framework for constructing finite temperature correlated wave function methods typical of ground state methods. We then introduce two distinct approaches to the resulting imaginary time Schrödinger equation, which we refer to as fixed-reference and covariant methods. As an example, we derive the two corresponding versions of thermal configuration interaction theory, and apply them to the Hubbard model, while comparing with exact benchmark results.

I. INTRODUCTION

The Schrödinger equation for an interacting many-electron system can almost never be solved exactly due to the exponential scaling of the Hilbert space.1 Over the years, several methods have been proposed to approximate solutions and properties for such systems. These methods (perhaps with the exception of density functional theory) fall into two broad categories: the path integral approach and the wave function approach. The path integral formulation, generally used in condensed matter physics, is particularly useful when thermodynamically large systems can be approximated using an effective mean-field theory in the presence of perturbing interactions. On the other hand, wave function methods (such as configuration interaction (CI), coupled cluster (CC), or matrix product states (MPS)) are often preferred for the study of finite many-body systems such as atoms and molecules - systems generally of interest in chemistry.

While the path integral formulation can be naturally extended to study the thermal behaviour of a system via Matsubara’s imaginary time formalism,6 the usage of typical wave function methods breaks down at non-zero temperatures. This is because at non-zero temperatures, a quantum system is described by an ensemble density matrix, and one would need to solve for the entire spectrum of the Hamiltonian, as opposed to finding just the ground state energy and the corresponding wave function at zero temperature. There are a number of reasons for developing finite temperature quantum chemistry, a subject that has recently attracted a lot of interest.7–12 The finite temperature variants of the coupled cluster method10,11 are of particular relevance to our present work. These techniques are based on an extension of the time-dependent CC method to imaginary time, make use of a finite-temperature generalization of Wick’s theorem, and are framed on similar lines as the Thermal Cluster Cumulant theory, proposed by Mukherjee et al.13,14

Umezawa et. al. proposed an alternative approach, known as thermofield dynamics,15–18 which provides a real-time approach as opposed to Matsubara’s imaginary time formalism. Thermofield dynamics (TFD) can be conveniently described in an operator or wave function formulation, and was originally proposed as a method to study time-dependent and non-equilibrium phenomena in many-body quantum systems, something which cannot be done conveniently with the Matsubara formalism. It has been used widely in high energy physics19–22 as well as for the study of time-dependent and open quantum systems.23–27

The wavefunction prescription of TFD holds a tremendous potential for studying thermal properties of quantum many body systems in physics and chemistry. However, its application to compute equilibrium thermal properties has been scarce and mostly limited to the mean-field level.28,29 In this paper, we present a general framework based on TFD to construct wave function methods, much similar to traditional ground state methods, to compute thermal averages of physical quantities.

II. THERMOFIELD DYNAMICS

At non-zero temperatures, the expectation value of an operator $A$ (i.e. its thermal average) must be evaluated as an ensemble average

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

$$
= \frac{1}{Z} \sum_m \langle m | A e^{-\beta H} | m \rangle,
$$

where $\beta$ is the inverse temperature, $H$ is the Hamiltonian, $\{|m\rangle\}$ forms a complete orthonormal basis and the partition function $Z$ is defined as the trace of $\hat{\rho}$, the density operator

$$
\hat{\rho} = e^{-\beta H}, \quad Z = \sum_m \langle m | \hat{\rho} | m \rangle.
$$

One can choose to work within the grand canonical or the canonical ensemble by appropriately defining the Hamiltonian $H$ with or without a chemical potential term. In this paper, unless mentioned otherwise, we shall work with the grand canonical ensemble.
The central idea in TFD is to express the ensemble average of an operator $A$ in Eq. 2 as an expectation value over just one state $|\Psi(\beta)\rangle$, known as the thermofield double state, thermal vacuum or just thermal state:

$$
\langle \hat{A} \rangle_\beta = \frac{\langle \Psi(\beta) | \hat{A} | \Psi(\beta) \rangle}{\langle \Psi(\beta) | \Psi(\beta) \rangle}
$$

(4)

This idea is realized by introducing a copy of the original Hilbert space $\mathcal{H}$, known as the auxiliary or tilde-conjugate space $\tilde{\mathcal{H}}$, such that:

1. For every state $|\psi\rangle$ in $\mathcal{H}$, there is a copy $|\tilde{\psi}\rangle$ in $\tilde{\mathcal{H}}$ and likewise for operators.

2. The tilde operators obey similar (anti-) commutation rules as their un-tilde counterparts. For instance, for a bosonic (fermionic) spin-orbital $k$, we have the extended set of field operators

$$
c_k, \ c_k^\dagger; \ \tilde{c}_k, \ \tilde{c}_k^\dagger
$$

following the (anti-)commutation rules given by

$$
[c_k, c_k^\dagger]_\mp = 1 = [\tilde{c}_k, \tilde{c}_k^\dagger]_\mp,
$$

(5a)

$$
[c_k, \tilde{c}_k]_\mp = 0 = [c_k^\dagger, \tilde{c}_k^\dagger]_\mp,
$$

(5b)

where the convention for commutator / anti-commutator is defined as

$$
[A, B]_{-\eta} = AB - \eta BA,
$$

(6)

such that $\eta = -1$ in Eq. 5 produces the anticommutation rules for fermions and $\eta = +1$ produces the commutation rules for bosons.

3. A tilde conjugation operation transforms operators between $\mathcal{H}$ and $\tilde{\mathcal{H}}$ with the following general rules:

$$
\tilde{(\alpha c_k + \delta c_q^\dagger)} = \alpha^* \tilde{c}_k + \delta^* \tilde{c}_q^\dagger
$$

(7)

$$
\tilde{\alpha c_k \delta c_q^\dagger} = \tilde{c}_k \tilde{c}_q^\dagger
$$

(9)

where $\alpha^*$, $\delta^*$ are complex conjugates of $\alpha$, $\delta$ respectively, and $\eta = \pm 1$ for bosons / fermions in Eq. 7. With these conjugation rules, a Hamiltonian for the tilde system can be defined, generally denoted by $\tilde{H}$.

4. The time-dependent Schrödinger equation in $\tilde{\mathcal{H}}$ becomes ($\hbar = 1$)

$$
-\frac{i}{\hbar} \frac{\partial}{\partial t} |\psi\rangle = \tilde{H} |\psi\rangle.
$$

(10)

5. Operators in the physical space do not act on states in the tilde space, and vice versa.

The conjugation and doubling of the Hilbert space has well justified connections with Hopf algebras.\cite{30,31}

In the expanded space, the thermal state in Eq. 4 can be expressed as

$$
|\Psi(\beta)\rangle = e^{-\beta H/2} \sum_m |m\rangle \otimes |\tilde{m}\rangle,
$$

(11)

where \{|$m\rangle$\} forms an orthonormal basis in $\mathcal{H}$ and $H$ is the Hamiltonian of the system (and so does not act on states in the tilde space). The norm of the thermal state gives the partition function

$$
Z = \langle \Psi(\beta) | \Psi(\beta) \rangle.
$$

(12)

Note that at infinite temperature or $\beta = 0$, the thermal state is merely given by

$$
|\tilde{1}\rangle = |\Psi(\beta = 0)\rangle = \sum_m |m\rangle \otimes |\tilde{m}\rangle.
$$

(13)

Since the Hamiltonian is no longer relevant, the state $|\tilde{1}\rangle$ only depends on the structure of the Hilbert space and can be computed exactly. Consequently, $|\tilde{1}\rangle$ is analogous to the identity operator and is independent of the choice of basis \{|$m\rangle$\}.

The $|\tilde{m}\rangle$ states in Eq. 11 perform the role of a tracer. That is, for some operator $\hat{A}$ which acts only on the physical states,

$$
\langle \hat{A} \rangle_\beta = \frac{\langle \Psi(\beta) | \hat{A} | \Psi(\beta) \rangle}{\langle \Psi(\beta) | \Psi(\beta) \rangle}\tag{14a}
$$

$$
= \frac{1}{2} \sum_{m,n} \langle m, \tilde{n}| e^{-\beta H/2} \hat{A} e^{-\beta H/2} |n, \tilde{n}\rangle \tag{14b}
$$

$$
= \frac{1}{2} \sum_{m} \langle m| e^{-\beta H/2} \hat{A} e^{-\beta H/2} |m\rangle \tag{14c}
$$

$$
= \frac{1}{2} \text{Tr} \left( e^{-\beta H/2} \hat{A} e^{-\beta H/2} \right) \tag{14d}
$$

$$
= \frac{1}{2} \text{Tr} \left( e^{-\beta H} \hat{A} \right) \tag{14e}
$$

where we have used the shorthand notation $|m, \tilde{m}\rangle = |m\rangle \otimes |\tilde{m}\rangle$.

Conventional applications of TFD have been mostly centered around the study of dynamics of quantum systems at finite temperatures which is governed by a new Hamiltonian

$$
H_{th} = H - \tilde{H},
$$

(15)

which drives the real-time dynamics of the thermal state through the Schrödinger equation

$$
i\hbar \frac{\partial}{\partial t} |\Psi(\beta)\rangle = H_{th} |\Psi(\beta)\rangle.
$$

(16)

This real-time Schrödinger equation does not provide any prescription to compute the thermal state $|\Psi(\beta)\rangle$ and hence cannot be used to compute the partition function.
and other equilibrium thermal properties for the original system. Instead, we realize that $|\Psi(\beta)\rangle$, while not being an eigenstate of the physical Hamiltonian $H$, obeys an imaginary time Schrödinger equation, given by

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

(17)

which allows us to construct the thermal state at any $\beta$ by integrating Eq. (17) starting from temperature $\beta_0$ where the thermal state $|\Psi(\beta_0)\rangle$ is known exactly. Similarly, if an explicit dependence on the chemical potential $\mu$ is considered, an equation for the evolution in $\mu$ can be established, i.e.

$$|\Psi(\beta, \mu)\rangle = e^{-\beta(H-\mu N)/2} |\Psi(\beta)\rangle,$$

(18)

$$\frac{\partial}{\partial \mu} |\Psi(\beta, \mu)\rangle = \frac{\beta}{2} N |\Psi(\beta, \mu)\rangle.$$  

(19)

In what follows, we shall explicitly describe only the $\beta$ evolution, but this work can be easily extended to the $\mu$ evolution in accordance with Eq. 19.

**A. Thermal Mean-Field Theory**

While Eq. 11 is formally exact, it is in practice impossible to determine the thermal state exactly except for the simplest model systems (it is a highly non-trivial problem to compute merely the ground state). Just as in ground state calculations, practical applications require a systematic way of approximating $|\Psi(\beta)\rangle$.

The most elementary approach one can invoke is the mean-field approach, wherein the Hamiltonian $H$ is approximated by a one-body mean-field Hamiltonian (or the Fock operator), and correspondingly, the mean-field thermal vacuum takes the form

$$|\Psi(\beta)\rangle_{\text{mf}} = |0(\beta)\rangle = e^{-\beta H_0/2} \sum_m |m\rangle \otimes |\tilde{m}\rangle,$$

(20)

where $H_0$ is the mean-field Hamiltonian. This mean-field state satisfies the imaginary time Schrödinger equation not for $H$ but for $H_0$:

$$\frac{\partial}{\partial \beta} |0(\beta)\rangle = -\frac{1}{2} H_0 |0(\beta)\rangle.$$  

(21)

If we choose the states $\{|m\rangle\}$ to be the eigenstates of the mean-field Hamiltonian $H_0$, which can generally be computed without much computational effort, the thermal vacuum takes the form

$$|0(\beta)\rangle = \sum_m e^{-\beta E_m/2} |m\rangle \otimes |\tilde{m}\rangle.$$  

(22)

The norm of $|0(\beta)\rangle$ gives the mean-field partition function

$$Z_0 = \langle 0(\beta) | 0(\beta) \rangle.$$  

(23)

Any quantity of interest, such as the energy, can then be approximately evaluated as an expectation value over $|0(\beta)\rangle$.

For fermions, working within the grand canonical formulation, the thermal state can also be expressed in terms of the single-particle Fock states:

$$|0(\beta)\rangle = e^{-\beta H_0/2} \prod_{p\in \text{levels}} (|0\rangle_p \otimes |\tilde{0}\rangle_p + |1\rangle_p \otimes |1\rangle_p).$$  

(24)

where $|0\rangle_p$ and $|1\rangle_p$ respectively denote that the single-particle level $p$ is empty or occupied. If the levels $p$ are chosen to be the eigenstates of $H_0$, a simple thermal Bogoliubov transformation can be defined to construct the thermal field operators $\{a_p(\beta), a_p^\dagger(\beta), \tilde{a}_p(\beta), \tilde{a}_p^\dagger(\beta)\}$ that create or annihilate quasi-particle excitations on to the thermal vacuum, i.e.

$$\begin{bmatrix} a_p(\beta) \\ \tilde{a}_p(\beta) \end{bmatrix} = \begin{bmatrix} w_p & -z_p \\ z_p & w_p \end{bmatrix} \begin{bmatrix} \epsilon_p^0 \\ \epsilon_p^1 \end{bmatrix},$$  

(25)

such that

$$a_p|0(\beta)\rangle = 0 = \tilde{a}_p|0(\beta)\rangle,$$

(26a)

$$\langle 0(\beta)|a_p^\dagger \tilde{a}_p^\dagger |0(\beta)\rangle = 0 = \langle 0(\beta)|\tilde{a}_p^\dagger a_p^\dagger |0(\beta)\rangle.$$  

(26b)

It is easy to show that $w_p = \sqrt{1 - f_F(\epsilon_p)}$ and $z_p = \sqrt{f_F(\epsilon_p)}$, where $f_F$ is the Fermi-Dirac distribution function. Here and in the following, we have dropped the explicit $\beta$-dependence in the operators $a_p, a_p^\dagger$, and their tilde counterparts.

A similar transformation can be defined for bosons, however, we shall confine ourselves to the many-electron problem in this paper. Furthermore, while such a transformation can also be built within the canonical ensemble, it is generally non-linear and introduces a new algebra for the thermal operators (see, e.g., the transformation for $SU(2)$ spin operators in Ref. 32).

The Bogoliubov transformation in Eq. 25 allows us to form a physical intuition about the thermal operators: in the low $T$ (or high $\beta$) limit, the annihilation of a particle in the original space $\mathcal{H}$ is equivalent to creating a particle in the tilde-space $\tilde{\mathcal{H}}$ and vice-versa, whereas for in the high $T$ limit, these operators are completely mixed.

A general 2-body Hamiltonian, written in terms of the spin-orbital creation and annihilation operators as

$$H = \sum_{p,q} h_{pq} c_p^\dagger c_q + \frac{1}{4} \sum_{p,q,r} v_{pqr} c_p^\dagger c_q^\dagger c_r,$$

(27)

can be expressed in terms of the thermal operators and takes the form

...
\[ H = \sum_p z_p^2 \left( h_{pp} + \frac{1}{2} \sum_{q} z_q^2 v_{pq} \right) + \sum_{pq} \left( h_{pq} + \sum_r z_r^2 v_{prq} \right) \left( w_p w_q a_p^\dagger a_q - z_p z_q a_p^\dagger a_q + w_p z_q a_p^\dagger a_q + w_q z_p a_p a_q \right) + 2\text{-body terms} \] (28)

Notice that the foregoing expression for the Hamiltonian is normal-ordered with respect to the thermal vacuum. The ordering we follow here is \( a^\dagger \to a^\dagger \to a \to a \). The thermal average of \( H \) at the mean-field level is simply found by extracting the scalar component from its normal ordered expression,

\[ E_{\text{hf}} = \sum_p z_p^2 h_{pp} + \sum_{p,q} \frac{1}{2} z_p^2 z_q^2 v_{pq} \] (29a)
\[ = \sum_p \frac{h_{pp}}{1 + e^{\beta (\epsilon_p - \mu)}} \] (29b)
\[ + \frac{1}{2} \sum_{p,q} \frac{v_{pq}}{\left(1 + e^{\beta (\epsilon_p - \mu)}\right)\left(1 + e^{\beta (\epsilon_q - \mu)}\right)}, \]

which recovers the standard thermal Hartree-Fock expression for the energy. One can find the appropriate one-electron basis or molecular orbitals by variationally minimizing the appropriate (i.e. Helmholtz or Gibbs) free energy.

### III. FRAMEWORK FOR CORRELATED METHODS

We have noted that a practical wave function-based framework for the study of the thermal properties of electronic systems is highly desirable, and have seen that thermofield dynamics allows such a framework at the mean-field level. Here, we wish to include correlation atop thermal mean-field.

Correlated methods frequently use a mean-field reference as the starting point, and we wish to do so here as well, but we face an additional choice which we wish to explore. Recall that the thermal state \( |\Psi(\beta)\rangle \) is obtained not from an eigenvalue problem but from an imaginary-time Schrödinger equation. We can choose as our reference the mean-field thermal state corresponding to a fixed temperature \( \beta_0 \), or we can instead use as our reference the mean-field thermal state corresponding to the temperature of interest. By analogy with similar frameworks for coordinates in fluid dynamics as well as general relativity, we call the former approach a fixed-reference formulation and the latter a covariant formulation. Mathematically, the exact thermal vacuum \( |\Psi(\beta)\rangle \) is represented as

\[ |\Psi(\beta)\rangle = \hat{\Gamma}(\beta, \beta_0) |0(\beta_0)\rangle, \] (30)

in the fixed-reference approach, where \( \hat{\Gamma} \) is a wave operator which builds correlation on the reference, and as

\[ |\Psi(\beta)\rangle = \hat{\Gamma}(\beta, \beta) |0(\beta)\rangle \] (31)

in the covariant approach.

On the one hand, the covariant approach would seem to be more sensible, as less is demanded of the wave operator \( \hat{\Gamma} \); on the other hand, the fixed-reference approach has the advantage that the quasiparticle creation and annihilation operators given by the thermal Bogoliubov transformation of Eq. 25 are not themselves temperature-dependent, which considerably simplifies the formulation of correlated methods. In principle any inverse temperature \( \beta_0 \) can be used in the fixed-reference case, but in practice the most convenient choice is \( \beta_0 = 0 \) for which the mean-field thermal state is exact and the wave operator \( \hat{\Gamma}(0,0) \) is simply the identity operator.

Beyond deciding between the fixed-reference and covariant cases, we have a second decision to make. The mathematical structure of the thermal averages expressed in the TFD formalism exhibits a great degree of flexibility in the way in which the bra and the ket thermal states can be split. This is a direct consequence of the cyclic property of the trace involved, or equivalently the freedom in the choice of the path integral representation of TFD.\(^{35}\)

Consider the thermal average of some physical quantity \( A \) which is written in TFD as

\[ \langle A \rangle = \frac{\langle \| e^{-\beta H/2} A e^{-\beta H/2} \| \rangle}{\langle \| e^{-\beta H} \| \rangle}. \] (32)

The numerator in Eq. 32 represents the trace of the operator \( A \) along with the density operator \( \hat{\rho} \). The cyclic property of the trace allows us to rewrite Eq. 32 as

\[ \langle A \rangle = \frac{1}{\| \|} \langle \| e^{-(1-\sigma)\beta H} A e^{-\sigma \beta H} \| \rangle, \] (33)

where we are free to chose \( 0 \leq \sigma \leq 1 \).\(^{15,35}\) The cyclic property of the trace is applicable to an expectation value here because \( A \) acts only on the states in \( \mathcal{H} \). Note that for \( \sigma \neq 1/2 \), we would require not one but two thermal states. Two values of \( \sigma \) are particularly useful: \( \sigma = 1/2 \) for which we require only a single thermal state, and \( \sigma = 1 \) for which one of the two requisite thermal states is simply \( \langle \| \rangle \). When this \( \sigma \)-dependence is needed to properly interpret the equations, we will hereafter indicate it by...
the inclusion of a subscript which for the sake of economy we will suppress when it is not needed.

We close this section by giving reasonably explicit recipes for the thermal state in the fixed-reference and covariant cases, assuming that we evolve in $\beta$ from $\beta = 0$. For the fixed-reference case, with $\beta_0 = 0$, we have

$$\vert \Psi_{\sigma}(\beta) \rangle = \hat{\Gamma}_{\sigma}(\beta, 0) \vert \mathbb{I} \rangle,$$

where we satisfy

$$\sigma H \vert \Psi_{\sigma}(\beta) \rangle = - \left( \frac{\partial}{\partial \beta} \hat{\Gamma}_{\sigma}(\beta, 0) \right) \vert \mathbb{I} \rangle,$$

$$\hat{\Gamma}_{\sigma}(0, 0) = \hat{1},$$

and where $\hat{1}$ is the identity operator. In contrast, for the covariant case we instead have

$$\vert \Psi_{\sigma}(\beta) \rangle = \hat{\Gamma}_{\sigma}(\beta, \beta) \vert 0_{\sigma}(\beta) \rangle,$$

and we satisfy

$$\sigma H_0 \vert 0_{\sigma}(\beta) \rangle = - \frac{\partial}{\partial \beta} \vert 0_{\sigma}(\beta) \rangle,$$

$$\sigma H \vert \Psi_{\sigma}(\beta) \rangle = - \left( \frac{\partial}{\partial \beta} \hat{\Gamma}_{\sigma}(\beta, \beta) \right) \vert 0_{\sigma}(\beta) \rangle - \hat{\Gamma}_{\sigma}(\beta, \beta) \frac{\partial}{\partial \beta} \vert 0_{\sigma}(\beta) \rangle,$$

$$\hat{\Gamma}_{\sigma}(0, 0) = \hat{1}. $$

Inserting Eq. 37a into Eq. 37b gives us an alternative expression:

$$\sigma \hat{H}_{\sigma}(\beta) \vert 0_{\sigma}(\beta) \rangle = - \left( \frac{\partial}{\partial \beta} \hat{\Gamma}_{\sigma}(\beta, \beta) \right) \vert 0_{\sigma}(\beta) \rangle $$

where the $\beta$-dependent effective Hamiltonian is

$$\hat{H}_{\sigma}(\beta) = H_0 \hat{\Gamma}_{\sigma}(\beta, \beta) - \hat{\Gamma}_{\sigma}(\beta, \beta) H_0 + V \hat{\Gamma}_{\sigma}(\beta, \beta) $$

and $V = H - H_0$ is the correction to the mean-field Hamiltonian $H_0$.

In the next section, we will show detailed formulations for these two approaches through the example of thermal configuration interaction (CI) theory.

### IV. THERMAL CI THEORY

Here, we specialize both the fixed-reference and the covariant versions of our general theory to the case of thermal CI. As will be clear, these approaches are quite similar to time-dependent CI at zero temperature. The construction of more sophisticated methods, such as thermal coupled cluster theory, is mathematically more involved and its details will be presented in a follow-up article. Nevertheless, we here present preliminary numerical results of thermal CCSD for the purpose of comparison with CISD.

#### A. Fixed-reference Thermal CI

In this first approach, let us express thermal averages with $\sigma = 1$, so that we use the asymmetric expectation value

$$\langle A \rangle_\beta = \frac{1}{Z_1} \langle \mathbb{I} \vert A \vert \psi(\beta) \rangle, \quad \vert \psi(\beta) \rangle = e^{-\beta H} \mathbb{I}, $$

where the state $\vert \psi(\beta) \rangle$ is governed by the imaginary-time Schrödinger equation

$$H \vert \psi(\beta) \rangle = - \frac{\partial}{\partial \beta} \vert \psi(\beta) \rangle $$

and is written as

$$\vert \psi(\beta) \rangle = \hat{\Gamma}(\beta, 0) \mathbb{I}, $$

$$\hat{\Gamma}(\beta, 0) = t_0 + \sum_{pq} t_{pq} \alpha_p^\dagger \alpha_q^\dagger$$

$$+ \frac{1}{(2!)} \sum_{pqrs} t_{pqrs} \alpha_p^\dagger \alpha_q^\dagger \alpha_s^\dagger \alpha_r^\dagger + \ldots, $$

where all the $\beta$-dependence is carried by the expansion coefficients. The $(\beta$-independent) quasiparticle operators $\alpha, \alpha^\dagger$, and so on are defined by Eq. 25 with

$$w_p = 1/\sqrt{1 + n_f} \quad \text{and} \quad z_p = w_p \sqrt{n_f}, $$

where $n_f$ is the filling fraction for a given basis set. It is interesting to note that the wave operator $\hat{\Gamma}$ in Eq. 42 is composed of terms that contain equal number of tilde and non-tilde quasiparticle creation operators. This is because, by virtue of the thermal Bogoliubov transformation in Eq. 25, the difference in the total number of tilde and non-tilde quasiparticles is a symmetry of the Hamiltonian, i.e.

$$[\hat{N}, H] = 0, \quad \hat{N} = \sum_p (\alpha_p^\dagger \alpha_p - \alpha_p^\dagger \alpha_p) $$

and therefore, only such terms would have a non-trivial contribution to the thermal state.

Substituting this ansatz into Eq. 41, we obtain the following set of working equations:

$$\frac{\partial t_0}{\partial \beta} = \frac{1}{Z_1} \langle \mathbb{I} \vert H \hat{\Gamma}(\beta, 0) \mathbb{I} \rangle, $$

$$\frac{\partial t_{pq}}{\partial \beta} = \frac{1}{Z_1} \langle \mathbb{I} \vert \alpha_q H \hat{\Gamma}(\beta, 0) \mathbb{I} \rangle, $$

$$\frac{\partial t_{pqrs}}{\partial \beta} = \frac{1}{Z_1} \langle \mathbb{I} \vert \alpha_r \alpha_s \alpha_p H \hat{\Gamma}(\beta, 0) \mathbb{I} \rangle, $$

and similarly for higher order terms, with the zero-temperature partition function $Z_1$ being given by

$$Z_1 = \langle \mathbb{I} \vert \mathbb{I} \rangle. $$

We can integrate these equations from $\beta = 0$, with the initial conditions

$$t_0 = 1; t_{pq} = 0; t_{pqrs} = 0, \ldots $$

to obtain the CI coefficients at any given inverse temperature $\beta$. 
operators are $\beta$-dependent. Because the operators $a_p$, $a_p^\dagger$, and so forth are $\beta$-dependent, they have non-trivial $\beta$ derivatives. For example, from the thermal Bogoliubov transformation of Eq. 25, we see that
\[
\frac{\partial a_p^\dagger}{\partial \beta} = \epsilon_p - \mu \omega_p z_p a_p, \quad \frac{\partial a_p}{\partial \beta} = -(\epsilon_p - \mu \omega_p z_p a_p),
\]
and so on.

Substituting the wave function ansatz of Eq. 47 into the imaginary time Schrödinger equation of Eq. 17, we find
\[
\frac{\partial s_0}{\partial \beta} = -\frac{1}{Z_0} \langle 0(\beta) \frac{1}{2} \bar{H} + \frac{\partial_{\text{op}} \Gamma(\beta, \beta)}{\partial \beta} | 0(\beta) \rangle, \quad (49a)
\]
\[
\frac{\partial s_{pq}}{\partial \beta} = -\frac{1}{Z_0} \langle 0(\beta) \bar{a}_q a_p \left( \frac{1}{2} \bar{H} + \frac{\partial_{\text{op}} \Gamma(\beta, \beta)}{\partial \beta} \right) | 0(\beta) \rangle, \quad (49b)
\]
and so forth, where $\partial_{\text{op}} \Gamma(\beta, \beta)/\partial \beta$ denotes the derivative of only the operator part of the wave operator $\Gamma(\beta, \beta)$ and where $\bar{H}$ is the effective Hamiltonian defined in Eq. 39. As with the fixed-reference case, we can integrate Eq. 49 from $\beta = 0$ with the initial conditions
\[
s_0 = 1; s_{pq} = 0; s_{pqrs} = 0; \ldots,
\]

V. RESULTS AND CONCLUSIONS

Just as for ground-state CI, the theories described above can be truncated at various levels of excitations to yield results with respective levels of accuracy. Here, we truncate after single (CIS) or double (CISD) excitations to study the temperature-dependence of the internal energy of the Hubbard model within the grand canonical ensemble. The Hamiltonian for the Hubbard model is given by
\[
H = \frac{t}{2} \sum_{(p,q),\sigma} (\epsilon_{p,\sigma} \epsilon_{q,\sigma} + \text{h.c.}) + U \sum_p \hat{n}_{p,\uparrow} \hat{n}_{p,\downarrow}, \quad (50)
\]
where $\langle \cdot \rangle$ 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 $\hat{n}_{p,\sigma} = \epsilon_{p,\sigma} c_{p,\sigma}^\dagger c_{p,\sigma}$ is the number operator for lattice site $p$ and spin $\sigma$. The correlation
Thermofield theory provides an honest wave function method from which the thermal density matrix may be extracted, and allows for a straightforward extension of any ground state method to compute properties at non-zero temperatures. This is achieved by integrating an imaginary time Schrödinger equation for the thermal state which has otherwise been scarce in the applications of TFD. Moreover, although the introduction of the fictitious \( \tilde{t} \) space results in a doubling of the Hilbert space, the overall computational cost of any method increases only by a multiple of the \( \beta - \mu \) grid size. The latter depends only on the desired accuracy in the integration and does not change the overall scaling of the cost. These features make this framework ideal for application to many-body quantum systems in physics and chemistry and provide a deterministic alternative to the more common stochastic Monte-Carlo methods. Our early results show that even thermal CI significantly improves upon thermal mean-field theory. This early work provides both the desire and the means to generalize more sophisticated wave function techniques to the case of finite temperature.

Figure 2 shows results for the six-site model at \( U/t = 2 \) and average half filling. The story is substantially the same as for the simpler two-site model: there are large errors at thermal HF and CIS level which are substantially reduced by thermal CI and CC. For large \( \beta \), thermal CISD reduces to the standard zero-temperature canonical ensemble CISD. Again, while the CIS and CISD results use the covariant formulation, the CCSD results uses a covariant formulation for \( \beta \)-evolution and a fixed-reference formulation for \( \mu \)-evolution.

As we have seen, covariant CI works well over the entire temperature range, particularly once we include double excitations. In contrast, for larger values of \( \beta \), fixed-reference CI quickly breaks down and for large enough \( \beta \) we can find no chemical potential \( \mu \) for which fixed-reference thermal CI has the right average particle number. This is emphasized in Fig. 3 which shows results for the six-site model at \( U/t = 2 \) with an average of two electrons.

Conclusions

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