Normal ordered exponential approach to thermal properties and time-correlation functions: general theory and simple examples

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ABSTRACT

A normal ordered exponential parametrisation is used to obtain equations for thermal one- and two-particle reduced density matrices, as well as free energies, partition functions and entropy for both Fermionic (electronic) and Bosonic (vibrational) Hamiltonians. A first principles derivation of the equations, relying only on a simple Wick’s theorem and starting from the differential equation \( \frac{d \hat{D}}{d \beta} = - (\hat{H} - \mu \hat{N}) \hat{D} \), is presented that yields a differential equation for the amplitudes representing density cumulants, as well as the grand potential. In contrast to other approaches reported in the literature, the theory does not use the interaction picture and an integral formulation as a starting point but rather requires a propagation of the resulting differential equation for the amplitudes in the Schrödinger representation. While the theory is applicable to general classes of many-body problems in principle, here, the theory is illustrated using simple model systems. As an application of the related time-dependent formulation numerically exact time-autocorrelation functions and absorption spectra are obtained for harmonic Franck–Condon problems. These examples illustrate the basic soundness of the scheme and are used for pedagogical purposes. Other approaches in the literature are only discussed briefly and no detailed comparative discussion is attempted.

1. Introduction

The calculation of thermal properties is important for many branches of chemistry and physics. The easiest realisation perhaps is in thermochemistry of (ideal) gases, in which nuclear motion is commonly treated through free particle, rigid rotor and harmonic approximations. The calculation of thermal properties due to nuclear motion in liquids or flexible proteins is most often treated using sampling of classical motion. Calculations of thermal electronic properties have a long history in the context...
of solid state physics, in particular for gap-less materials, e.g. metals, and/or small gap materials, for example, in Hubbard-like models for strongly correlated materials, e.g. [1], or phase-transitions, e.g. [2]. For molecules, magnetic properties can be of interest, e.g. spin crossover phenomena [3]. Hartree–Fock or more commonly density functional theory is widely applied in the convenient grand-canonical formulation in which one obtains fractional occupation numbers according to the Fermi–Dirac distribution, \[ n_p = \frac{1}{1 + e^{\beta E_p}}. \] The chemical potential in such calculations is adjusted to achieve electrical neutrality. The other most widely applied strategies to obtain thermal properties for solids use a variety of approximations rooted in many-body Green’s function theory, e.g. [4–7]. Such approaches apply to both Fermionic (i.e. electronic) and Bosonic (e.g. vibrational) degrees of freedom and in this paper we will likewise explore both types of problems from a unified perspective.

Thermal electronic properties are also of interest for molecular systems, e.g. gases or liquids that contain low-lying electronic states, and recent years have witnessed an increased interest in the calculation of thermal properties using first principles theories, e.g. through perturbation theory [8–13], second-order Green’s function approaches, e.g. [14–17], variations of thermal coupled cluster theory [18–24], or thermal mean field approaches, e.g. [25,26] and references in these papers. While Coupled Cluster theory today is arguably the most versatile and accurate wave function based theory for electronic ground states, the theoretical foundation of the various Coupled Cluster formulations to obtain thermal properties are somewhat curious, and perhaps ad hoc. Hirata and coworkers have addressed some of the issues in recent work on perturbation theory including the limit at zero temperature [27,28].

Most of the formulations are justified broadly according to the following principles:

(a) At zero temperature, the thermal coupled cluster approach reduces to the conventional single reference coupled cluster formulation for the ground state.

(b) A low-order perturbation expansion of the thermal CC approach agrees with established finite temperature perturbation theory (e.g. in the Matsubara formulation).

(c) The formulations explicitly use the interaction picture to derive equations, and involve an integration over inverse temperature. The use of the interaction picture implies the partitioning of the full Hamiltonian into a zeroth-order and perturbed part, and it is not always clear if final results depend on this choice of zeroth-order Hamiltonian.

(d) Thermal energies and other thermal properties are obtained as a function of the inverse temperature \( \beta \) and the chemical potential \( \mu \), and are not strictly limited to systems with a specified number of electrons in their ensemble average (i.e. they employ the grand-canonical formulation).

It would appear that this state of affairs has mainly historical origins. Much of the original work on thermal properties has been done based on a quantum field theoretical framework, extending time-dependent propagator or Green’s function theory to thermal properties, using in essence a Wick rotation, in addition to further analysis. In this historical context, a perturbative diagrammatic starting point is the essential point of departure, and any resulting theory is naturally rooted in perturbative expansions and partial re-summations. The PhD work of one of the authors took exactly this point of view for purely electronic problems, starting from perturbative diagrammatic expansions and back-engineering to infinite order theories like Coupled Cluster theory and the Coupled Cluster Green’s function, using recursive diagrammatic procedures [29–31]. Interestingly, in this process, the Green’s function was obtained directly, and not through an approximation to the irreducible self-energy and a subsequent solution of Dyson’s equation. Moreover, this approach is basically equivalent to Coupled Cluster linear response theory, e.g. [32] or equation of motion CC theory [33]. This suggests that the methods of quantum field theory, which are defined from the outset in terms of a perturbation expansion may benefit from a reformulation when a closed form Hamiltonian is known. In the context of quantum chemistry, the picture is usually reversed. One has easy direct ways to define Coupled Cluster theory, as an approximation to full CI, and a perturbative expansion of the theory leads to many-body perturbation theory, in a manifestly connected form, e.g. [34–36].

The tight connection to essentially single reference perturbation theory is likely not desirable if the goal is to calculate thermal properties for molecular systems, including explicitly electronic degrees of freedom. Molecular systems of interest will have multiple low-lying electronic states, otherwise one need not bother with electronic contributions to thermal properties beyond the ground state. The most likely realistic systems would require a multireference description for their ground states and would be poorly described by (low-rank) single reference coupled cluster theory or many-body perturbation theory. The logical conclusion would be that...
if one is interested in efficient methodologies to calculate thermal properties (of strongly correlated systems), methods should not reduce to conventional single-reference Coupled Cluster theory at zero temperature, and/or one would prefer low-order perturbative schemes that do not reduce to conventional finite temperature perturbation theory, as these methods do not work well for strongly correlated systems. We think this is a fair assessment for molecular systems, although the situation for metallic solids may be different.

We think the above arguments strongly suggest one should take an alternative tack, avoiding the conventional routes. Rather than starting from a complicated framework rooted in Quantum Field Theory the basic starting point for molecular calculations can be the full CI formulation in a finite basis set, using either canonical or grand-canonical formulations. For small, but meaningful, strongly correlated systems full CI thermal properties are readily obtained, and the goal of more efficient, approximate formulations would be to approach the full CI results, implying one needs to design a formulation that can work with low-rank, e.g. singles and doubles substitution operators. There does not seem to be any pressing need to use the interaction picture and the resulting theory may be simpler without invoking it. It may be that newly derived approaches could be reformulated using the interaction picture, but we do not want to make this a point of departure.

This paper is largely pedagogical in nature. We present a general theory to calculate thermal properties for both Fermionic and Bosonic systems and will also consider closely related time-dependent formulations. The approach is based on a normal ordered exponential ansatz to represent the many-body reduced density matrices and the use of a simple Wick’s theorem (i.e. no interaction picture) to derive ordinary coupled differential equations (in terms of a single parameter τ) for the amplitudes that can simply be solved for numerically, given suitable initial conditions. The goal of the paper is to clearly explain the theory from simple principles, and we will use simple examples like one-electron Hamiltonians and displaced harmonic oscillators for which exact (analytical) solutions are known. As an example of a time-dependent property, we will discuss the calculation of time-autocorrelation functions and related absorption spectra for general harmonic Franck-Condon problems. The implementation of these methods for more general problems is of course of real interest, but a number of issues are expected to arise and here we focus on simple problems for which the proposed methods are numerically exact.

This paper is organised as follows. In Section 2, we discuss the general thermal NOE (thermal normal-ordered exponential) formulation of the electronic problem for the grand-canonical ensemble. In Section 3, we apply the Fermionic theory to one-electron Hamiltonians and discuss how the results reduce to conventional single refer-

2. Thermal normal ordered exponentials for fermions and the grand canonical ensemble

The starting point for the discussion is the differential equation for the thermal density matrix in the grand canonical formulation

\[
\frac{d \hat{D}}{d \beta} = (\hat{H} - \mu \hat{N}) \hat{D} = \beta \hat{D}_0
\]

(1)

\[
\hat{D}(\beta = 0) = \hat{D}_0 = \alpha \hat{1}
\]

(2)

We define a uniform fermionic density operator, \( \hat{D}_0 \) at \( \beta = 0 \), and this serves as the vacuum for the many-body theory. In the definition above \( \alpha \) is a (formal) normalisation constant such that \( Tr(\hat{D}_0) = 1 \). To derive equations, we trace over the complete Fock space using the uniform density, but using Wick’s theorem, we only require the notion of normal order and contractions between elementary annihilation and creation operators. We define the non-zero contractions as

\[
\hat{p}^\dagger \cdot \hat{q} = Tr \left( \hat{p}^\dagger \hat{q} \hat{D}_0 \right) \equiv \left( \hat{p}^\dagger \hat{q} \right) = f_p \delta_{pq} = f \delta_{pq}
\]

(3)

\[
\hat{p} \cdot \hat{q}^\dagger = \delta_{pq} - \left( \hat{q}^\dagger \hat{p} \right) = (1 - f_q) \delta_{pq} \equiv f_q \delta_{pq} = \bar{f} \delta_{pq}
\]

(4)

Due to the uniformity of the density operator the value of the single parameter \( f \) is determined by the condition that the trace of the one-body density matrix should equal the
number of electrons, \( n_{\text{el}} \). If we have \( M \) orbitals in total in the orthonormal one-particle basis set, we have

\[
\sum_{\mathbf{p}} f = n_{\text{el}}, \quad f = \frac{n_{\text{el}}}{M} \hat{f} = \frac{M - n_{\text{el}}}{M} \tag{5}
\]

The theory we will develop is completely based on a simple form of Wick’s theorem where the product of two normal operators is defined as their normal product with all possible contractions. Another important property is that the vacuum expectation value of any normal-ordered operator vanishes except for the constant part

\[
\text{Tr}(\{\hat{\Omega}_k\} \hat{D}_0) \equiv \langle \{\hat{\Omega}_k\} \rangle = 0 \tag{6}
\]

for any nonempty string of annihilation and creation operators \( \hat{\Omega}_k \). In this work, we can use a very familiar version of Wick’s theorem, where the only generalisation is that all orbitals are treated equivalently and there is no distinction between occupied and virtual orbitals.

The finite temperature many-body density operator is parameterised using a normal ordered exponential as

\[
\hat{D} = \left\{ e^{\hat{S}(\beta)} \right\} \hat{D}_0 \tag{7}
\]

where the braces indicate normal ordering and \( \hat{S}(\beta) \) is expanded in terms of normal ordered substitution operators and a constant term

\[
\hat{S}(\beta) = s_0(\beta) + \sum_{\lambda} s_{\lambda}(\beta) \left\{ \hat{\Omega}_k \right\} \tag{8}
\]

The expansion can be truncated after some highest rank of substitution. The complete untruncated operator may require an expansion up to the dimension of the Fock space. To work with the normal ordered exponential, one can simply use the Taylor series expansion for the exponential and use that there are no contractions between \( \hat{S} \) operators when evaluating Wick’s theorem, e.g.

\[
\left\{ e^{\hat{S}(\beta)} \right\} = \sum_{n=0}^{\infty} \frac{1}{n!} \left( \hat{S}(\beta) \right)^n \tag{9}
\]

To facilitate the discussion we partition normal ordered operators in a constant part and the remaining part of the operator, which has non-trivial (normal ordered) substitution operators. This non-trivial part of the operator will be denoted through a dot rather than a carrot, e.g.

\[
\hat{S}(\beta) = s_0(\beta) + \check{\hat{S}}(\beta) \tag{10}
\]

\[
\check{\hat{N}} = n_{\text{el}} + \check{N} \tag{11}
\]

\[
\check{H} = E_0 + \check{H} \tag{12}
\]

Due to the normal ordering convention, the trace of the density matrix is easily evaluated as

\[
\text{Tr}(\hat{D}) = \text{Tr} \left\{ \exp(s_0(\beta) + \check{\hat{S}}(\beta)) \right\} \hat{D}_0
\]

\[
= e^{s_0(\beta)} \left\{ \exp(\check{\hat{S}}(\beta)) \right\}
\]

\[
= e^{s_0(\beta)} \tag{13}
\]

To evaluate the thermal expectation value of any operator \( \check{O} = O_0 + \check{O} \) one evaluates

\[
\langle \check{O} \rangle = \frac{\text{Tr}(\hat{\check{O}} \hat{D})}{\text{Tr}(\hat{D})}
\]

\[
= \left\{ \langle O_0 + \hat{\check{O}} \rangle \left\{ e^{s_0(\beta)} \exp(\check{\hat{S}}(\beta)) \right\} \right\} e^{-s_0(\beta)}
\]

\[
= O_0 + \left\{ \hat{\check{O}} \left\{ \exp(\check{\hat{S}}(\beta)) \right\} \right\} \tag{14}
\]

where we note that the partition function \( Z = e^{s_0} \) cancels between numerator and denominator. This is convenient as the partition function depends on an arbitrary choice for zero energy and may diverge for low \( T \), if that zero of energy is above the ground state energy of the system. It follows that if one knows the amplitudes of the operator \( \check{S}(\beta) \) one can evaluate expectation values over the thermal density matrix, while

\[
s_0(\beta) = \ln(\text{Tr}(\hat{D})) = \ln \text{Tr}(e^{-\beta(\check{H} - \check{\hat{N}})}) = \ln(Z(\beta, \mu)) \tag{15}
\]

is the grand potential, relating to the (Helmholtz) free energy, \( A = -k_B T \ln(Z) = -\frac{1}{\beta} \ln(Z) \).

As we will see the constant term, \( E_0 \), in the Hamiltonian is easily incorporated, like a shift in energy scale, and we will use as a starting equation for the \( S \) amplitudes

\[
-\frac{d\hat{D}}{d\beta} = (\check{H} - \mu \check{\hat{N}}) \hat{D} \tag{16}
\]

Substituting the normal ordered exponential parameterisation in the differential equation for the density matrix,

\[
-\frac{d}{d\beta} \left\{ \exp(\check{\hat{S}}(\beta)) \right\} \hat{D}_0 = (\check{H} - \mu \check{\hat{N}}) \left\{ \exp(\check{\hat{S}}(\beta)) \right\} \hat{D}_0
\]

\[
\tag{17}
\]

we can simplify immediately, using Wick’s theorem (see Appendix)

\[
-\left\{ \frac{d}{d\beta} \exp(\check{\hat{S}}(\beta)) \right\} \hat{D}_0 = \left[ (\check{H} - \mu \check{\hat{N}}) \left\{ \exp(\check{\hat{S}}(\beta)) \right\} \right]_{\text{connected}} \hat{D}_0
\]

\[
\tag{18}
\]

which implies the connected form of the equation

\[
-\frac{d\check{S}}{d\beta} \hat{D}_0 = \left[ (\check{H} - \mu \check{\hat{N}}) \left\{ \exp(\check{\hat{S}}(\beta)) \right\} \right]_{\text{connected}} \hat{D}_0
\]

\[
\tag{19}
\]

The subscript ‘connected’ implies the string of operators is written in normal order, and one keeps only connected
terms. The usual combinatorics of the exponential regenerates a normal ordered exponential as indicated above. We can equate the connected parts on both sides of the equation and project against a complete set of normal ordered substitution operators commensurate with the definition of maximum substitution rank to get a differential equation for the amplitudes

\[ - \left( \frac{d}{d\beta} \Omega_v \right) = \left( \Omega_v \left[ \left( \hat{H} - \mu \hat{N} \right) \left\{ \exp(\hat{S}(\beta)) \right\} \right] \right)_{\text{connected}} \]

\[ - \frac{d s_0}{d\beta} = \left\{ \left( \hat{H} - \mu \hat{N} \right) \left\{ \exp(\hat{S}(\beta)) \right\} \right\}_{\text{connected}} \]

In our replacement of \( \hat{N} \) by \( \hat{\tilde{N}} \) in the amplitude equations, we have used that a constant term cannot be connected to, or contracted against, other operators. The number of electrons is determined as

\[ N_{el} = n_{el} + \left[ \left\{ \hat{N} \left\{ \exp(\hat{S}(\beta)) \right\} \right\} \right]_{\text{connected}} \]

and the parameter \( \mu(\beta) \) is to be determined such that \( N_{el} \) evaluates to \( n_{el} \) for all \( \beta \). This implies the convenient relation

\[ \left[ \left\{ \hat{N} \left\{ \exp(\hat{S}(\beta)) \right\} \right\} \right]_{\text{connected}} = 0 \]

Equations (20), (21) and (23) have to be solved in a coupled fashion. We note that \( s_0(\beta) \), which is an extensive quantity, does not enter the amplitude Equations (20), which is to be expected if a theory is to scale correctly with the size of the system. The initial condition for the integration over \( \beta \) is simply \( s_\lambda(\beta = 0) = 0 \) \( \forall \lambda \), starting from the high (or infinite) \( T \) limit \( \beta = 0 \).

The thermal internal energy is given by

\[ U(\beta) = E_0 + \left[ \left\{ \hat{H} \left\{ \exp(\hat{S}(\beta)) \right\} \right\} \right]_{\text{connected}} \]

The grand canonical partition function then satisfies the differential equation

\[ - \frac{\ln(Z)}{d\beta} = E_0 - \frac{d s_0}{d\beta} \]

By integrating \( \frac{d s_0}{d\beta} \), we obtain (the ln of) the grand canonical partition function

\[ \ln(Z(\beta)) = -\beta E_0 + s_0(\beta) \]

Identifying temperature \( T = (k_B \beta)^{-1} \), we can make the connection to thermodynamic electronic properties in the grand canonical ensemble through

\[ - k_B T \ln(Z(T)) = U(T) - T S(T) + \mu(T) n_{el} \]

It follows that entropy can be obtained from the above formulation. The above relations will be verified numerically for a simple one-electron model problem in Section 3, in which we can explicitly perform a sum over states expression and use elementary methods to obtain all quantities. For one-electron problems, we are recovering the correct results known from Fermi-Dirac statistics.

The one- and two-body reduced thermal density matrices can be obtained in a similar fashion as the internal energy, and only require the one- and two-body operators in \( \hat{S}(\beta) \). If we define

\[ \hat{S}_1(\beta) = \sum_{p \neq q} s_{pq}(\beta) \left\{ \hat{p}_p^+ \hat{q}_q \right\} \]

\[ \hat{S}_2(\beta) = \frac{1}{4} \sum_{p \neq q \neq s} s_{pq}^{pq}(\beta) \left\{ \hat{p}_p^+ \hat{q}_q^+ \hat{s}_s \right\} \]

One obtains explicitly

\[ D_q^p = \left\{ \hat{p}_p^+ \hat{q}_q(1 + \hat{S}_1) \right\} = f s_{pq}^0 + f f s_{pq}^q \]

\[ D_{pq}^{qs} = \left\{ \hat{p}_p^+ \hat{q}_q^+ \hat{s}_s(1 + \frac{1}{2} \left\{ \hat{s}_{qs}^+ \right\} + \hat{s}_2) \right\} \]

\[ = \cdots = D_q^p D_s^p - D_{pq} D_s^p + f f q^p s_{pq}^{rs} \]

It follows that the two-body amplitudes \( s_{pq}^{pq}(\beta) \) represent the two-body cumulant up to a scaling factor. One can think of the normal-ordered exponential ansatz as a reduced density cumulant ansatz, and this is the perspective of Mukerjee and coworkers [18–21]. Moreover, the above identification suggests that the operator \( \hat{S} \) should be Hermitian. This aspect is not clear, however, at the moment of writing this paper. It is possible that it is better for the operator \( \hat{S} \) to remain non-Hermitian, and to obtain density matrices that are formally not necessarily Hermitian. Since operators that represent properties are Hermitian, only the Hermitian part of the reduced density matrix would survive when taking the trace, and one can Hermitize after the fact. Alternatively, one could explicitly Hermitize the residual equations, and if we define

\[ \Omega_v^+ = \frac{1}{2} \left( \Omega_v - \Omega_v^+ \right) \]

the Hermitized residual equations are given by

\[- \left( \frac{d}{d\beta} \Omega_v^+ \right) = \left( \Omega_v^+ \left[ \left\{ \hat{H} - \mu \hat{N} \right\} \left\{ \exp(\hat{S}(\beta)) \right\} \right\} \right)_{\text{connected}} \]

\[ - \frac{d s_0}{d\beta} = \left\{ \left( \hat{H} - \mu \hat{N} \right) \left\{ \exp(\hat{S}(\beta)) \right\} \right\}_{\text{connected}} \]

Curiously, nothing in the formal theory imposes this Hermitized form and it appears Hermitization is a choice, on
which we remain agnostic at the moment. The issue will not be resolved in this paper. In particular in the simple model applications to be discussed in this paper, which serve mostly as illustrations and sanity checks of the theory, the hermitization does not do anything. Let us note, however, that if we would consider the detailed singles and doubles equations we would observe a strong formal analogy between the present theory and conventional single reference coupled cluster, and it would appear that the non-Hermitean version of the theory is perhaps the better choice. In the formal development, we will keep using projection against $\Omega^+_v$ to emphasise the issue, but the actual preferred projection of choice will have to await more detailed numerical studies.

The zero temperature, or $\beta \to \infty$ limit is obtained by setting the $\beta$ derivative (or left hand side of the amplitudes equations Equation (20)) to 0, hence, the pair of equations

$$\langle \Omega^+_v \left[ (\hat{H} - \mu \hat{N}) \left\{ \exp(\hat{S}(\beta)) \right\} \right] \rangle_{\text{connected}} = 0 \quad (35)$$

$$\langle [\hat{N} \exp(\hat{S}(\beta))] \rangle = 0 \quad (36)$$

defines a ground state methodology, which has many similarities with the contracted Schrödinger equation or many-body cumulant theory. In particular, there is no preferred set of occupied Hartree–Fock orbitals in the theory. It can be shown that the zero temperature limit yields exactly the same equations as the connected cumulant formulation to the contracted Schrödinger equation by Nooijen et al. [37]. We will not discuss this aspect further in this pedagogically oriented paper. The N-representability problem is a major issue with cumulant based contracted Schrödinger theory, and it is not unlikely this will also plague the present thermal or ground state theory.

The general formulation making extensive use of the concept of normal ordering and solving a differential equation is really quite nimble and elegant in our opinion. The zero temperature formulation can be tested in a straightforward way against full CI or other accurate results that have been obtained for many systems. Here the main difficulty perhaps lies in solving the equations, which may require special care. The testing of the finite temperature methodology is less straightforward as this problem has not been widely studied for molecular systems. The most straightforward way is to perform sum over states calculations (of varying number of electrons) in small finite basis sets, or restricting the problem to a complete active space (CAS). Magnetic model systems may be particularly suitable for this purpose. The $\beta$-dependent formulation is daunting perhaps, because one has to integrate the differential equation from $\beta = 0$, where all electronic state are populated equally, to large values of $\beta$ where only few states carry significant population. Applications of the theory to all-electron situations with large one-particle basis sets may be challenging.

The reader may be surprised by the apparent power of the formulation and the concept of normal-ordering, e.g. when comparing the left and right hand side of the equation

$$\frac{1}{Z} \text{Tr} (\hat{O} e^{-\beta \hat{H}}) = \langle \hat{O} (\hat{S}(\beta)) \rangle \quad (37)$$

On the left-hand side, we have a very complicated expression even when $\hat{H}$ is a known two-body operator. On the right-hand side, we essentially have the solution when $\hat{S}(\beta)$ is known. The essential difference is those innocuous braces denoting normal ordering. There is no trace to be taken over a gigantic Hilbert space. The above equations provide essentially a recipe to calculate directly the thermal reduced density matrices. Powerful indeed.

In the next section, we will first perform some sanity tests for the theory. Our focus will be on one-electron Hamiltonians that are easily solved using simple computer implementations and concerns the case of non-interacting fermionic particles in the traditional grand canonical formulation, for which we expect to obtain the one-electron Fermi-Dirac result.

### 3. Detailed equations for grand canonical formulation using non-interacting one-body Hamiltonian

Let us derive detailed equations for the one-body problem that should yield the usual solution given by the one-particle Fermi-Dirac partition function. The various operators in normal order are given by

$$\hat{h} = h_0 + \sum_{p,q} h_{pq} \left\{ \hat{p}^+ \hat{q} \right\} ; \quad h_0 = f \sum_p h_{pp} \quad (38)$$

$$\hat{N} = n_0 + \sum_{p,q} \delta_{pq} \left\{ \hat{p}^+ \hat{q} \right\} ; \quad n_0 = f \sum_p \delta_{pp} = n_{el} \quad (39)$$

$$\hat{S}(\beta) = s_0(\beta) + \sum_{pq} s_{pq}(\beta) \left\{ \hat{p}^+ \hat{q} \right\} \quad (40)$$

Applying Wick’s theorem, we can evaluate properties from the general formulas as

$$U(\beta) = h_0 + \hat{f} \sum_{p,q} h_{pq}s_{qp}(\beta) \quad (41)$$

$$N_{el} = n_{el} + \hat{f} \sum_{p,q} \delta_{pq}s_{qp} = n_{el} + \hat{f} \sum_p s_{pp}(\beta) \quad (42)$$
Since $N_{el}$ should evaluate to $n_{el}$, we obtain a constraint for the $s$-coefficients:

$$\sum_p s_{pp} = 0 \quad (43)$$

The equation for $U(\beta)$ indicates also the proper expression for the one-particle reduced density matrix of the system.

$$D_{pq}(\beta) = f\delta_{pq} + \bar{f} s_{pq}(\beta) \quad (44)$$

This quantity can directly be compared with the exact result: If one diagonalises the one-particle Hamiltonian one obtains eigenvalues $\epsilon_p$, and the density matrix takes the diagonal Fermi-Dirac form $n_p = [1 + \exp(\beta(\epsilon_p - \mu))]^{-1}$. If one transforms this back to the original basis one obtains the density matrix which should agree with the expression for $D(\beta)$.

The amplitude equations are obtained from

$$\left\{ \hat{q}^+ \hat{p} \right\} \frac{d\vec{S}}{d\beta} = \left\{ \hat{q}^+ \hat{p} \right\} \left( [\hat{h} - \mu \hat{N}] \{\exp(\hat{S}(\beta))\} \right)_{\text{connected}} \quad (45)$$

$$-\frac{ds_0}{d\beta} = \left( [\hat{h} \{\exp(\hat{S}(\beta))\}]_{\text{connected}} \right) - \mu n_{el} \quad (46)$$

Substituting the detailed second quantised expressions and evaluating using Wick's theorem one finds

$$-\bar{f} \frac{ds_{pq}}{d\beta} = \bar{f} \left( h_{pq} + \bar{f} \sum_r h_{pq} s_{rq} \right)$$

$$- f \sum_r s_{pr} h_{rq} - \bar{f} \sum_r s_{pr} h_{rs} s_{sq} \right)$$

$$- \mu f \bar{f} \left( \delta_{pq} + \bar{f} s_{pq} - f s_{pq} - \bar{f} \sum_r s_{pr} s_{rq} \right)$$

$$-\frac{ds_0}{d\beta} = h_0 + \bar{f} \sum_{p,q} h_{pq} s_{qp}(\beta) - \mu n_{el} \quad (47)$$

One can cancel a common factor $\bar{f} \bar{f}$ from the amplitude equations and abbreviate the equations as

$$-\frac{ds_{pq}}{d\beta} = R_{pq}(h, s) - \mu R_{pq}(\delta, s) \quad (49)$$

The parameter $\mu(\beta)$ is determined from the condition that the trace of $s$ should vanish, hence

$$\mu(\beta) = \frac{\sum_p R_{pp}(h, s)}{\sum_p R_{pp}(\delta, s)} \quad (50)$$

The differential equation can be solved in a simple numerical fashion using a leap frog scheme with a fixed step size $\Delta \beta$.

$$S_{pq}(\beta_{i+1}) = S_{pq}(\beta_{i-1}) + 2\Delta \beta \frac{ds_{pq}}{d\beta}(\beta_i)$$

$$= S_{pq}(\beta_{i-1}) - 2\Delta \beta \left( R_{pq}(h, s(\beta_i)) - \mu(\beta_i) R_{pq}(\delta, s(\beta_i)) \right) \quad (51)$$

$$s_0((\beta_{i+1}) = s_0((\beta_{i-1}) + 2\Delta \beta \frac{ds_0}{d\beta}(\beta_i) \quad (52)$$

These equations have been implemented in a simple Fortran code, and it has been verified that the results reproduce the analytical results corresponding to Fermi–Dirac results obtained using a sum over states formulation and exact diagonalisation of the finite basis Hamiltonian. We used simple e.g. 20 × 20 Hamiltonian matrices. It has also been verified that the natural occupation numbers do not become less than 0, nor do they exceed 1, and this is an interesting aspect, that deserves some further discussion.

The equations take on a simplified form in the basis in which $h$ is diagonal. Let us denote the orbital values as $\epsilon_p$. The operator $\hat{S}$ is diagonal, and we will simply refer to the amplitudes as $s_p$. The amplitude equations and natural occupation numbers then read

$$-\frac{ds_p}{d\beta} = (\epsilon_p - \mu) \left( 1 + \bar{f} s_p - f s_p - \bar{f} \bar{f} s_p^2 \right)$$

$$= (\epsilon_p - \mu) R(s_p) \quad (53)$$

$$R(s) = 1 + \bar{f} s - f s - \bar{f} \bar{f} s^2 \quad (54)$$

$$\frac{dR}{ds} = \bar{f} - f - 2\bar{f} \bar{f} s \quad (55)$$

$$n_p = f + \bar{f} \bar{f} s_p \quad (56)$$

The critical values for $s_p$ are

$$n_p = 0; \quad s_p = -\bar{f}^{-1} \quad (57)$$

$$n_p = 1; \quad s_p = f^{-1} \quad (58)$$

We can see that at these extremal values we have

$$s = -\bar{f}^{-1}: R(s) = 0; \quad \frac{dR}{ds} = 1 \quad (59)$$

$$s = f^{-1}: R(s) = 0; \quad \frac{dR}{ds} = -1 \quad (60)$$

The meaning of these equations is that the rate of change $\frac{ds_p}{d\beta}$ goes to zero as the occupation numbers reach their extremal values. For these extreme values, the value of $(\epsilon_p - \mu)$ will be far from zero, and so the sign of $\frac{ds_p}{d\beta}$ is uniform. As $\beta$ increases the values will approach the extremal values closer. As long as the integration step is not too large, the occupation numbers will fall in the interval [0, 1]. The solution of the equations in the
We define normal ordering and contractions automatically converge to the ground state. The thermal differential equation. The ground state corresponds to the value. Anysuch determinantal statesatisfiesthe zerotemperature, or all occupation numbers take on their extremal values, and $d \theta/d\beta = 0 \quad \forall \beta$. The ground state amplitudes and associated chemical potential can be determined directly from the equations

$$\langle \{ q^+ p \} (h - \mu N) \exp(\delta S) \rangle_{\text{connected}} = 0 \quad (61)$$

$$\sum_p S_{pp} = 0 \quad (62)$$

These conditions, in the diagonal basis, imply $R(s_p) = 0 \quad \forall p$, or all occupation numbers take on their extremal value. Any such determinantal state satisfies the zero temperature equation. The ground state corresponds to the lowest energy solution. The thermal differential equations automatically converge to the ground state. The excited state solutions for the zero-temperature equations are additional solutions associated with the non-linearity of the equations.

In principle, we could present some numerical results here but we learn nothing more than that the results agree exactly with one-electron Fermi-Dirac theory. This is a very satisfying, boring, result that proves the essential validity of the theory.

### 4. General theory for pure bosonic systems

We assume bosonic creation and annihilation operators that satisfy the usual commutation relations

$$\hat{i}^+ \hat{j} = \delta_{ij} \quad (63)$$

We define normal ordering and contractions

$$\langle \{ \hat{i}^+ \hat{j} \} \rangle = f \delta_{ij}; \quad \langle \hat{i}^+ \hat{j} \rangle = \bar{f} \delta_{ij}$$

$$\hat{j}^+ \hat{i} = \{ \hat{j}^+ \hat{i} \} + f \delta_{ij}; \quad \hat{j}^+ = \{ \hat{j}^+ \} + \bar{f} \delta_{ij}$$

$$\hat{f} = 1 + f \quad (64)$$

Within a normal ordered product the operators commute, and the last relation can be derived from the commutation relations. The factor $f$ is as yet not defined. We assume here for simplicity that it is the same for all modes $i$, but the theory is easily generalised.

For definiteness, we might be interested in vibrational problems and the second quantised operators would be associated with dimensionless normal mode coordinates $q_i$ in the usual way, based on an underlying quadratic potential around an equilibrium geometry. We will use a very similar second quantised approach to tackle both thermal properties and time-autocorrelation functions to gain access to spectroscopy.

The Hamiltonian is expressed in second quantisation and can be written in normal order, e.g.

$$\hat{H} = h_0 + \sum_i h_i \{ \hat{i} \} + \sum_i h_{ij} \{ \hat{i}^+ \hat{j} \}$$

$$+ \sum_{ij} h_{ij} \{ \hat{i}^+ \hat{j}^+ \} + \sum_{ij} h_{ij} \{ \hat{i} \hat{j} \} + \cdots$$

$$= h_0 + \sum_{\lambda} h_\lambda \{ \hat{\Omega}_\lambda \} \quad (65)$$

The procedure we use to calculate thermal properties is very similar to the procedure discussed in the previous section. The main difference is that we do not include a constraint on the number of particles, and the use of commutation rather than anticommutation relations, of course. Given the form of the Hamiltonian, we define an operator $\hat{\tilde{S}}(\tau)$ in a similar way

$$\hat{\tilde{S}} = s_0 + \sum_{\lambda} s_\lambda(\tau) \{ \hat{\Omega}_\lambda \} \equiv s_0 + \hat{\tilde{S}} \quad (66)$$

The parameters that define the operator $\hat{\tilde{S}}$ are defined from the differential equation

$$\langle \hat{\Omega}_\mu^+ d\hat{\tilde{S}} \rangle = \frac{1}{k_B \tau^2} \langle \hat{\Omega}_\mu^+ (\hat{H} \{ e^{\tilde{S}} \}) \rangle_{\text{connected}} \quad (67)$$

To evaluate the thermal expectation value of any operator $\hat{O}$, we evaluate

$$\langle \{ \hat{O} \} \rangle = \frac{\langle \{ \hat{O} \{ e^{\tilde{S}} \} \rangle_{\text{connected}} \}}{\{ e^{\tilde{S}} \} \rangle_{\text{connected}}} \quad (68)$$

The quantity $e^{\tilde{S}_0}$ represents the partition function. Please note the use of the (non-constant) operator component $\hat{\tilde{S}}$ in the last equation. We formulate the theory in terms of an integration over temperature $(\tau)$ from $0_+$ to $T$. This means we have to specify the initial value of the amplitudes $s_\lambda(\tau = 0_+)$. In addition, we have to define the contraction $f$. Here the symbol $0_+$ indicates a small finite temperature different from 0. The initial condition for the bosonic theory is a little cumbersome. We cannot (easily)
start from the infinite T limit as the occupation numbers of bosons have no upper limit. Moreover, we cannot start exactly at T = 0, as the initial S-amplitudes solving the ground state would yield vanishing residuals and hence the propagation cannot get started, related to the essential flatness at 0 K: all derivatives of the function $e^{-\beta \omega}$ vanish at $T = 0$. The solution might be to solve for a few excited states that have some population at small T, (e.g. $T = 20$ K). We can calculate the thermal reduced density matrices for this ensemble and extract the corresponding S-amplitudes. We will provide an example based on a general multidimensional displaced harmonic oscillator in Section 6.

If one integrates the equations using temperature as a variable some care will be needed to obtain a stable numerical procedure. The equations of interest are coupled ordinary differential equations that can be expressed as

$$\frac{dS_\lambda}{d\tau} = \frac{1}{k_B \tau^2} R_\lambda(S(\tau))$$  \hspace{1cm} (69)

If we would use a leap frog-type algorithm where we integrate between $\tau_{i-1}$ and $\tau_{i+1}$, we can approximate

$$S_\lambda(\tau_{i+1}) - S_\lambda(\tau_{i-1}) = \int^{\tau_{i+1}}_{\tau_{i-1}} d\tau \frac{1}{k_B \tau^2} R_\lambda(S(\tau))$$

$$S_\lambda(\tau_{i+1}) = S_\lambda(\tau_{i-1}) - \left( \frac{1}{k_B \tau_{i+1}} - \frac{1}{k_B \tau_{i-1}} \right) R_\lambda(S(\tau_{i}))$$  \hspace{1cm} (70)

Here we assume the factor $\frac{1}{\tau^2}$ varies more quickly than $R_\lambda(S(\tau))$. More sophisticated integration schemes may have to be explored. These equations clearly have troubles near $\tau = 0$, indicating once again that the propagation should be started from $\tau_0 = 0_+$ and using a suitable set of initial S-amplitudes.

The theory can also be developed in real time. We would obtain the differential equation

$$i\left\langle \hat{\Omega}_\mu^\dagger \frac{d\hat{S}}{d\tau} \right\rangle = \left\langle \hat{\Omega}_\mu \left( \hat{H} \left\{ e^{\hat{S}(\tau)} \right\} \right) \right\rangle_{\text{connected}}$$  \hspace{1cm} (71)

Taking a Fourier transform of $\hat{S}_0(\tau)$ would yield information on eigenvalues. Again one needs to provide a suitable set of initial amplitudes at $\tau = \tau_0$.

Given the definition of contractions, normal order and Wick’s theorem the equations can also be formulated as operator equations, rather than through a projection. Hence we can write

$$\frac{d\hat{S}}{d\tau} = \frac{1}{k_B \tau^2} \left( \hat{H} \left\{ e^{\hat{S}(\tau)} \right\} \right)_{\text{connected}}$$  \hspace{1cm} (72)

This equation is to be viewed as an equation for the amplitudes, where the left-hand and right-hand amplitudes are equated component by component. Let us note that the notion of connected in this context implies as usual that the expression is written in normal ordering. The same type of alternative viewpoints have been discussed in the context of Coupled Cluster theory for electronic structure theory, and for example, similarity transformed equation of motion coupled cluster is preferably discussed in this fashion (see e.g. [38,39] for pedagogical discussions). However, for single reference theory, the alternate approaches of derivation lead to equivalent equations. The same is true here, as the projection by $\hat{\Omega}_\mu$ simply picks out a unique component and multiplies left and right hand of equation by the same combination of factors $f_i \tilde{f}_i$.

5. Bosonic harmonic oscillator examples in 1d

At this point, the theory appears to be very general but also quite abstract. What would be appropriate definitions of $f$? Can one actually integrate the equations? In the thermal case could one instead use $\beta$ as the variable and start from the high $T$ or $\beta = 0$ limit (or small $\beta$)? These are interesting questions and we will address some of them using exceedingly simple but instructive examples. To illustrate the thermal case, we will look at simple harmonic oscillators, starting with a one-dimensional problem before discussing the general multidimensional problem. For time-dependent problems we will formulate a procedure to calculate time-autocorrelation functions for Franck–Condon spectra based on harmonic oscillators for ground and excited electronic states.

In this section, we will discuss the simple example of a one-dimensional (undisplaced) harmonic oscillator. The equations are derived in detail, and the integration can be done analytically.

$$\hat{H} = \omega \left( \hat{\gamma}_i^+ + \frac{1}{2} \right) = h_0 + \omega \left( \hat{\gamma}_i^+ \right); h_0 = \frac{1}{2} + f ; \omega$$  \hspace{1cm} (73)

Defining the operator $\hat{S}$ in a similar way, we obtain equations

$$\left\langle \left\{ \hat{\gamma}_i^+ \right\} \frac{d\hat{S}}{d\tau} \right\rangle = \frac{1}{k_B \tau^2} \left( \left\{ \hat{\gamma}_i^+ \right\} \left( \hat{H} \left\{ e^{\hat{S}} \right\} \right) \right)_{\text{connected}}$$

$$\frac{dS_0}{d\tau} = \frac{1}{k_B \tau^2} \left( \left\{ \hat{H} \left\{ e^{\hat{S}} \right\} \right\} \right)_{\text{connected}}$$  \hspace{1cm} (74)
which can be evaluated as
\[
\begin{align*}
\frac{\partial \rho}{\partial \tau} &= \frac{1}{k_B T^2} \omega (\rho f + f \rho t) + \rho f \frac{\partial f}{\partial \tau} \\
\frac{\partial s_0}{\partial \tau} &= \frac{1}{k_B T^2} (\rho f + f \rho t)
\end{align*}
\]
(75)

If we use that the operator \( \hat{S} \) is always contracted in the same manner we can substitute \( t = \rho f \) (we also could have done this in the section on the fermionic case, see later) and obtain
\[
\begin{align*}
\frac{dt}{d\tau} &= \frac{1}{k_B T^2} \omega (f \hat{f} + (f + \hat{f}) t + t^2) \\
&= \frac{1}{k_B T^2} \omega (t + f) (t + \hat{f}) \\
\frac{ds_0}{d\tau} &= \frac{1}{k_B T^2} \omega \left( \frac{1}{2} f + t \right)
\end{align*}
\]
(76)

The differential equation for \( s \) can be solved analytically
\[
\begin{align*}
\frac{dt}{(t + f)(t + \hat{f})} &= \frac{1}{k_B T^2} \omega d\tau \\
\frac{dt}{(t + f)} - \frac{dt}{(t + \hat{f})} &= \frac{1}{k_B T^2} \omega d\tau
\end{align*}
\]
(77)

This equation can be integrated, replacing \( \tau \) by \( T \) and introducing an integration constant \( C \), which we set to zero quickly, using hindsight
\[
\begin{align*}
(t + f) &= e^{-\frac{\omega}{k_B T^2}} + C \\
(t + f) &= e^{-\frac{\omega}{k_B T^2}} (t + 1 + f) \\
(t + f)(1 - e^{-\frac{\omega}{k_B T^2}}) &= e^{-\frac{\omega}{k_B T^2}} \\
(t + f) &= \frac{e^{\frac{\omega}{k_B T^2}} - 1}{e^{\frac{\omega}{k_B T^2}} - 1} \\
(t + f) &= \frac{1}{e^{\frac{\omega}{k_B T^2}} - 1}
\end{align*}
\]
(78)

The partition function can be obtained by integrating the corresponding equation for \( \frac{d\rho}{d\tau} \). The expectation value of any operator \( \hat{O} = \hat{O}^{\dagger} \hat{O} \) is evaluated as
\[
\left\langle \hat{O} \right\rangle = \left\langle \hat{O} \left| \hat{s} \right\rangle \right\rangle_{\text{connected}} = \hat{O} = \hat{O}(f + \hat{f}) = \rho(t + f) = e^{\frac{\omega}{k_B T^2}} - 1
\]
(79)

This is the expected result, and \( t + f \) represents the thermal density matrix. The above equations indicate that the contraction \( f \) is essentially arbitrary. The initial value for \( t \) can be taken to be \( -f \), while the initial value for \( s_0 = -\frac{1}{2} \omega/(k_B T) \), related to the ground state energy. While the solutions for the problem can be obtained analytically, they also indicate that the initial conditions for the bosonic problem are not trivial, and at low \( T \) the amplitudes diverge or grow very slowly due to the behaviour of the Boltzmann-factor. These issues will be addressed in subsequent sections. The above simple calculation indicates that we can expect the essential theory to work as advertised. As discussed more extensively below one can anticipate exact results for any Hamiltonian that is harmonic (or even more general: at most quadratic in annihilation/creation operators). Presumably the Hamiltonian does not even have to be Hermitean. As long as the parameters defining the Hamiltonian are real, the \( t \)-amplitudes and reduced density matrices are real too.

Let us re-emphasize that the essential result is independent of the factor \( f \). The value of \( t \) depends on \( f \), but the physically relevant quantity is \( n = f + t \), the reduced density matrix (or population in the 1-d case) is independent of \( f \). However, if one assumes (perhaps most naturally) that \( f = 0 \), using the traditional ground state of the harmonic oscillator to define normal ordering, some unexpected issues do arise. If we look at the equation for amplitudes \( s \), Equation (75) and divide first by \( f \hat{f} \) on both sides, one obtains, setting \( f = 0 \) afterwards,
\[
\frac{ds}{d\tau} = \frac{1}{k_B T^2} \omega (1 + (f + \hat{f}) s + f \hat{f} s^2) = \frac{1}{k_B T^2} \omega (1 + s)
\]
(80)

The right-hand side is now linear in \( s \) and has as a solution the Boltzmann distribution \( 1 + s(t) = e^{\frac{\omega}{k_B T^2}} \). Incidentally, the exact same equation is obtained if one uses the many-body formulation. Clearly this result, setting \( f = 0 \) is not correct. Rather one would have to solve the equation for non-zero \( f \) and then take \( \lim \omega f \to 0 \) in the end result. This result would be correct, and the result are identical to before if one substitutes \( t = f \hat{f} \). However, if one examines the equations for \( t \), one can take the limit before integrating, yielding
\[
\frac{dt}{d\tau} = \frac{1}{k_B T^2} \omega (\hat{f} t + t^2) = \frac{1}{k_B T^2} \omega (1 + t^2)
\]
(81)

This differential equation has the solution
\[
t(t) = \frac{1}{e^{\frac{\omega}{k_B T^2}} - 1}
\]
which is correct. The situation is delicate because \( f \hat{f} s = t \) is finite, even in the limit \( f \to 0 \). In summary, to derive
the equations we need to use \( \hat{S} \). In the case that we use \( f \neq 0 \) one can use either many-body or projected equations. However, when we use \( f = 0 \), only the projected equations will work and only if we first make the substitution \( \sum_{s} f s = t \). It might seem most pertinent to avoid the case \( f = 0 \). However, in the case of solving the Franck–Condon problem, the use of \( f = 0 \) is most convenient. The procedure of deriving equations using \( s \) and then redefining variables to introduce \( t \) yields the simplest equations in practice. Let us note that the case \( f = 0 \) is very natural as it corresponds to a legitimate normal ordering in which annihilation operators are always to the left of creation operators. It is the normal ordering used for example in work by Facheaux and Hirata, [40–42], and is commonly used in conjunction with second quantisation for vibrational problems. The above analysis shows it may actually (rather easily) lead to erroneous equations, at least in the thermal case.

6. Explicit amplitude equations for thermal equations for Bosons in a singles and doubles approximation

Let us next discuss the general problem for the multidimensional Harmonic oscillator addressing a numerical way to find suitable initial conditions for the amplitudes. The results are compared numerically with sum over states results and we will again achieve the satisfying, but boring, result that everything works as advertised.

The harmonic oscillator Hamiltonian expressed in normal order (assuming some \( f \)) is given by

\[
\hat{H} = h_0 + \sum_{i} h_i \hat{a}_{\hat{i}}^{\dagger} + \sum_{i} h_i \hat{a}_{\hat{i}} + \sum_{ij} h_{ij} \{ \hat{a}_{\hat{i}}^{\dagger} \hat{a}_{\hat{j}} \}
\]

where \( h_0 = E_0 + f \sum_{i} \omega_i \), where \( E_0 \) is the ground state energy (including the zero point energy) of the harmonic oscillator. Likewise the operator \( \hat{S} \) is parameterised as

\[
\hat{S} = s_0 + \sum_{i} s_i \hat{a}_{\hat{i}}^{\dagger} + \sum_{i} s_i \hat{a}_{\hat{i}} + \sum_{ij} s_{ij} \{ \hat{a}_{\hat{i}}^{\dagger} \hat{a}_{\hat{j}} \}
\]

The equations are derived by evaluating the following equations through an application of Wick’s theorem and keeping only fully contracted and connected terms

\[
-\left\langle \frac{d\hat{S}}{d\beta} \right\rangle = \left\langle \hat{S}^{\dagger} \left\langle \hat{H} \left| e^{\hat{S}} \right\rangle \right\rangle_{\text{connected}} \right\rangle
\]

Here the operator manifold is given by

\[
\hat{\Omega}_k \equiv \left\{ 1, \hat{a}_i, \hat{a}_i^{\dagger}, \hat{a}_i \hat{a}_j, \hat{a}_i^{\dagger} \hat{a}_j, \left\{ \hat{a}_i^{\dagger}, \hat{a}_j \right\} \right\}
\]

Since the expressions are always fully contracted, each \( s \) amplitude always carries the corresponding factors of \( f, \tilde{f} \). In addition the operators on the Hamiltonian that are contracted with the external projection operators carry corresponding factors \( f \) and \( \tilde{f} \). We replace the \( s \)-amplitudes by \( t \)-amplitudes using the completely systematic substitutions \( fs \rightleftharpoons t_i, \tilde{f}s \rightleftharpoons t^i, f^2 s^2 \rightleftharpoons t^i_j, \tilde{f}^2 s^2 \rightleftharpoons t^l_i \). An external creation operator (upper index) on \( h \) retains a factor \( \tilde{f} \), while lower external indices on \( h \) carry a factor \( f \) from the original evaluation of Wick’s theorem. These rules (that are easy to prove) facilitate the evaluation of terms. The detailed results are given below. Note that we use Einstein summation to express the sums over the labels of the tensors. We obtain the following.

Zero-order equation:

\[
-\frac{d s_0}{d\beta} = h_0 + h_i t_k^i + h_k t^i_k + h_k t^k
\]

\[
+ \frac{1}{2} h_{kl} t^i_l + \frac{1}{2} h_{kl} t^k_l + \frac{1}{2} h_{kl} t^i_l t^k_l + \frac{1}{2} h_{kl} t^k_l t^i_l
\]

Single equations:

\[
-\frac{d f^i}{d\beta} = \tilde{f} h^i + h^i f^k + \tilde{f} h_k t^i_k + h^i_t_k t^i + h^i t_k t^i + h^i t_k t^i_l + \frac{1}{2} h_{kl} t^i_l
\]

Double equations:

\[
-\frac{d f^i_j}{d\beta} = \tilde{f} h^i_j + h^i_j f^k + \tilde{f} h_k t^i_j + h^i_j t^k + h^i_j t^k_j + h^i_j t^k_l + \frac{1}{2} h_{kl} t^i_j t^k
\]

The thermal quantities could be determined through the \( \beta \) or imaginary time integration over the amplitudes. The
primary remaining issue is the determination of initial conditions. If we define the thermal density matrices at a particular value of $\beta$, as well as the partition function $Z = \sum_v e^{-\beta E_v}$ using a small sum over states expression, valid at low temperature (large $\beta$)

$$d_\nu = \frac{1}{Z} \sum_v \langle \Psi, \hat{S}_\nu^\dagger | \Psi_v \rangle e^{-\beta E_v} \quad (92)$$

One can extract the initial conditions for the propagation (valid for any $f$).

$$s_0 = \ln(Z)$$
$$t_i = d_i$$
$$t_i = d_i$$
$$t_i^j = d_i^j - t_i^j$$
$$t_i^j = d_i^j - t_i^j$$

Upon integration, thermal properties can be obtained. Most notably, the partition function $Z$ and Helmholtz Free energy $A = -k_B T \ln Z$

$$Z(\beta) = \text{Tr}(D) = e^{s_0(\beta)} \quad (94)$$

as well as the thermal internal energy $U$ and hence entropy $(TS = U - A)$

$$U = \text{Tr}(\hat{H} \hat{D}) = (\hat{H} e^S)_{\text{f.c.}} = -\frac{ds_0}{d\beta} \quad (95)$$

The heat capacity can be obtained using differentiation of $U$, if desired. Also thermal density matrices and cumulants are easily obtained using the (inverse) of the formulas above, relating density matrices and $t$-amplitudes.

Let us emphasise one more aspect of interest. For quadratic Hamiltonians (containing up to two annihilation and/or creation operators), these propagation equations are exact (up to numerical precision of the integration, and depending on the validity of initial conditions). The reason is that the ansatz is in principle exact, but using up to two-body amplitudes the three-body results are zero as $(\hat{H}(e^S))_{\text{connected}}$ cannot lead to three-body terms under these conditions.

Of course, by itself these results are not very interesting. The approach is expected to be a good approximation also for more complicated Hamiltonians. The main drawback is that the initialisation of the thermal density matrices would currently require an external source for a few low lying states. It is to be noted that low-lying states are generally more easily obtained than higher lying states, e.g. harmonic oscillator may be sufficiently accurate, or a perturbative approach can be adopted to include anharmonic effects. It is interesting that using the thermal NOE approach one recovers the complete, basis set free, partition function even when the starting point only includes a few states that have significant thermal population at low $T$. This latter aspect is not obvious form the theoretical considerations alone, and so it will be good to provide evidence through a numerical example.

We implemented the scheme described above and tested the scheme for a general (non-diagonal) harmonic oscillator Hamiltonian with two vibrational modes (corresponding to vibrational frequencies of $300$ and $360$ cm$^{-1}$). Using a small number of states (2 or 3 for comparison), obtained from a finite basis full CI calculation, we extracted the thermal densities at the initial temperature of $60K$ and the propagated the thermal NOE equations up to $500$ K. The results for the partition function $Z$ and the internal energy $U$ are compared to the complete sum over states finite basis set calculation. It is easily seen from Figure 1 that the result are indeed numerically very accurate if the initial set of states is large enough. Including the three lowest vibrational states suffices to obtain the full partition function, while including two states is clearly not enough. At higher $T$, we anticipate the (basis set free) NOE result to remain accurate while the full CI result will (eventually) suffer from the finite basis set used.

7. Simulation of harmonic Franck–Condon spectra

It is clear that solving the thermal differential equations is not the preferred way for solving the simple pedagogical problems discussed thus far (one-electron problems for Fermions, harmonic oscillator for Bosons). Let us turn next to a problem that might be of actual interest to the quantum chemistry community: the simulation of harmonic Franck–Condon spectra using time-autocorrelation functions using the present NOE approach.

The math of time-dependent formalism resembles the thermal density matrix formalism but with different goals. In this case, our goal is to solve the time-dependent Schrödinger equation (TDSE) by simply switching the imaginary time integration in the thermal case to real time integration. We will here demonstrate the theory using the simple example of the calculation of a vibronic absorption spectra in the vertical Hessian harmonic Franck–Condon approximation. We assume the initial ground state wave function is described by the ground state of a harmonic oscillator, while the electronic transition moments are constant. The second quantised operators are the dimensionless normal modes of the
Figure 1. Comparison of thermal NOE and sum over states approach to thermal properties for 2d harmonic oscillator. The thermal NOE is initialised using the thermal density for either two states (dashed line) or 3 states (solid line). The latter matches the sum over states results. (a) Partition function and (b) internal energy.

ground state and we use as a vacuum state for Wick’s theorem the corresponding ground vibrational state \( |0\rangle \), such that the only non-zero contractions are given by

\[
\overline{ii} = \langle 0\,\overline{ii}\,|0\rangle = \bar{f} = 1; \tag{96}
\]

while \( f = \overline{i\,i} = 0 \). To obtain the spectrum we calculate the autocorrelation function based on the excited state harmonic Hamiltonian, shifted by the ground state energy (vertical excitation energy plus ground-state zero-point frequency). This excited state Hamiltonian is represented as usual

\[
\hat{H} = h_0 + \sum_i h_i \hat{a}_i^{\dagger} + \sum_i h'_i \hat{a}_i + \sum_{ij} h_{ij} \{\hat{a}_i^{\dagger} \hat{a}_j\} + \frac{1}{2} \sum_{ij} h'_{ij} \hat{a}_i^{\dagger} \hat{a}_j + \frac{1}{2} \sum_{ij} h_{ij} \hat{a}_i \hat{a}_j \tag{97}
\]

The TDSE we wish to solve is given by

\[
i \frac{d}{d\tau} | \Psi(\tau) \rangle = \hat{H} | \Psi(\tau) \rangle \tag{98}
\]
If we apply the normal-ordered exponential ansatz to parameterise the time dependent wavefunction, we have

\[ |\Psi(\tau)\rangle = e^{\hat{T} \tau} |\Psi(0)\rangle = e^{\hat{T} \tau} |0\rangle \]

(99)

Due to the normal-ordered exponential and the fact that \( \hat{\Omega}|0\rangle = 0 \), it follows that the only non-trivial contributions in \( \hat{S} \) contain creation operators only and such operators all commute, such that we do not need the normal ordering but can parameterise the wave function as

\[ |\Psi(\tau)\rangle = e^{\hat{T} \tau} |0\rangle \]

(100)

We can obtain suitable working equations by substituting the ansatz into the TDSE, multiplying by \( e^{-\hat{T} \tau} \) and projecting again \( |0\rangle \Omega \),

\[ i\langle 0|\hat{\Omega}_\lambda \frac{d}{d\tau} |0\rangle = \langle 0|\hat{\Omega}_\lambda e^{-\hat{T} \tau} \hat{H} e^{\hat{T} \tau} |0\rangle \]

\[ = \langle 0|\hat{\Omega}_\lambda \hat{H}_c \rangle_{\text{connected}} |0\rangle \]

(101)

It can be seen that in this case the normal ordered ansatz reduces to traditional Coupled Cluster equations for vibrational problems. Using the projection manifold \( \hat{\Omega}_\lambda = \{1, \hat{t}, \hat{t}_j\} \), we obtain CC amplitude equations as follows:

\[
\begin{align*}
\frac{i ds_0}{d\tau} &= h_0 + h_k t_k^l + h_k t_l^k + h_t^k + h^k t_k \\
&\quad + \frac{1}{2} h_k t_l^k + \frac{1}{2} h_k t_l^l + \frac{1}{2} h_t^l t_k^l + \frac{1}{2} h^l t_k^l \\
&\text{connected} = \frac{t_i}{d\tau} = \hat{f} h_i + h^k t_k^i + \hat{f} h_k t_i^k + h_i t_k^l + h^k t_i^l + h_i t_k^l + h^l t_i^l + h_i t_k^l + h^l t_i^l \\
&\quad + h_k t_i^l + h_t^i t_k^l + h^k t_i^l + h_i t_k^l + h^l t_i^l + h_i t_k^l + h^l t_i^l \\
&\quad + \hat{f} h_k t_i^l + \hat{f} h_i t_k^l + \hat{f} h_k t_i^l + \hat{f} h_i t_k^l + \hat{f} h_i t_k^l + \hat{f} h_i t_k^l + \hat{f} h_i t_k^l \\
&\quad + \hat{f} h_i t_k^l + \hat{f} h_i t_k^l + \hat{f} h_i t_k^l + \hat{f} h_i t_k^l + \hat{f} h_i t_k^l \\
&\quad (102)
\end{align*}
\]

(103)

(104)

At time \( \tau = 0 \) all cluster amplitudes are zero and it is a simple matter to propagate the equations in time. The time-autocorrelation function \( ACF(\tau) \) is given by

\[ ACF(\tau) = \langle \Psi(0) | \Psi(\tau) \rangle = e^{\beta \mu} \]

(105)

One can obtain zero temperature Harmonic Franck–Condon spectra by taking the Fourier transform of \( ACF(\tau) \) and multiplying by the square of the electronic transition moment. In the literature, there are a large number of methods available to calculate harmonic Franck-Condon spectra, including hot bands and Hertzberg–Teller effects. The above time-dependent CC approach yields numerically exact results for the simplest type of spectra and is perhaps the simplest approach among them. It appears possible to generalise the approach to (i) more complicated surfaces, (ii) hot bands, (iii) Hertzberg–Teller effects. It is also possible to apply this approach to more general potential energy surfaces, expressed as a Taylor series expansion. In that case, one has to keep in mind that the approach is no longer numerically exact and in particular the evolution is not unitary and also energy is not conserved. One may have to modify parameterisations to preserve the norm and energy. In our group, we are aiming to generalise the approach to multi-state vibronic models including non-adiabatic coupling.

As an example of a harmonic FC problem, we simulated the photo-electron spectrum of the formaldehyde molecule, comparing the CC result to an MCTDH calculation in a large single particle basis set. The excited state Hamiltonian was obtained many years ago through an IP-EOMCC calculation. Here our goal is to show such calculations can indeed be done routinely, and they take mere minutes (or seconds) of computation time. The number of parameters (complex \( t_0, t_i^j, t_l^i \)) is similar to a full (exact) Gaussian wave packet calculation, which require, norm and phase, real position and momentum and width parameters (Figure 2).

8. Further reflections

The above formulation of the calculation of thermal properties or time-dependent auto-correlation functions from solving coupled differential equations shows great unity between the approaches discussed for electronic structure theory and for pure vibrational problems. The basic difference between approaches discussed refers to the use of anti-commutation relations for Fermions, and commutation relations for Bosonic problems, and the associated relations \( \hat{f} = 1 \pm \hat{f} \). Moreover, in electronic problems, we have introduced the chemical potential \( \mu \) to ensure the average electron count. Finally, in electronic structure problems, we have found it convenient to start from the infinite temperature limit (\( \beta = 0 \)), while for Bosonic problems, the more convenient starting point is \( T = 0 \), and solving for the ground and low-lying excited states first, and extract initial values for the amplitudes from the associated thermal reduced density matrices. We have seen in the bosonic case that if one uses the (natural) value \( f = 0 \), using the true vacuum, the equations
should be phrased in terms of the ‘renormalised’ amplitudes \( t \). Let us collect the relevant equations here, both in terms of \( s \) and \( t \) amplitudes for the simplest type of problem, to show the basic unity.

**Bosons**, including \( s \to t \) substitution:

\[
\begin{align*}
\frac{df}{d\tau} &= \frac{\omega}{k_B \tau^2} \bar{f} \bar{f} (1 + (f + \bar{f})s + \bar{f} \bar{f} s^2) \\
\frac{d\bar{f}}{d\tau} &= \frac{\omega}{k_B \tau^2} (f \bar{f} + (f + \bar{f})t + t^2) \\
\lim_{t \to 0} f &= \frac{dt}{d\tau} = \frac{\omega}{k_B \tau^2} (t + t^2)
\end{align*}
\]

(106)

With bosonic solution (Bose-Einstein distribution)

\[
n(t) = (t + f)(\tau) = \frac{1}{e^{\frac{\mu}{k_B \tau}} - 1}
\]

(107)

**Fermions**, including \( s \to t \) substitution

\[
\begin{align*}
\frac{df}{d\tau} &= \frac{\epsilon_i - \mu}{k_B \tau^2} \bar{f} \bar{f} (1 + (f + \bar{f})s_i - \bar{f} \bar{f} s_i^2) \\
\frac{d\bar{f}}{d\tau} &= \frac{\epsilon_i - \mu}{k_B \tau^2} (f \bar{f} + (f + \bar{f})t_i - t_i^2) \\
\lim_{t \to 0} f &= \frac{dt_i}{d\tau} = \frac{\epsilon_i - \mu}{k_B \tau^2} (t_i - t_i^2)
\end{align*}
\]

(108)

With Fermionic solution (Fermi-Dirac distribution)

\[
n_i(t) = (t_i + f)(\tau) = \frac{1}{e^{\frac{\epsilon_i - \mu}{k_B \tau}} + 1}
\]

(109)

Boltzman \((f = 0)\) limit of Bosonic equation without \( s \to t \) substitution:

\[
\frac{df}{d\tau} = \frac{\omega}{k_B \tau^2} f \bar{f} (1 + (f + \bar{f})s + \bar{f} \bar{f} s^2) \\
\frac{d\bar{f}}{d\tau} = \frac{\omega}{k_B \tau^2} (f \bar{f} + (f + \bar{f})t + t^2) \\
\lim f \to 0 : \frac{d\bar{f}}{d\tau} = \frac{\omega}{k_B \tau^2} (1 + s)
\]

(110)

With solution (Boltzman distribution)

\[
n(\tau) = (1 + s)(\tau) = e^{\frac{\mu}{k_B \tau}}
\]

(111)

The same Boltmann distribution is obtained if one uses the same \( f = 0 \), no \( s \to t \) substitution in the Fermionic case. The Boltmann distribution (linear equation) is also obtained if one uses a Hamiltonian matrix (no second quantisation).

All of these equations have the fundamental numerical problem that if they are initiated by first obtaining the ground state solution, and subsequently a first-order scheme is used to numerically integrate, the solution is dead as the derivatives at \( T = 0 \) are all equal to zero, and the amplitudes from a first-order numerical integration scheme will remain zero. As was shown before the diagonal one-body problems can easily be solved analytically, but numerical approaches, needed in practice, may suffer.

We think it is insightful to obtain the three fundamental statistics in Physics related to these simple linear or quadratic differential equations, where the difference in statics relates to the factor of the quadratic term. A factor of \(+1\) yields Bose-Einstein Statistics, A factor of \(-1\) yields...
Fermi-Dirac statistics, while a factor of 0 yields Boltzmann statistics. Most surprisingly is that we are not aware of this discussion in the literature. It seems likely that it has been discussed before but we authors are not aware of it. The same notion is of course there if we write the general formula \( n^p_\alpha (\tau) = (e^{\beta \tau} + \alpha)^{-1} \), where \( \alpha = \pm 1 \), 0 yields the various statistics. The novelty is the existence of the differential equations, which allows the generalisation to more complicated Hamiltonians.

**8.1. Comparison of thermal NOE and coupled cluster in the limit of zero temperature**

There is substantial room for confusion in regards to the extreme values of \( f, f = 0, 1 \) and the zero temperature limit of the theory for the Fermionic problem. Let us try to lay our finger on the critical issues. To make the comparison we have to first allow for the fact that the contractions can become orbital specific and if we introduce factors \( f_p, f_p = 1 - f_p \), the detailed one-electron equations read, in terms of \( s \)-amplitudes denoted as \( S = \sum_{p,q} s_p^q \) here

\[
- \frac{d s_p^q}{d \beta} = f_p \sum_{r} h_{p}^{r} s_{p}^{r} - \mu f_p \left( \delta_q^p + f_p s_p^q - f_q s_q^p \right) 
- f_q \left( \sum_{r} s_p^r \right) 
- \frac{d s_0}{d \beta} = h_0 + \sum_{p,q} \frac{d s_p^q}{d \beta} \left( \beta \right) - \mu n_{el} 
\]

As before we make the substitution \( f_p \sum_{q} s_p^q \rightarrow t_p^q \) and we obtain

\[
- \frac{d t_p^q}{d \beta} = f_p h_{p}^{q} t_{p}^{q} + \sum_{r} h_{p}^{r} t_{p}^{r} - \mu \left( f_p \sum_{q} h_{p}^{q} t_{p}^{q} - f_q t_{q}^{p} - \sum_{r} t_{r}^{q} h_{r}^{q} \right) 
- \frac{d s_0}{d \beta} = h_0 + \sum_{p,q} h_{p}^{q} t_{p}^{q} \left( \beta \right) - \mu n_{el} 
\]

Let us note one more substitution that completely eliminates the factors \( f_p, f_p \), namely \( d_q^p = f_p \delta_q^p + t_p^q, \bar{d}_q^p = \delta_q^p - d_q^p = \bar{f}_p \delta_q^p - t_p^q \), and write the equations as

\[
- \frac{d_0^p}{d \beta} = h_0 + \sum_{p,q} \frac{d_0^p}{d \beta} (\beta) - \mu n_{el} 
\]

We think these equations are perhaps most fundamental as the arbitrary dependency on the definition of \( f_p \) is eliminated. This final identification of the singles amplitudes with the reduced one-particle density matrix is also how the relation to the connected contracted Schrödinger equation [37] can be made in the general.

To arrive at Coupled Cluster at zero temperature we return to the previous Equation (114), we now partition the orbitals into occupied, \( i, j_k \), having \( f_i = 1, f_j = 0 \) and virtual, \( a, b, c \) having \( f_a = 0, f_b = 1 \). We are not using subtle reasoning that certain \( s \)-amplitudes might go to \( \infty \) at \( T = 0 \), but simply argue that with this choice of \( f_p \) the only surviving amplitudes are excitation operators, \( \tilde{T} = \sum_{a,i} t_{a}^{i} \hat{\alpha}^{\dagger} i \) and replacing indices accordingly, it is easy to show that the only surviving terms are as follows

\[
- \frac{d t_i^q}{d \beta} = h_i^q + \sum_{c} t_{c}^{i} - \mu \left( t_i^q \right) 
- \frac{d s_0}{d \beta} = h_0 + \sum_{a,i} h_{i}^{a} t_{i}^{a} \left( \beta \right) - \mu n_{el} 
\]

Not surprisingly, the chemical potential does not play a role since \( \tilde{T} \) only excites and preserves the number of electrons. Setting the derivative equal to zero, these equations are exactly the single reference CC equations that would yield the correct ground state. It is easy to analyse the thermal energy in the case that the Hamiltonian is (block)-diagonal such that \( h_{i}^{a} = 0 \). We would find \( h_{i}^{a} + t_{i}^{a} \), which would be the ground state energy in that case and this is clearly incorrect at finite temperature. It follows this theory is only applicable at zero temperature, and there it agrees with the thermal NOE equation for the energy. Even at zero \( T \), the density matrices are completely different (to such an extent that one does not have density matrices in CC, only excitation amplitudes).

We can make some pertinent observations to address confusing aspects in the literature (speaking in general terms).

(1) It is perfectly valid to integrate the equations starting from finite (non-extremal) \( f_p \) and adjusting the \( \beta = 0 \) limit to have equal populations \( n_p = f_p + t_p^p = \frac{n_p^e}{M} \). These equations would yield the correct (Hermitean) reduced density matrix \( d_q^p = f_p \delta_q^p + t_p^q \) that are independent of \( f_p \), even as one would approach extremal values.
(2) Setting the contraction factors $f_p$ to 1 for some nominally occupied orbitals and to zero for nominally virtual orbitals completely changes the character of the equations. It is impossible to extract the thermal density matrices from the excitation coefficients $t_{\mu}^\alpha$. One would have to solve some response equations in addition.

(3) At zero temperature, both approaches yield correct results for the energy, but the solutions for the $t$–amplitudes are different.

(4) One could develop a perturbation theory for one-electron problems using either approach as a starting point. We think these perturbation theories would be different, although the ground state energy would be correct for either approach, and the resulting energies should be the same.

(5) The discussion is essentially the same for interacting systems. The thermal NOE approach is expected to yield different limits in the zero temperature limit than single reference Coupled Cluster Theory (both approximations). In fact we know from our unpublished work that the zero temperature limit from the thermal NOE approach is the connected cumulant approach to the contracted Schrödinger equation discussed almost two decades ago [37]. Unfortunately, this approach was abandoned as it appears to have major issues with $N$–representability. Initial investigations in our group seem to indicate that thermal NOE has similar issues. Let us also mention that thermal NOE appears to be very similar to the approaches suggested by White and Chan [23] or Mukherjee and coworkers [19–21], except for numerical convergence strategies, and (perhaps) the use of $\beta$–dependent contractions. Many of the subtleties of these methods can be studied using one-electron Hamiltonians for which they are potentially exact. It would be more interesting if they are not exact in that limit perhaps.

Nearing the end of this story, we can make a comparison to other non-perturbative approaches developed in the literature that invariably invoke the interaction picture. There are very significant similarities between these approaches and our thermal NOE approach but also some significant differences.

### 8.2. Interaction picture starting point

In this section, we will adapt a description of the interaction picture approach that allows us to make easy comparisons to our current approach. Following the literature we define $\hat{K} = \hat{H} - \mu \hat{N}$ and a corresponding zeroth-order $\hat{K}_0 = \hat{H}_0 - \mu_0 \hat{N}$. We note that in general $\mu$ is not a constant but varies with $\tau$. Consider the following definition of the density matrix in the interaction picture

$$D_I(\tau) = e^{\hat{K}_0 \tau} e^{-\hat{K} \tau} e^{-\hat{K}_0 \tau} D_0$$  \hspace{1cm} (119)

It is easy to see that $Z = \text{Tr}(D_I(\tau))$ as $D_0$, the density matrix at $\tau = 0$, is a multiple of the identity matrix. To evaluate expectation values, operators have to be written in the interaction picture too

$$\frac{1}{Z} \text{Tr}(A_I(\tau) D_I(\tau)) = \frac{1}{Z} \text{Tr}(e^{\hat{K}_0 \tau} A e^{-\hat{K}_0 \tau} e^{\hat{K} \tau} e^{-\hat{K}_0 \tau} D_0)$$

$$= \frac{1}{Z} \text{Tr}(A e^{-\hat{K}_0} D_0) = A(\tau)$$  \hspace{1cm} (120)

These equations hold for all values of $\tau$. The equation of motion for the density matrix is given by

$$-\frac{dD_I(\tau)}{d\tau} = -\hat{K}_0 D_I(\tau) + e^{\hat{K}_0 \tau} \hat{K} e^{-\hat{K}_0 \tau} e^{-\hat{K}_0 \tau} D_0$$

$$+ D_I(\tau) \hat{K}_0$$

$$= [-\hat{K}_0 + e^{\hat{K}_0 \tau} \hat{K} e^{-\hat{K}_0 \tau}] D_I(\tau) + D_I(\tau) \hat{K}_0$$  \hspace{1cm} (121)

We can now define $\hat{V} = \hat{K} - \hat{K}_0$ and $V_I(\tau) = e^{\hat{K}_0 \tau} \hat{V} e^{-\hat{K}_0 \tau}$ to obtain the equation of motion in the interaction picture.

$$-\frac{dD_I}{d\tau} = -\hat{K}_0 D_I + e^{\hat{K}_0 \tau} \hat{K} e^{-\hat{K}_0 \tau} D_I + D_I \hat{K}_0$$

$$= \hat{V}_I(\tau) D_I + D_I \hat{K}_0$$  \hspace{1cm} (122)

If we parameterise $D_I = \{e^{\hat{S}}\} e^{-\hat{K}_0 \tau} D_0$, we find as the derivative

$$-\frac{dD_I}{d\tau} = -\left\{ \frac{d\hat{S}}{d\tau} e^{\hat{S}} \right\} e^{-\hat{K}_0 \tau} D_0 + D_I \hat{K}_0$$  \hspace{1cm} (123)

Equating the derivatives and defining $D_0(\tau) = e^{-\hat{K}_0 \tau} D_0$, we observe that the last term cancels and we obtain a differential equation for $\hat{S}$

$$-\left\{ \frac{d\hat{S}}{d\tau} e^{\hat{S}} \right\} D_0(\tau) = \hat{V}_I(\tau) \left\{ e^{\hat{S}} \right\} D_0(\tau)$$  \hspace{1cm} (124)

or in the connected form

$$-\left\{ \frac{d\hat{S}}{d\tau} e^{\hat{S}} \right\} D_0(\tau) = \left[ \hat{V}_I(\tau) \left\{ e^{\hat{S}} \right\} \right]_{\text{Connected}} D_0(\tau)$$  \hspace{1cm} (125)

One obtains correct results from a single propagation, using a normal ordering associated with $D_0(\tau)$, which
explicitly depends on \( \tau \). Importantly, the above derivation shows there are no additional \( \tau \) derivatives associated with the changing contractions or zeroth-order density matrix, due to the cancellation of the respective \( D_I K_0 \) term (for fixed \( \tilde{H}_0, \mu_0 \) at least). The normal ordering is defined with respect to \( D_0(\tau) \), hence the contractions have to be defined as \( f_p = \text{Tr}(\hat{p}^\dagger \hat{p} D_0(\tau)) = n_p(\tau) \). The amplitude equations are defined as

\[
- \text{Tr} \left( \hat{\Omega}_2 \frac{d\hat{S}}{d\tau} D_0(\tau) \right) = \text{Tr}(\hat{\Omega}_2 \left[ V_I(\tau) \left\{ e^{\hat{S}(\tau)} \right\} \right]_{\text{connected}} D_0(\tau) )
\]  

Using the notation \( \hat{S} = S_0 + \hat{S} \), the partition function is given by \( Z = e^{\hat{S}(\tau)} \), while the thermal reduced density matrices are obtained from

\[
d_s(\tau) = \text{Tr}(e^{\tau \hat{K}_0} \hat{\Omega}_2 e^{-\tau \hat{K}_0} \left\{ e^{\hat{S}(\tau)} \right\} D_0(\tau))
\]  

All these equations can be evaluated as before, and we can also substitute amplitudes \( T \), rather than \( S \), which include the contraction coefficients. This is the approach adopted in [23], (including private communications) although we note that the derivation of these equations is less clear and deduced from Feynman diagrams. In both the interaction picture and in the thermal NOE approach a single equation is propagated and it has physical meaning for all temperatures. There is a substantial difference in the propagation, as in thermal NOE, we use the full Hamiltonian to propagate and using (essentially) arbitrary contractions, while in the interaction picture one uses the \( \tau \)-dependent contractions and \( V_I(\tau) \). It may be that the equations in the interaction picture require fewer \( \tau \) steps, or one may use an integral equation in the interaction picture. It is unlikely that for thermal problems this yields many advantages. The zero temperature limit uses occupation numbers 0,1 in the interaction picture and would yield CC theory, not the cumulant based CSE theory. That is a singular point, however, as discussed before.

There is an alternative formulation which can provide more insight in this work and which one might refer to as a static interaction picture. Consider the following definition of the density matrix in this modified interaction picture

\[
D_I(\tau; \beta) = e^{\hat{K}_0 \beta} e^{-\hat{K}_0} D_0
\]  

The notation is meant to imply that \( D_I \) is a function of \( \tau \) and parametrically depends on a fixed value of \( \beta \). Again \( Z(\tau) = \text{Tr}(D_I(\tau; \beta)) \), while expectation values can be obtained from \( A(\tau) = \frac{1}{2} \text{Tr}(A_I(\beta) D_I(\tau; \beta)) \). These equations hold for all values of \( \tau \) as before. Moreover, the (exact) results for the physically relevant quantities are independent of \( \beta \). The equation of motion for the density matrix is given by

\[
- \frac{dD_I}{d\tau} = e^{\hat{K}_0 \beta} \hat{K} e^{-\hat{K}_0} D_I(\tau; \beta) = \hat{K}_I(\beta) D_I(\tau; \beta)
\]  

If we parameterise \( D_I(\tau; \beta) = \{ \hat{S} \} e^{-\hat{K}_0 \beta} D_0 \), we find as the derivative

\[
- \frac{dD_I}{d\tau} = - \left\{ \frac{d\hat{S}}{d\tau} \hat{S} \right\} e^{-\hat{K}_0 \beta} D_0
\]  

Equating the derivatives, we obtain a differential equation for \( \hat{S} \)

\[
- \left\{ \frac{d\hat{S}}{d\tau} \hat{S} \right\} D_0(\beta) = \hat{K}_I(\beta) \left\{ \hat{S} \right\} D_0(\beta)
\]  

or in the connected form

\[
- \left\{ \frac{d\hat{S}}{d\tau} \hat{S} \right\} D_0(\beta) = \left[ \hat{K}_I(\beta) \left\{ \hat{S} \right\} \right]_{\text{Connected}} D_0(\beta)
\]  

Again we can obtain correct results from a single propagation, using a normal ordering associated with \( D_0(\beta) \). This density matrix is valid for every value of \( \tau \). In fact, this derivation is a little more comfortable as the definition of normal ordering is not changing with \( \tau \). We ignored potential complications previously. The known uniform density at \( \tau = 0 \) provides an initial condition for \( \hat{S}(\tau = 0) \). To calculate the initial \( \hat{S} \), one can propagate back from \( \tau = \beta \) to \( \tau = 0 \) using \( \hat{K}_0 \) as the Hamiltonian and \( \hat{S} = 0 \) at initial \( \tau = \beta \). Alternatively, one can use that \( \text{Tr}(\hat{p}^\dagger \hat{q} \{ \hat{S} \} D_0(\beta)) = \int \delta_{nq} f \), where \( f = \frac{2g}{hf} \) as before and solve for the diagonal elements \( s_{pp} \). In this latter formulation, we obtain a similar result as discussed throughout this paper. The definition of the contractions and zeroth-order thermal (diagonal) density operator is essentially arbitrary, i.e. both \( \hat{K}_0 \) and \( \beta \) can be chosen arbitrarily. One starts propagation from the suitably initialised \( \hat{S}(\tau = 0) \) and can obtain results for all \( \tau \). Moreover, using infinite \( \beta \) as a reference one clearly recovers CC at zero temperature.

Clearly, such a static interaction procedure has a lot in common with the thermal NOE approach and introduces similar freedoms in the definitions of contractions. Moreover, the full (transformed) Hamiltonian \( \hat{K}_I(\beta) \) is involved in both propagation schemes. It is likely that with a few straightforward redefinitions involving factors \( e^{\tau (\epsilon_p - \epsilon_q)} \), the equations can be made identical. In light of
the findings of this paper, it seems unlikely that the static interaction picture yields additional benefits and is likely to yield (essentially) the same results as thermal NOE.

For a thermofield formulation, however, there is potentially an advantage using the static interaction picture. Using \( \tau \)-dependent quasiparticle operators to parameterise the wave operator, one can use formally a single reference formulation, without invoking normal ordering. This may reduce the N-representability issues of the approach, at least for the quasiparticles. The \( \tau \)-dependence of the second quantised quasiparticle operators in the original interaction picture complicate the equations. The static interaction picture might provide the benefits of a more optimal reference state around temperature \( \beta \), but without the additional complexity of the \( \tau \)-dependence of the Bogliubov transformation and the quasi-particle operators, simplifying the theory. We think this would be interesting to explore. It is beyond the scope of this paper, however, to make any detailed comparison of thermal NOE and the thermofield formulation [25,26].

In conclusion we find few arguments in favour of the original interaction picture representation, which has been used almost exclusively in many-body thermal physics. We suspect results will be exactly the same in all of the thermal coupled cluster, thermal cumulant, or thermal NOE methods as long as numerical integration is done properly, but we have not investigated the issue carefully, beyond this theoretical analysis. We suspect the situation may be different for thermofield approaches, but this remains to be investigated.

9. Concluding remarks and outlook

We have come a long way using tools like normal ordering and Wick’s theorem that are easy to use, but conceptually hard, or, one might say, deep. In the few instances that people teach normal ordering in the Chemistry curriculum it is usually in the context of single reference Coupled Cluster theory, and the normal ordering is simply a resorting of annihilation and construction operators, using the (anti-)commutation rules such that so-called quasi-particle annihilation operators are to the right (annihilating the ket \(|0\rangle\)), while quasi-particle creation operators are to the left, such that they yield 0 when acting on the bra \(|0\rangle\). As a result \( \langle 0 | \Omega_\lambda \rangle | 0 \rangle = 0 \) for any non-empty string of operators \( \Omega_\lambda \) or linear combinations. Upon the introduction (seldom proved) of Wick’s theorem we know then that only \textit{fully connected} terms contribute. In the context of this paper, \textit{normal ordering} is a misnomer. It is not possible to write the operator \( \hat{p}^\dagger \hat{q} \) as a particular order of \( \hat{p}^\dagger \) and \( \hat{q} \). The only way to think about it is as \( \{ \hat{p}^\dagger \hat{q} \} = \hat{p}^\dagger \hat{q} - C_{pq} \), where \( C_{pq} \) is a constant (or sometimes a function), called the contraction of the operators. It is not hard to understand the definition, but it can be hard to really understand the power of such a simple devise.

Starting from the most traditional quantum chemistry approaches using Slater rules or elementary second quantisation it appears impossible to tackle the problems of Statistical Mechanics that involve taking the trace over all determinants (in Fock space!). That is Full CI on steroids. Using the mechanism of normal ordering, as we advertise here, one defines a constant zero-order density matrix \( D_0 \) (a multiple of the unit matrix in Fock space) and defines the contraction as \( \hat{p}^\dagger \cdot \hat{q} = \text{Tr}(\hat{p}^\dagger \hat{q} D_0) \) and as a result \( \text{Tr}(\{ \hat{p}^\dagger \hat{q} \} D_0) = 0 \). Wick’s theorem does not depend in any way on the initial poetry to set things up. It is not physics but rather a mathematical theorem that works on algebraic structures such as we are employing here.

The other ingredient is the use of the normal ordered exponential to parameterise the true density matrix \( \hat{D} = \{ e^\delta \} D_0 \). Could we not have used an ordinary exponential? Yes, in fact we can! \( \hat{D} = \frac{1}{\text{Tr}(D_0)} e^{-\beta \hat{H}} D_0 \). Unfortunately, that is just a restatement of the problem. The normal ordering is key to the solution. Most of the other manipulations in this paper are merely technical, in particular, the convenient reduction of the propagation equations to a connected form (see appendix).

\[
\left\langle \Omega_\lambda \right| \frac{d\hat{S}}{d\tau} = \left\langle \Omega_\lambda \right| \left\{ \hat{H} \left\{ e^\delta \right\}_{\text{connected}} \right\}
\]

We spend quite some time on the fact that the choice of the contraction \( f \) is essentially arbitrary. The \( s \) or \( t \)-amplitudes adjust such that the reduced density matrix \( d_{q\lambda}^f(\tau) = f_{pq} + t_{q\lambda}^f(\tau) \) are invariant under the choice of \( f \). With a little extra work one can in fact remove all singles \( t_{p\lambda}^f \) amplitudes and factors \( f \) and use \( d_{q\lambda}^f = f \tilde{d}_{q\lambda}^p + t_{q\lambda}^f \) and \( \tilde{d}_{q\lambda}^p = f - t_{q\lambda}^f \). This would constitute a proof that the results do not depend on the choice of \( f \) and in addition this would have allowed us to make a clear connection to the connected cumulant formulation [37] at zero temperature. We also emphasised here the pitfalls one can fall into if one makes the choice \( f = 0 \), or rather, if one makes this choice too quickly.

In this paper, we discussed a number of illustrative examples that all yield the exact (numerical) result provided the differential equations are initialised properly. For Fermionic one-electron problems one obtains the usual results from Fermi-Dirac theory, initialising the theory at the high T limit or \( \beta = 0 \). For harmonic oscillators the high T-limit is less appropriate, while also \( T = 0 \) is hard because the initial propagation is essentially flat (all derivatives are zero). We started the propagation by...
extracting the $t$-amplitudes from reduced density matrices obtained from a small sum over state calculation at low temperature. Another interesting illustration is the calculation of harmonic Franck–Condon spectra, where we also show that we do not need to use the normal-ordered exponential, but it is more convenient to use the usual exponential and (commuting) excitation operators only (using $f = 0$).

These exactly solvable problems are useful to illustrate the validity of the theory but other problems are truly of interest. The most obvious candidate is the many-body electronic structure case. There is one glaring problem and this is that the residual equations are exactly the same (or can be interconverted by simple substitutions) as connected cumulant theory [37]. This theory was such a major disappointment that it took one of the authors two years to publish it (i.e. to write the paper) after the work was completed. Moreover, this paper essentially killed the field as more recent approaches in this area are currently more wave function like in spirit (in spite of terminology). In the present thermal context, we spent another 3 months on its implementation and application to strongly correlated systems with similar disappointments and clear violations of N-representability. That was also two years ago. The theory as expounded here is too beautiful not to publish. Better ideas are needed to push it towards application for relevant electronic structure problems. We note that it may work for metallic systems in the current form. The multireference nature of metals is not sufficiently clear to these authors. In particular, close lying states may all have different translational symmetry (k-point), and the vertical energy gap (same k-point value) may be sufficiently large that each state can be represented well in a single reference picture.

Another application is to vibrational and also non-adiabatic vibronic problems. We think the application to (anharmonic) vibrational problems is in principle straightforward. In our group, we are working on the application of both time-autocorrelation functions and thermal properties for non-adiabatic vibronic problems. The theory is less straightforward here, in particular, we did not find a connected form of the equations and this remains work-in-progress.

A very appealing application would be to electron-phonon models in a solid state context, see also [43]. The theory is tailor-made for these problems using both bosonic and Fermionic second quantisation. We think the main issue is the same as the problems plaguing the pure electronic theory: N-representability. Moreover, the initial conditions for electronic structure problems (high T) and vibrational problems (low T) are opposite, and a solution to this issue is not yet clear to us.

Let us conclude by pointing out that the connections to other work are not entirely clear to us, although we have resolved some of the issues. A lot of work is ongoing in the recent quantum chemistry literature that tackles the same problems as we do here. There are clearly close connections in regards to the use of normal ordered exponentials and the use of Wick’s theorem. As far as we are aware, the other approaches use time- or temperature-dependent contractions, starting from the interaction picture. That requires some changes and it is not completely straightforward to connect these theories, e.g. [19–23]. We know for sure the zero-temperature limit of our electronic structure formulation is the connected contracted Schrödinger equation and not single reference coupled cluster theory. Due to the ‘vagueries’ of the temperature-dependent contractions, we are not sure at present about other formulations, in the low-temperature regime, but not exactly zero temperature. We would caution care in claiming the connection to Coupled Cluster, referring to our analysis in Section 8. We tried hard here to have this paper be self-contained. The only assumptions are second quantisation and Wick’s theorem. All the rest can be (and is essentially) derived in this paper. This suffices for now and we forgo more detailed comparisons or reflections on the extent literature.

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Appendix. Reduction of amplitude equations to connected form

One of the important features that greatly simplify the CC amplitude equations is the reduction of the equation to a connected form in which each amplitude is contracted to the Hamiltonian. In this appendix, we prove the crucial relation

\[
\hat{H} \left\{ \hat{S}(\beta) \right\} = \left\{ \left[ \hat{H} \left\{ \hat{S}(\beta) \right\} \right]_{\text{connected}} \hat{S}(\beta) \right\} \tag{A1}
\]

For the left-hand side, expand the exponential ansatz into Taylor series

\[
\hat{H} \left\{ \hat{S}(\beta) \right\} = \sum_{n} \frac{1}{n!} \hat{H} \left\{ \hat{S}(\beta)^{n} \right\} \tag{A2}
\]

Applying Wick’s Theorem, each term in the Taylor series can be expanded and we can distinguish \( \hat{S} \) amplitudes that are connected to the Hamiltonian and those that are not. If in a particular term of power \( n \), \( k \) amplitudes \( \hat{S} \) are connected to \( \hat{H} \), indicated by an overbar, while \( n-k \) are not connected to \( \hat{H} \), the number of distinct such contributions is given by

\[
\binom{n}{k} = \frac{n!}{k!(n-k)!} \tag{A3}
\]

and one can write

\[
\sum_{n} \frac{1}{n!} \hat{H} \left\{ \hat{S}(\beta)^{n} \right\} = \sum_{n} \frac{1}{n!} \sum_{k=0}^{n} \binom{n}{k} \left\{ \hat{H} \left\{ \hat{S}(\beta)^{k} \right\} \right\} \left( \hat{S}(\beta)^{n-k} \right) = \sum_{m} \sum_{k} \frac{1}{(m+k)!} \binom{m+k}{k} \right)
\]

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\]
\[
\times \left\{ \left( \hat{H} \hat{S}(\beta)^k \right) \right\} \hat{S}(\beta)^m \right\} \quad (A4)
\]

From Equations (A4) and (A3), we get the desired result:
\[
\hat{H} \left\{ \hat{S}(\beta) \right\} = \sum_k \frac{1}{k!} \left\{ \hat{H} \hat{S}(\beta)^k \right\} \sum_m \left( \frac{1}{(m)!} \hat{S}(\beta)^m \right) = \left\{ \left[ \hat{H} \hat{S}(\beta) \right] \right\}_{\text{connected}} \hat{S}(\beta) \right\} \quad (A5)
\]

It may be instructive to do the same proof for an ordinary exponential of commuting operators, as occurs, for example, in single reference coupled Cluster theory
\[
\hat{H} e^{\hat{T}} = e^{\hat{T}} \left( e^{\hat{H}} \hat{T} \right) = e^{\hat{T}} \left( \hat{H} e^{\hat{T}} \right)_{\text{connected}} = \left\{ \left( \hat{H} e^{\hat{T}} \right)_{\text{connected}} e^{\hat{T}} \right\} \quad (A6)
\]

The second line is then usually proven by applying the Baker–Campbell–Hausdorff expansion to obtain a nested commutator, and showing that each commutator implies only terms survive in which \( \hat{T} \) is contracted to the Hamiltonian. The above proof based on Wick’s theorem is in some sense easier and highlights the role of the \( \frac{1}{n!} \) coefficients in combination with the binomial ‘choose’ factors.