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ABSTRACT

Equations are derived for the time evolution of time-dependent vibrational coupled cluster (TDVCC) wave functions covering both the TDVCC ket state and the associated so-called Λ bra state. The equations are implemented in the special case of both the Hamiltonian and the cluster operator containing at most two-mode coupling terms. The nontrivial behavior of the evolution of norm, energy, and expectation values due to the nonunitary time-evolution of the nonvariational TDVCC theory is analyzed theoretically and confirmed in numerical experiments that also include time-dependent Hamiltonians. In the spirit of time-independent size-consistency analysis, the separability of both the coupled cluster and Λ states for noninteracting systems is studied. While the coupled cluster state clearly has the correct behavior, the behavior of the Λ state is more intricate, and the consequence for different properties is shown theoretically and numerically. Overall, the numerical experiments show that TDVCC in incomplete expansions gives higher accuracy than a standard linear variational wave function parameterization with the same number of independent parameters, while equivalent results are obtained for complete expansions. The efficiency of the methodology is illustrated in computations on polycyclic aromatic hydrocarbons with up to 156 modes.

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I. INTRODUCTION

With the continuously increasing focus on dynamics in the study of molecular systems, it is important to establish new accurate computational methods for predicting nuclear motion. The standard approach to solving the time-dependent Schrödinger equation (TDSE) in the context of quantum molecular dynamics (QMD) is to employ a linear expansion of the wave function in a direct product of time-independent one-mode basis functions. This approach becomes exact in the limit of an untruncated basis. Such quantum dynamical computations can, in both time-independent and time-dependent contexts, be used to accurately compute spectra and dynamics of low-dimensional systems. Progressing to higher dimensionality, this direct approach is, however, hampered by the curse of dimensionality as the state-space and the computational

cost increases exponentially with the number of modes in the systems. Accordingly, it is an important task to develop methods that avoid this exponential scaling in order to be able to treat molecules with more than a few (say, 5) atoms.

Perhaps the simplest approximate quantum mechanical method for computing the time evolution of many-mode molecular systems is time-dependent Hartree (TDH).^{1,2} The great simplification of TDH lies in the use of a single direct product wave function in conjunction with the time-dependent variational principle (TDVP) for determining the evolution of the one-mode functions of the direct product. In the considerably more accurate and versatile multiconfigurational time-dependent Hartree (MCTDH) approach,^{2,3} the TDVP is used to determine the evolution of both the coefficient and the one-mode basis functions for several such Hartree products. Fundamentally, MCTDH still comes with

an exponential increase in computational cost, but with a much reduced base, due to the variational optimization. Many variants of MCTDH and Gaussian wave packet methods have been developed aiming at efficient treatment of time-dependent problems.^{4–12}

We have recently presented a many-mode second quantization (SQ)¹³ based exponentially parameterized formulation and implementation of TDH,¹⁴ which paved the way for an implementation with a significant reduction in computational cost. This allowed computations to be carried out for model system with more than 10^5 dimensions and for polycyclic aromatic hydrocarbon (PAH)s with many-term potentials and more than 250 modes. However, the accuracy limitation of TDH is the same as before, and in ongoing studies, we are seeking to extend this line of work to more advanced wave functions. In this study, we turn to time-dependent vibrational coupled cluster (TDVCC) for computing the time-dependent wave function (TD-WF), focusing on the coupled cluster (CC) parameterization in configuration space with a fixed (i.e., time-independent) one-mode basis.

CC theory has a long history by now. Originally developed in nuclear physics in the late 1950s,^{15,16} CC theory was introduced into quantum chemistry for the description of electron correlation from 1966 and onwards.^{17,18} Decades later, CC theory is still an active field in nuclear physics¹⁹ and CC methods for molecules are widespread and generally appreciated for their high accuracy for electronic wave functions dominated by a single configuration. Today, electronic CC methods are further developed for applicability to large molecular systems^{20–22} at the same time as research addresses the key theoretical limitation of electronic CC, the multireference problem.²³ From 2003 and onwards, vibrational coupled cluster (VCC) theory^{24,25} was developed to solve the time-independent Schrödinger equation (TISE) for a set of coupled distinguishable modes using a coupled cluster parameterization. The anharmonic vibrational problem can thereby be solved by approximate but accurate and efficient VCC methods. The formulation and implementation are based on a many-mode SQ formulation constructed for this purpose, which can be conveniently applied to any basis set and any Hamiltonian operator. The basic foundation allows extension to the time-dependent case as well, but the present work presents the first such TDVCC study. In the VCC approach, a vibrational self-consistent field (VSCF) reference state and VSCF one-mode functions are often used, which, in turn, are constructed from a primitive basis (B-splines, harmonic oscillators, or others). It is similar in spirit to the electronic case in the sense that a cluster operator excites to virtual states generated from a set of electronic self-consistent field (SCF) orbitals which, in turn, can be expanded in any suitable basis.

There are other early attempts^{26–28} on constructing coupled-cluster-like parameterizations for the time-independent vibrational problem. Following these early works, Durga-Prasad and co-workers^{29–31} have developed what can be denoted³¹ boson CC theory. Durga-Prasad and co-workers have described time-dependent extensions as well.^{32–34} The boson CC theory is limited to a harmonic oscillator basis and a reference constructed from an optimized harmonic oscillator basis. Later, Hirata and co-worker³⁵ presented their XVCC approach which in certain typical limits is similar to the boson CC theory of Prasad but allows the use of other reference states. The XVCC approach proceeds, however, still through reference to a harmonic oscillator and the corresponding

basis/ladder operators, and is furthermore based on reduced Taylor-expanded potentials which, although perhaps useful for solids, will limit the accuracy and usefulness in practical molecular computations.

The overwhelming majority of previous CC work has been on solving time-independent quantum equations. The present work is to our knowledge the first CC treatment of the dynamics of nuclear motion (with the exception of the rather different work of Durga-Prasad). There has been some previous work of time-dependent CC theory in other contexts.^{19,36–46} In response theory, the response of molecular systems in the presence of external fields is studied. In this context, the wave function is formally parameterized in a time-dependent fashion, but the final computation takes place in the frequency domain and within a perturbational expansion. Nevertheless, time-dependent CC equations have been discussed since long ago in this context.^{47–50} The work by Koch and Jørgensen⁴⁹ is interesting therein that it reports considerations of the CC state and the so-called Λ -state as being the solution of projected Schrödinger equations. The work by Arponen³⁹ introduced a so-called bivariational approach⁴¹ that has been followed in several electronic structure works.^{41,44,46}

In this work, we will derive working equations for TDVCC in a nuclear dynamics framework, following the idea of Arponen. When discussing correlated wave function dynamics, one can employ either time-independent or time-dependent one-mode basis functions (modals). In this paper, we consider TDVCC employing time-independent modals. The introduction of time-dependent modals gives a number of extra considerations, which will be taken up in a future work. We will compare the TDVCC method to a corresponding linear-variational approach in the same space, which will be denoted time-dependent vibrational configuration interaction (TDVCI). The time-evolution of TDVCC is neither (truly) variational nor unitary, and we accordingly investigate the key features of the method with respect to the evolution of norms, energies, and expectation values. The size-consistency of CC theory is well-known in time-independent theory. Similar behavior has been stated in the time-dependent context without analysis. We analyze separability for noninteracting systems theoretically and numerically and discuss some consequences of the nontrivial behavior found. Although performed in the context of QMD, the results of these analyses could be of interest in electronic dynamics. Integration of the TDVCC equations of motion (EOMs) are implemented using a standard adaptive integrator, which in the tested cases is stable and performing even better than similarly for TDVCI wave functions, even though this was done without exploiting the symplectic structure, as was reported to be important for integration of CC equations of motion in the electronic case.⁴⁶

In Sec. II, we describe the theory behind TDVCC before the implementation is briefly described in Sec. III. In Sec. IV, we present a number of numerical experiments demonstrating the key features of the theory and implementation, and a summary and outlook is given in Sec. V.

II. THEORY

A. Second-quantization and definition of spaces

We consider a system described by M distinguishable coordinates q_m . Each coordinate associated a (potentially complete) set

of one-mode basis functions, $\phi_{s^m}(q_m)$. We shall denote these one-mode functions as modals. In standard first quantization quantum mechanics, we consider for the full system the space of Hartree-products,

$$\Phi_s(\mathbf{q}) = \prod_{m=1}^M \phi_{s_m}^m(q_m) = \phi_{s_1}^1(q_1) \phi_{s_2}^2(q_2) \dots \phi_{s_M}^M(q_M). \quad (1)$$

In the SQ formulation of Ref. 13, many-mode wave functions and operators are described based on a one-to-one correspondence between Hartree-products and occupation number vectors. In this representation, all relevant states and operators can be given in terms of one common set of creation and annihilation operators, $a_{s^m}^{m\dagger}$ and $a_{s^m}^m$, that, respectively, create and annihilate occupation in the one-mode function indexed by s^m . The creation and annihilation operators satisfy the commutator relations,

$$[a_p^{m\dagger}, a_q^{m'\dagger}] = [a_p^m, a_q^{m'}] = 0, \quad (2)$$

$$[a_p^m, a_q^{m'\dagger}] = \delta_{mm'} \delta_{pq}. \quad (3)$$

The space is complete with the definition of the vacuum state, $|\text{vac}\rangle$, satisfying orthonormality, $\langle \text{vac} | \text{vac} \rangle = 1$, and the killer condition,

$$a_r^m |\text{vac}\rangle = 0. \quad (4)$$

Usually some convention is adopted in labeling modals. Thus, i^m is used for indexing the occupied modals of mode m in some reference Hartree-product, a^m , b^m , c^m , d^m for the unoccupied/virtual modals, while p^m , q^m , r^m , s^m are used for modals of unspecified occupancy. The reference Hartree-product can in SQ be written in terms of a string of creation operators,

$$|\Phi_i\rangle = \prod_{m=1}^M a_{i_m}^{m\dagger} |\text{vac}\rangle. \quad (5)$$

All other M -mode Hartree-products can be reached by applying excitation operators of the form

$$\tau_\mu = \tau_{\mathbf{a}\mathbf{i}\mathbf{m}}^{\mathbf{m}} = \prod_{m \in \mathbf{m}} a_{a_m}^{m\dagger} a_{i_m}^m \quad (6)$$

to the reference ket. That is, it excites all modes in the set given by $\mathbf{m}$ from the reference levels $\mathbf{i}$ to the specific excited levels given by $\mathbf{a}$. Thus, the dimensions of the $\mathbf{i}$ and $\mathbf{a}$ vectors are the same as for $\mathbf{m}$. Most often, we simply use one compound index μ to simply denote some excitation. Also for simplicity, we will in the following suppress the $\mathbf{i}$ vector in the reference ket and simply use $|\Phi\rangle$ instead of $|\Phi_i\rangle$ and denote excited kets simply as $|\mu\rangle = \tau_\mu |\Phi\rangle$. From Eqs. (3) and (4) follows, respectively, the commutator and killer conditions for the τ_μ operators,

$$[\tau_\mu, \tau_\nu] = 0, \quad (7)$$

$$\tau_\mu^\dagger |\Phi\rangle = 0, \quad \langle \Phi | \tau_\nu = 0. \quad (8)$$

The Hamiltonian can similarly be expressed in the second quantization for any first quantization format¹³ such that identical matrix elements and thereby predictions are obtained in the first and second quantization. We shall in the implementation and computation use a sum-of-products form

$$\hat{H} = \sum_{t=1}^T c_t \prod_{m \in \mathbf{m}^t} \hat{h}^{m,t} = \sum_{t=1}^T c_t \prod_{m \in \mathbf{m}^t} \sum_{r^m, s^m} h_{r^m s^m}^{m,t} a_{r^m}^{m\dagger} a_{s^m}^m, \quad (9)$$

where the one-mode integrals $h_{r^m s^m}^{m,t}$ are

$$h_{r^m s^m}^{m,t} = \langle \phi_{r^m}^m(q_m) | \hat{h}^{m,t} | \phi_{s^m}^m(q_m) \rangle, \quad (10)$$

giving the link to the corresponding first quantization representation in terms of one mode operators $^{FQ}\hat{h}^{m,t}$. Thus, each term is a product of one-mode operators $\hat{h}^{m,t}$, and each term will generally only have nontrivial (different from unity) operation in a limited set of modes, given by the set of modes in $\mathbf{m}^t$. Furthermore, in this work, we restrict ourselves to the case of at most two-mode couplings, i.e., the sets $\mathbf{m}^t$ are restricted to at most a dimension of two.

The above operator setup follows the many-mode second quantization of Ref. 13 which we refer to for details. Note that this framework is fundamentally different from standard ladder operators of the harmonic oscillator problem, and the formulation is not restricted to harmonic oscillator basis functions or reference states (i.e., a multidimensional Gaussian), which would otherwise be the case. In this work, the modals are time-independent throughout and therefore the creation and annihilation operators, and the excitation operators, are also all time-independent, with the theory for time-dependent modals deferred to future work (but note the recent SQ TDH work¹⁴).

The space spanned by the SQ formulation is larger than the physically relevant space for our use. The physically relevant space corresponds to each mode occupied once (or in other words that all one-mode number operators, $N^m = \sum_{s^m} a_{r^m}^{m\dagger} a_{r^m}^m$, have eigenvalue 1). All states are automatically confined to the physically relevant space, by constructing such states from the outset (e.g., the given reference state) and using only number conserving operators for all further manipulations. That is, operators like the given excitation operator and the $a_{r^m}^{m\dagger} a_{s^m}^m$ combinations of the Hamiltonian that transfer occupation unit from level s^m to r^m in the same mode m . These operators preserve unit occupation of each mode, even though they may change modal occupations for the modes. The many-mode second-quantization theory shares similarities with what in other contexts is denoted hard-core boson theory.⁵¹ In the context of the latter, the restriction to the physical part of space has been included in the fundamental commutator relations. Since, as described, we from the outset consider only states and operators working in the relevant space, there is no current need for these additional considerations.

At a high level of abstraction, we consider in our formulation dynamics generated by a Hamiltonian and a state space that is obtained from a reference state and a set of excitation operators satisfying Eqs. (7) and (8). We shall write most of the equations at this level of abstraction, covering both the dynamics of distinguishable modes of nuclear motion above and employing modes, modals, and Hartree-products as well as the electronic case, i.e., employing electrons, orbitals, and Slater-determinants. While the excitation operators satisfy identical equations to Eqs. (7) and (8) and therefore the high-level results are transferable, it should not be forgotten that the cases refer to fundamentally different spaces and Hamiltonians, e.g., in deriving the actual detailed equations, the

basic creation and annihilation operator commutator algebra is different, as is the Hamiltonian, leading to very different equations and implementations.

B. Wave function ansatz

We now consider the wave function $|\Psi\rangle$ in a CC ansatz,

$$|\Psi(t)\rangle = |\text{CC}(t)\rangle = \exp(-i\epsilon(t)) \exp(T) |\Phi\rangle = \exp(-i\epsilon(t)) |\tilde{\text{CC}}\rangle. \quad (11)$$

Here, $|\Phi\rangle$ is a unit-normalized reference state given in terms of a string of time-independent creation operators in the second quantization, corresponding to a Hartree-product or Slater determinant depending on the case as discussed in Subsection II A. The time-dependent cluster operator T is

$$T = \sum_{\mu} s_{\mu}(t) \tau_{\mu}, \quad (12)$$

given in terms of time-independent excitation operators and the time-dependent and generally complex amplitudes s_{μ} . It is customary to denote the amplitudes t_{μ} in quantum chemistry, but this is avoided here, to avoid confusion with the time t . As in many previous works,^{50,52–54} we choose to separate out overall phase and normalization factors—we do this here by the $\exp(-i\epsilon(t))$ factor, where the real part of the generally complex ϵ is associated with phase and the imaginary part is associated with norm.

We further define a second “bra” state in terms of s_{μ} and the yet undetermined variable l_{μ} ,

$$\begin{aligned} \langle\Psi'(t)| &= \langle\Lambda| = \langle\tilde{\Lambda}| \exp(i\epsilon'(t)) \\ &= (\langle\Phi| + \sum_{\mu} l_{\mu}(t) \langle\mu|) \exp(-T) \exp(i\epsilon'(t)) \\ &= \langle\Phi|(1+L) \exp(-T) \exp(i\epsilon'(t)). \end{aligned} \quad (13)$$

Here, the L operator has been introduced as

$$\hat{L} = \sum_{\mu} l_{\mu}(t) \tau_{\mu}^{\dagger}. \quad (14)$$

It has become common to denote such a state as $\langle\Lambda|$. Similar to the phase-and-norm separated state $|\tilde{\text{CC}}\rangle$, we also define a $\langle\tilde{\Lambda}| = \langle\Lambda| \exp(-i\epsilon'(t))$ state. Since the $\exp(-T)$ operator is invertible, the state $\langle\Lambda|$ is a general bra state, provided that $\langle\Phi|$, $\langle\mu|$ span the full Hilbert space.

C. Equations of motion

Following Arponen,³⁹ we now define a functional $\mathcal{I}[\Psi, \Psi']$ of two functions, whose unconstrained simultaneous variations yield the TDSE and its complex conjugate

$$\mathcal{I}[\Psi, \Psi'] = \int_{t_0}^{t_1} \langle\Psi'| \left(i \frac{\partial}{\partial t} - \hat{H} \right) |\Psi\rangle dt, \quad (15)$$

$$\delta\Psi'(t_0) = \delta\Psi'(t_1) = \delta\Psi(t_0) = \delta\Psi(t_1) = 0. \quad (16)$$

Following previous works,^{39,41,55} we denote this a bivariational principle. If $\Psi = \Psi'$, this reduces to a standard time-dependent variational principle. The functional $\mathcal{I}[\Psi, \Psi']$ can be written as the integral of the Lagrangian

$$\mathcal{L}(\Psi', \Psi, \dot{\Psi}) = \langle\Psi'| \left(i \frac{\partial}{\partial t} - \hat{H} \right) |\Psi\rangle. \quad (17)$$

According to the calculus of variations, the stationarity conditions can be obtained from the corresponding Euler-Lagrange equations. The Lagrangian can with the $|\Psi\rangle$ and $\langle\Lambda|$ states of Eqs. (11) and (13) be written as

$$\begin{aligned} \mathcal{L}(s, \dot{s}, l) &= \langle\Phi|(1+L) \exp(-T) e^{i\epsilon'} \left(i \frac{\partial}{\partial t} - \hat{H} \right) e^{-i\epsilon} \exp(T) |\Phi\rangle \\ &= [\langle\Phi|(1+L)(\dot{T} - i\dot{\epsilon})|\Phi\rangle - \langle\Phi|(1+L)\hat{H}|\Phi\rangle] e^{-i(\epsilon-\epsilon')} \\ &= \left[i \sum_{\mu} l_{\mu} \dot{s}_{\mu} + \dot{\epsilon} - \mathcal{H}(s, l) \right] e^{-i(\epsilon-\epsilon')}, \end{aligned} \quad (18)$$

introducing also what we shall denote a Hamiltonian energy function (as has also been employed for variational theory⁵⁶),

$$\mathcal{H}(s, l) = \langle\Phi|(1+L)\hat{H}|\Phi\rangle = \langle\tilde{\Lambda}|\hat{H}|\tilde{\text{CC}}\rangle. \quad (19)$$

We here and in the following use a bar over an operator to denote a similarity transformed operator,

$$\bar{H} = \exp(-T) \hat{H} \exp(T). \quad (20)$$

The Euler-Lagrange equations can now be concisely written as

$$0 = \frac{\partial \mathcal{L}}{\partial l_{\mu}} - \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{l}_{\mu}} = \left(i \dot{s}_{\mu} - \frac{\partial \mathcal{H}}{\partial l_{\mu}} \right) e^{-i(\epsilon-\epsilon')}, \quad (21)$$

$$0 = \frac{\partial \mathcal{L}}{\partial s_{\mu}} - \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{s}_{\mu}} = \left(-i \dot{l}_{\mu} - l_{\mu}(\dot{\epsilon} - \dot{\epsilon}') - \frac{\partial \mathcal{H}}{\partial s_{\mu}} \right) e^{-i(\epsilon-\epsilon')}, \quad (22)$$

$$0 = \frac{\partial \mathcal{L}}{\partial \epsilon} - \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\epsilon}} = -i\mathcal{L} + i(\dot{\epsilon} - \dot{\epsilon}') e^{-i(\epsilon-\epsilon')}, \quad (23)$$

$$0 = \frac{\partial \mathcal{L}}{\partial \epsilon'} - \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\epsilon}'} = i\mathcal{L}, \quad (24)$$

using in the first that the Lagrangian does not depend on $\dot{l}$ and in the second that the time-derivative term from the Lagrangian is independent of s .

Comparing the last two Euler-Lagrange equations, we see clearly that the time-evolution of ϵ and ϵ' must be identical,

$$\dot{\epsilon} = \dot{\epsilon}'. \quad (25)$$

The first two Euler-Lagrange equations then lead to the symplectic equations of motion (EOMs) for s_{μ} and l_{μ} ,

$$\dot{s}_{\mu} = -i \frac{\partial \mathcal{H}}{\partial l_{\mu}} = -i \langle\mu|\bar{H}|\Phi\rangle \equiv -ie_{\mu}, \quad (26)$$

$$\dot{l}_{\mu} = +i \frac{\partial \mathcal{H}}{\partial s_{\mu}} = +i \langle\tilde{\Lambda}|[\hat{H}, \tau_{\mu}]\tilde{\text{CC}}\rangle \equiv i \left(\eta_{\mu} + \sum_{\nu} l_{\nu} A_{\nu\mu} \right), \quad (27)$$

where $e_{\mu} = \langle\mu|\bar{H}|\Phi\rangle$, $\eta_{\mu} = \langle\Phi|[\bar{H}, \tau_{\mu}]|\Phi\rangle$, and $A_{\mu\nu} = \langle\mu|[\bar{H}, \tau_{\nu}]|\Phi\rangle$ are the error- and η -vectors and the error-vector Jacobian matrix, well-known from VCC ground state and response theory. The last Euler-Lagrange equation determines the evolution of ϵ (and hence also of ϵ'),

$$\dot{\epsilon} = \mathcal{H}(s, l) - i \sum_{\mu} l_{\mu} \dot{s}_{\mu} = \langle\tilde{\Lambda}|\hat{H} - i \frac{\partial}{\partial t}|\tilde{\text{CC}}\rangle = \langle\Phi|\bar{H}|\Phi\rangle, \quad (28)$$

where we in the last step have used the s_μ equations of motion in Eq. (26).

Considering the overlap between the $\langle\Lambda|$ and the $|\Psi\rangle$ states, we see that they have constant overlap

$$\begin{aligned}\langle\Psi'(t)|\Psi(t)\rangle &= \langle\tilde{\Lambda}|\tilde{C}\tilde{C}\rangle e^{-i(\epsilon-\epsilon')} \\ &= \langle\Phi|(1+L)\exp(-T)\exp(T)|\Phi\rangle e^{-i(\epsilon-\epsilon')} \\ &= \langle\Phi|\Phi\rangle e^{-i(\epsilon-\epsilon')} = e^{-i(\epsilon-\epsilon')} = 1\end{aligned}\quad (29)$$

at all times, and if we choose $\epsilon'(t_0) = \epsilon(t_0)$, then $\epsilon'(t) = \epsilon(t)$ at all times and the last equality gives us the unit overlap. Note that this does not necessarily imply (e.g., based on the Cauchy-Schwarz inequality) that $|\Lambda\rangle$ and $|\Psi\rangle$ are parallel because their norms squared, $\langle\Psi|\Psi\rangle$ and $\langle\Lambda|\Lambda\rangle$, are generally not unity (to be discussed further in Sec. II E).

As stated in the Introduction, Eqs. (26) and (27) have been derived in previous works using various approaches, including direct projection of the TDSE. Thus, solving the bivariational (V)CC equations can be proven in a few steps to correspond to solving the projected TDSEs,

$$\hat{P}\left(i\frac{\partial}{\partial t} - \hat{H}\right)|\Psi\rangle = 0, \quad (30)$$

$$\left(\langle\Lambda|\hat{H} + i\frac{\partial}{\partial t}\langle\Lambda|\right)\hat{P} = 0. \quad (31)$$

The projection is carried out by the projection operator

$$\hat{P} = e^T \hat{P} e^{-T} = \sum_\mu e^T |\mu\rangle \langle\mu| e^{-T} + e^T |\Phi\rangle \langle\Phi| e^{-T} \quad (32)$$

that is a similarity transformation of the projection onto the reference and the allowed excitations

$$\hat{P} = |\Phi\rangle\langle\Phi| + \sum_\mu |\mu\rangle\langle\mu|. \quad (33)$$

Note that $\hat{P}$ is inverse transformed compared to $\tilde{P}$, i.e., $\hat{P} = \tilde{P}$. Corresponding to $\hat{P}$ projection operators, there are corresponding projection operators on the orthogonal complement, $\hat{Q} = 1 - \hat{P}$, and similarly $\tilde{Q} = 1 - \tilde{P}$. In this manner, we have for time-independent modal TDVCC explicitly shown equivalence in the equations of motion obtained from the bivariational principle with two different types of parameters s_μ and l_μ and an explicit wave function view, where the equations of motion are obtained from the projected Schrödinger equations. The bivariational principle offers good possibilities for generalization in various ways such as time-dependent modals, which will be exploited in forthcoming works. The wave function/projection point of view offers explicit insight into the $\langle\Lambda|$ and $|\Psi\rangle$ states as solutions to the projected Schrödinger equations, thereby converging to the exact limit and offering a basis for interpretation with some care. The need for a ket state in computing a bra state (i.e., for s_μ in computing l_μ) makes it apparent that that they are not individually representative of the complete wave function of the system, but rather should be considered together for the description of the system and all its properties. It is with this understanding in mind that we use the simple bra and ket state terminology.

Finally, we note that the above derived time-dependent equations straightforwardly reduce to the time-independent CC equations,

$$0 = \langle\mu|\tilde{H}|\Phi\rangle, \quad (34)$$

$$0 = \langle\Phi|(1+L)\exp(-T)[\tilde{H}, \tau_\mu]\exp(T)|\Phi\rangle. \quad (35)$$

D. Energy evolution and conservation

Let us now consider the so-called Hamiltonian energy expression. In the time-independent context, one can also denote that the variational Lagrangian energy and its variational conditions lead exactly to Eqs. (34) and (35). We will now study it in its own right as an energy expression in the time-dependent case,

$$E_V = \mathcal{H}(s, l) = \langle\tilde{\Lambda}(t)|\hat{H}|\tilde{C}\tilde{C}(t)\rangle = \langle\Phi|\tilde{H}(t)|\Phi\rangle + i\sum_\mu l_\mu \dot{s}_\mu. \quad (36)$$

The time-derivative of E_V is easily found

$$\begin{aligned}\frac{dE_V}{dt} &= \frac{d\mathcal{H}(s, l)}{dt} = \langle\tilde{\Lambda}(t)|\dot{\hat{H}}|\tilde{C}\tilde{C}(t)\rangle + \sum_\mu \left(\frac{\partial\mathcal{H}(s, l)}{\partial s_\mu} \dot{s}_\mu + \frac{\partial\mathcal{H}(s, l)}{\partial l_\mu} \dot{l}_\mu \right) \\ &= \langle\tilde{\Lambda}(t)|\dot{\hat{H}}|\tilde{C}\tilde{C}(t)\rangle + \sum_\mu (-i\dot{l}_\mu \dot{s}_\mu + i\dot{s}_\mu \dot{l}_\mu) = \langle\tilde{\Lambda}(t)|\dot{\hat{H}}|\tilde{C}\tilde{C}(t)\rangle\end{aligned}\quad (37)$$

using the CC equations (26) and (27).

In the case where the Hamiltonian has no explicit time-dependence, this means that the energy is a conserved quantity. Thus, in such computations evolving the l_μ and s_μ in time, we should see E_V stable to within the numerical noise from the time-integration. With a time-dependent Hamiltonian, the above equation can be used to understand and verify the Lagrangian energy evolution, as we shall see in Sec. IV F.

The common CC energy from equivalent standard electronic ground state theory

$$E_{NV} = \langle\Phi|\tilde{H}(t)|\Phi\rangle \quad (38)$$

is not conserved even for a time-independent Hamiltonian with $\dot{\hat{H}} = 0$ as

$$\begin{aligned}\frac{dE_{NV}}{dt} &= \langle\Phi|[\tilde{H}, \dot{T}]|\Phi\rangle = -i\sum_\mu \langle\Phi|\tilde{H}|\mu\rangle \langle\mu|\tilde{H}|\Phi\rangle \\ &= i[\langle\Phi|\tilde{H}|\Phi\rangle^2 - \langle\Phi|\tilde{H}\hat{P}\tilde{H}|\Phi\rangle] \neq 0.\end{aligned}\quad (39)$$

The E_{NV} energy will therefore generally not be conserved, though it is conserved in the full space limit in the special case when $|\tilde{C}\tilde{C}\rangle$ is an eigenstate, i.e., $\tilde{H}\Phi = E\Phi$. The fact that the energy expression in Eq. (38) is not the appropriate energy is not surprising. Also in time-independent theory, it can be discussed what is the appropriate energy expression. For a converged ground state, we have $\langle\mu|\tilde{H}|\Phi\rangle = 0$ and then $E_{NV} = \langle\Lambda|\hat{H}|\tilde{C}\tilde{C}\rangle = E_V$ for the time-independent states. However, when we depart from this very special point, it is another issue, and, for example, also when the nonlinear interaction with a solvent is taken into account, the Lagrangian energy expression must be used to obtain the correct exact limit, as opposed to the simpler E_{NV} expression.⁵⁷

E. The evolution of norm

Recall that the phase/norm isolated CC ket $|\tilde{\Psi}\rangle$ is intermediate normalized at any point in time

$$1 = \langle \Phi | \tilde{\Psi} \rangle, \quad (40)$$

and for $\langle \tilde{\Psi}' |$, we have

$$\langle \tilde{\Psi}' | \Psi \rangle = \langle \Lambda | \text{CC} \rangle = \langle \tilde{\Lambda} | \tilde{\text{CC}} \rangle = \langle \Phi | \Phi \rangle = 1. \quad (41)$$

Let now $N_{\text{CC}}^2(t)$ and $N_{\Lambda}^2(t)$ be the squared norms of the Ψ and Ψ' states, respectively,

$$N_{\text{CC}}^2(t) = \langle \Psi | \Psi \rangle = \langle \tilde{\Psi} | \tilde{\Psi} \rangle \exp(2 \text{Im}\{\epsilon\}) = \langle \Phi | e^{T^\dagger} e^T | \Phi \rangle e^{i\epsilon^*} e^{-i\epsilon}, \quad (42)$$

$$\begin{aligned} N_{\Lambda}^2(t) &= \langle \Lambda | \Lambda \rangle = \langle \tilde{\Lambda} | \tilde{\Lambda} \rangle \exp(-2 \text{Im}\{\epsilon\}) \\ &= \langle \Phi | (1 + L) e^{-T} e^{-T^\dagger} (1 + L^\dagger) | \Phi \rangle e^{-i\epsilon^*} e^{i\epsilon}. \end{aligned} \quad (43)$$

The norms of the states are connected with the imaginary part of the ϵ . Thus, we can, for example, in principle, fix the initial norm of the Ψ state at $t = 0$ by the appropriate choice of $\text{Im}\{\epsilon(t = 0)\}$, though we do not want to do this in practice (computing $\langle \Phi | e^{T^\dagger} e^T | \Phi \rangle$ would be very costly even for truncated T).

Instead we will now focus on the norm evolution to understand what happens over time. For that purpose, we can, using Eq. (30), obtain

$$\begin{aligned} \langle \Psi | \frac{\partial}{\partial t} \Psi \rangle &= \langle \Psi | \dot{\Psi} + \dot{\tilde{Q}} | \frac{\partial}{\partial t} \Psi \rangle = \langle \Psi | \dot{\Psi} (-i\hat{H}) | \Psi \rangle + \langle \Psi | \dot{\tilde{Q}} (\dot{T} - i\epsilon) | \Psi \rangle \\ &= \langle \Psi | (1 - \tilde{Q}) (-i\hat{H}) | \Psi \rangle + \langle \Psi | e^{-T} \dot{\tilde{Q}} (\dot{T} - i\epsilon) | \Phi \rangle e^{i\epsilon} \\ &= -i\langle \Psi | \hat{H} | \Psi \rangle + i\langle \Psi | \dot{\tilde{Q}} \hat{H} | \Psi \rangle + 0, \end{aligned} \quad (44)$$

using in the last step that $(\dot{T} - i\epsilon) | \Phi \rangle$ lies in the space of the reference and included excitations and thus gives zero when projected on the orthogonal complement by $\tilde{Q}$. Similarly, we have using Eq. (31)

$$\begin{aligned} \langle \frac{\partial}{\partial t} \Lambda | \Lambda \rangle &= \langle \frac{\partial}{\partial t} \Lambda | \dot{\tilde{P}} + \dot{\tilde{Q}} | \Lambda \rangle = \langle \Lambda | (i\hat{H}) \dot{\tilde{P}} | \Psi \rangle + \langle \frac{\partial}{\partial t} \Lambda | \dot{\tilde{Q}} | \Lambda \rangle \\ &= i\langle \Lambda | \hat{H} (1 - \tilde{Q}) | \Psi \rangle + \langle \Lambda | (-\dot{T} + i\epsilon) \dot{\tilde{Q}} | \Lambda \rangle + \langle \Phi | \dot{L} e^{-T} e^{i\epsilon} \dot{\tilde{Q}} | \Lambda \rangle \\ &= i\langle \Lambda | \hat{H} | \Lambda \rangle - i\langle \Lambda | \hat{H} \tilde{Q} | \Psi \rangle + \langle \Phi | (1 + L) e^{i\epsilon} (-\dot{T} + i\epsilon) \\ &\quad \times \dot{\tilde{Q}} e^{-T} | \Lambda \rangle + \langle \Phi | \dot{L} e^{i\epsilon} \dot{\tilde{Q}} e^{-T} | \Lambda \rangle \\ &= i\langle \Lambda | \hat{H} | \Lambda \rangle - \langle \Lambda | \hat{H} \tilde{Q} | \Lambda \rangle \end{aligned} \quad (45)$$

canceling again terms in the null space of $\tilde{Q}$.

We can now find the time derivatives of the squared norms

$$\begin{aligned} \frac{d(N_{\text{CC}}^2)}{dt} &= \langle \Psi | \frac{\partial}{\partial t} \Psi \rangle + c.c. = -2i \text{Im}\{\langle \Psi | \dot{\tilde{Q}} \hat{H} | \Psi \rangle\} \\ &= -2i \text{Im}\{\langle \Phi | e^{T^\dagger} e^T \dot{\tilde{Q}} \hat{H} | \Phi \rangle\} \exp(2 \text{Im}\{\epsilon\}), \end{aligned} \quad (46)$$

$$\begin{aligned} \frac{d(N_{\Lambda}^2)}{dt} &= \langle \frac{\partial}{\partial t} \Lambda | \Lambda \rangle + c.c. = -2i \text{Im}\{\langle \Lambda | \hat{H} \tilde{Q} | \Lambda \rangle\} \\ &= -2i \text{Im}\{\langle \Phi | (1 + L) \hat{H} \tilde{Q} e^T e^{-T^\dagger} (1 + L^\dagger) | \Phi \rangle\} \exp(-2 \text{Im}\{\epsilon\}). \end{aligned} \quad (47)$$

In both, it has been used that $\langle \Psi | \hat{H} | \Psi \rangle$ is real and therefore not contributing after adding complex conjugate terms. Also for both,

the variation in the norm is zero when the full excitation space is included and $\dot{Q} = 0$ (i.e., in the FVCI case). However, in approximate computations, the $|\Psi\rangle$ and $\langle\Lambda|$ states cannot be expected to conserve their norms.

F. Expectation values and correlation functions

In standard exact or approximate variational quantum theory, the expectation value of an operator $\hat{A}$ for the state $|\alpha\rangle$ is

$$\langle A \rangle \equiv \frac{\langle \alpha | \hat{A} | \alpha \rangle}{\langle \alpha | \alpha \rangle}. \quad (48)$$

This has the property that the expectation values for physical quantities are always real, as they should be, because their corresponding operators are Hermitian.

In the context of TDVCC, we consider the corresponding expectation value definition

$$\langle A \rangle \equiv \frac{\langle \Lambda | \hat{A} | \Psi \rangle}{\langle \Lambda | \Psi \rangle} = \langle \Lambda | \hat{A} | \Psi \rangle \quad (49)$$

and variants thereof. With the choice in Eq. (49), we seemingly lose the guaranteed real nature of the expectation value of a Hermitian operator because the bra and ket states are generally not adjoints of each other. Obviously, in the full vibrational configuration interaction (FVCI) limit where $\langle \Lambda | = \langle \Psi | \Psi \rangle^{-1} \langle \Psi |$, we recover the equivalence with the variational formulation, but we also wish to be able to handle the general case where $\langle \Lambda |$ and $|\Psi\rangle$ are not identical and the operator is general (i.e., potentially non-Hermitian).

Any operator can be decomposed into Hermitian and anti-Hermitian parts as

$$\hat{A} = \frac{1}{2}(\hat{A} + \hat{A}^\dagger) + \frac{1}{2}(\hat{A} - \hat{A}^\dagger) \equiv \hat{A}_H + \hat{A}_{AH}, \quad (50)$$

and we can in the variational case write (for a normalized state)

$$\langle A \rangle = \langle \alpha | \hat{A}_H | \alpha \rangle + \langle \alpha | \hat{A}_{AH} | \alpha \rangle = \text{Re}[\langle \alpha | \hat{A}_H | \alpha \rangle] + i \text{Im}[\langle \alpha | \hat{A}_{AH} | \alpha \rangle]. \quad (51)$$

Inspired by the exact variational case, we redefine the CC expectation value as another possible analogy to the exact limit departing from Eq. (51) as opposed to Eq. (48),

$$\begin{aligned} \langle A \rangle &= \text{Re}[\langle \Lambda | \hat{A}_H | \Psi \rangle] + i \text{Im}[\langle \Lambda | \hat{A}_{AH} | \Psi \rangle] \\ &= \frac{1}{2}(\langle \Lambda | \hat{A}_H | \Psi \rangle + \langle \Lambda | \hat{A}_H | \Psi \rangle^*) + \frac{1}{2}(\langle \Lambda | \hat{A}_{AH} | \Psi \rangle - \langle \Lambda | \hat{A}_{AH} | \Psi \rangle^*) \\ &= \frac{1}{2}(\langle \Lambda | \hat{A} | \Psi \rangle + \langle \Lambda | \hat{A}^\dagger | \Psi \rangle^*). \end{aligned} \quad (52)$$

In the limit where $\langle \Lambda | = \langle \Psi | \Psi \rangle^{-1} \langle \Psi |$, we recover $\langle A \rangle = \langle \Psi | \hat{A} | \Psi \rangle / \langle \Psi | \Psi \rangle$ as we should. For Hermitian operators, Eq. (52) amounts to simply taking the real part of $\langle \Lambda | \hat{A} | \Psi \rangle$, i.e.,

$$\langle A \rangle = \frac{1}{2}(\langle \Lambda | \hat{A} | \Psi \rangle + \langle \Lambda | \hat{A} | \Psi \rangle^*). \quad (53)$$

The raw CC expectation value of Eq. (49) is widely used and was, for example, introduced already by Arponen³⁹ in a Lagrangian context, by Salter *et al.*⁵⁸ for electronic energy gradients, and by Koch and Jørgensen in a dual state derivation of response functions.⁴⁹ The symmetrization for Hermitian operators in Eq. (53) was introduced in Ref. 50 to ensure real expectation values and corresponding

requirements for response functions (as well as for enforcing the realness of the energy in magnetic fields). The full equation (52) was also given by Pedersen and Kvaal in Ref. 46.

The only operator under consideration in this study, which is neither purely Hermitian nor anti-Hermitian, is the (formal) time evolution (from $t' \rightarrow t$) operator $\hat{U}(t, t')$, of which we indirectly calculate expectation values when computing the autocorrelation function. Fourier transformation of correlation functions is a convenient method for obtaining time-independent properties from a wave packet evolution (see Ref. 59 for many examples).

In the exact quantum theory, the autocorrelation function $C(t, t')$ of a general time-dependent state $|\alpha\rangle$ can be expressed as

$$C(t, t') = \langle \alpha(t') | \alpha(t) \rangle = \langle \alpha(t') | \hat{U}(t, t') | \alpha(t') \rangle. \quad (54)$$

As the exact time evolution operator is unitary, this corresponds also to

$$\begin{aligned} C(t, t') &= \frac{1}{2} (\langle \alpha(t') | \hat{U}(t, t') | \alpha(t') \rangle + \langle \alpha(t') | \hat{U}^\dagger(t, t') | \alpha(t') \rangle^*) \\ &= \frac{1}{2} (\langle \alpha(t') | \alpha(t) \rangle + \langle \alpha(t) | \alpha(t') \rangle^*). \end{aligned} \quad (55)$$

In the context of coupled cluster theory, the equation analogous to Eq. (54) is

$$C(t, t') = \langle \Lambda(t') | \Psi(t) \rangle, \quad (56)$$

while the coupled cluster analogy to Eq. (55) naturally corresponds to the autocorrelation function as defined through (52),

$$C(t, t') = \frac{1}{2} (\langle \Lambda(t') | \Psi(t) \rangle + \langle \Lambda(t) | \Psi(t') \rangle^*). \quad (57)$$

Although similar in the exact limit, the terms behave differently with respect to size consistency. Hence, we study both terms *and* their average in this study.

G. Separability

The exact quantum state $|\alpha\rangle$ satisfies some, in some sense trivial, features with respect to separability of noninteracting subsystems, and somewhat related, the correct scaling of properties and wave functions with the number of degrees of freedom. Obviously, the correct behavior in this sense is a strongly desirable feature for an approximate theory that is to treat both small and large molecular systems. It is one of the hallmarks of both CC and VCC that they excel in this regard compared to competing theories. The words normally associated with this behavior are size-consistency and size-extensivity, in ways that are not always completely clear or relevant. In this section, we shall therefore primarily use the terms additive and multiplicative separability, which are somewhat in line with the use of the term size-consistency, but which are more concise for our purpose.

In the time-independent case, the correct separability for a system consisting of noninteracting subsystems, A and B, is easily established. With an additively separable Hamiltonian, $\hat{H}_{\text{tot}} = \hat{H}_A + \hat{H}_B$, the energy is additively separable, $E_{\text{tot}} = E_A + E_B$, and the quantum state is multiplicatively separable, $|\alpha_{\text{tot}}\rangle = \hat{W}_A \hat{W}_B |\text{vac}\rangle$. Here, E_I , $|\alpha_I\rangle$ (for $I = A, B$) are the ground state solutions for the respective subsystems, $\hat{H}_I |\alpha_I\rangle = E_I |\alpha_I\rangle$, with $|\alpha_I\rangle = \hat{W}_I |\text{vac}\rangle$.

Thus, $\hat{W}_I$ are the second-quantization wave-operators that generate the appropriate wave functions when acting on the vacuum, based on an appropriate linear combination of strings of creation operators. In this manner, we can write intuitive equations without specifying further whether vibrational coordinates or electrons are considered and in the latter case without further need to be explicit about particular antisymmetry. All modes/orbitals are assumed localized to the specific subsystems I . Creation and annihilation operators on different subsystems therefore commute, thereby also all operators belonging to different subsystems, $[\hat{O}_A, \hat{O}_B] = 0$.

In the time-dependent case, there are two considerations: (i) the multiplicative separability of the initial state and (ii) the additive separability (and hence decoupling) of the EOMs. For the exact case, assume that the state is product separable at *some* time t ,

$$|\alpha_{\text{tot}}\rangle = \hat{W}_A \hat{W}_B |\text{vac}\rangle. \quad (58)$$

Inserting this into the TDSE, one obtains

$$\begin{aligned} 0 &= \left(\hat{H}_{\text{tot}} - i \frac{\partial}{\partial t} \right) \hat{W}_A \hat{W}_B |\text{vac}\rangle \\ &= \hat{W}_B \left(\hat{H}_A - i \frac{\partial}{\partial t} \right) \hat{W}_A |\text{vac}\rangle + \hat{W}_A \left(\hat{H}_B - i \frac{\partial}{\partial t} \right) \hat{W}_B |\text{vac}\rangle, \end{aligned} \quad (59)$$

which upon projection with $\langle \alpha_B |$ and $\langle \alpha_A |$ (assumed normalized), respectively, produces

$$0 = \left(\hat{H}_A - i \frac{\partial}{\partial t} \right) |\alpha_A\rangle, \quad (60)$$

$$0 = \left(\hat{H}_B - i \frac{\partial}{\partial t} \right) |\alpha_B\rangle. \quad (61)$$

Consequently, if the quantum state is initially product separable, it will remain so, and the time evolution will be determined by how each subsystem evolves separately.

Note that the multiplicative separability of the quantum state ensures the additive separability of the expectation value of *any* additively separable operator $\hat{A} = \hat{A}_A + \hat{A}_B$ (not just the ground state energy usually studied in time-independent theory),

$$\begin{aligned} \langle \hat{A} \rangle &= \langle \text{vac} | \hat{W}_A^\dagger \hat{W}_B^\dagger (\hat{A}_A + \hat{A}_B) \hat{W}_A \hat{W}_B | \text{vac} \rangle \\ &= \langle \alpha_A | \hat{A}_A | \alpha_A \rangle + \langle \alpha_B | \hat{A}_B | \alpha_B \rangle, \end{aligned} \quad (62)$$

as well as the multiplicative separability of the expectation value of *any* multiplicatively separable operator $\hat{M} = \hat{M}_A \hat{M}_B$,

$$\begin{aligned} \langle \hat{M} \rangle &= \langle \text{vac} | \hat{W}_A^\dagger \hat{W}_B^\dagger \hat{M}_A \hat{M}_B \hat{W}_A \hat{W}_B | \text{vac} \rangle \\ &= \langle \alpha_A | \hat{M}_A | \alpha_A \rangle \langle \alpha_B | \hat{M}_B | \alpha_B \rangle. \end{aligned} \quad (63)$$

We now turn to the TDVCC[k] model and assume that the states $\langle \Lambda_I |$ and $|\Psi_I\rangle$ (for $I = A, B$) describe the time evolution of each subsystems, respectively. We then consider the following questions:

1. Are the initial product states $|\Psi_{\text{tot}}\rangle$ and $\langle \Lambda_{\text{tot}} |$ representable within the chosen TDVCC[k] model?
2. Can the EOMs for the total system be decoupled into EOMs for the subsystems?
3. Are expectation values of additively/multiplicatively separable operators accordingly separable?

1. Product state representations

Looking first at the initial states, we see that $|\Psi_{\text{tot}}\rangle$ is properly represented, thanks to the properties of the exponential operator,

$$\begin{aligned} |\Psi_{\text{tot}}\rangle &= e^{-i\epsilon_A} e^{T_A} \hat{W}_A^{\text{Ref}} e^{-i\epsilon_B} e^{T_B} \hat{W}_B^{\text{Ref}} |\text{vac}\rangle \\ &= e^{-i(\epsilon_A + \epsilon_B)} e^{T_A + T_B} |\Phi_{\text{tot}}\rangle, \end{aligned} \quad (64)$$

noting that the total cluster operator $T_A + T_B$ is also truncated at the k th excitation level. Here, $\hat{W}_I^{\text{Ref}}$ generates the reference state for subsystem I , and the total reference state satisfies $|\Phi_{\text{tot}}\rangle = \hat{W}_A^{\text{Ref}} \hat{W}_B^{\text{Ref}} |\text{vac}\rangle$. On the other hand, we have for the $\langle\Lambda_{\text{tot}}|$ that

$$\begin{aligned} \langle\Lambda_{\text{tot}}| &= \langle\text{vac}| (\hat{W}_A^{\text{Ref}})^\dagger (1 + L_A) e^{-T_A} e^{i\epsilon_A} (\hat{W}_B^{\text{Ref}})^\dagger (1 + L_B) e^{-T_B} e^{i\epsilon_B} \\ &= \langle\Phi_{\text{tot}}| (1 + L_A + L_B + L_{AB}) e^{-(T_A + T_B)} e^{i(\epsilon_A + \epsilon_B)}, \end{aligned} \quad (65)$$

where L_{AB} consists of all terms of the form $l_{\mu^A \mu^B}^{\text{AB}} \tau_{\mu^A}^{\text{A}} \tau_{\mu^B}^{\text{B}}$, i.e., which contains an up-to- k -mode de-excitation operator for both subsystems. We initially have $L_{AB} = L_A L_B$, and thus, $l_{\mu^A \mu^B}^{\text{AB}} = l_{\mu^A}^{\text{A}} l_{\mu^B}^{\text{B}}$. Thus, the $\langle\Lambda_{\text{tot}}|$ is generally *not* representable within the chosen TDVCC[k] method because of the partially linear parametrization of the $\langle\Lambda|$ states—the cross-term L_{AB} generally extends beyond the chosen truncation level k , up to $2k$.

The situation is not so dire yet, for as we will see momentarily, the L_{AB} does not have an impact on all of the considerations to follow. To appreciate this, we leave the offending L_{AB} term as it is, so as to note when it will and will not make a contribution in the following derivations. For a proper treatment, we also formally include a T_{AB} term consisting of excitation operators of the form $s_{\mu^A \mu^B}^{\text{AB}} \tau_{\mu^A}^{\text{A}} \tau_{\mu^B}^{\text{B}}$. It is, however, initially zero and will remain so, as we will show, which is important for the derivations to follow.

2. Decoupling of equations of motion

We next turn to the EOMs using the full system $T = T_A + T_B + T_{AB}$ and $L = L_A + L_B + L_{AB}$. We will first show that the $s_{\mu^A \mu^B}^{\text{AB}}$ are constantly zero. From the equations in Sec. II C, we get

$$\begin{aligned} 0 &= \langle\mu^A \mu^B| e^{-(T_A + T_B + T_{AB})} (\hat{H}_A + \hat{H}_B) e^{T_A + T_B + T_{AB}} |\Phi_{\text{tot}}\rangle - i s_{\mu^A \mu^B}^{\text{AB}} \\ &= \langle\mu^A \mu^B| e^{-T_{AB}} (e^{-T_A} H_A e^{T_A} + e^{-T_B} H_B e^{T_B}) e^{T_{AB}} |\Phi_A \Phi_B\rangle - i s_{\mu^A \mu^B}^{\text{AB}}. \end{aligned} \quad (66)$$

If the $s_{\mu^A \mu^B}^{\text{AB}}$ (and consequently T_{AB}) are zero initially, this leads to $\dot{s}_{\mu^A \mu^B}^{\text{AB}} = 0$, due to the commutativity of operators on different systems and the fact that $\langle\mu^A|\Phi_A\rangle = \langle\mu^B|\Phi_B\rangle = 0$. In that case, the $s_{\mu^A \mu^B}^{\text{AB}}$ will thus remain zero at all times.

Furthermore, the phase and norm controlling ϵ is additively separable,

$$\begin{aligned} \dot{\epsilon}_{\text{tot}} &= \langle\Phi_{\text{tot}}| e^{-T_A - T_{AB}} \hat{H}_A e^{T_A + T_{AB}} |\Phi_{\text{tot}}\rangle + \langle\Phi_{\text{tot}}| e^{-T_B - T_{AB}} \hat{H}_B e^{T_B + T_{AB}} |\Phi_{\text{tot}}\rangle \\ &= \langle\Phi_A| \hat{H}_A |\Phi_A\rangle + \langle\Phi_B| \hat{H}_B |\Phi_B\rangle \\ &= \dot{\epsilon}_A + \dot{\epsilon}_B, \end{aligned} \quad (67)$$

but only because $T_{AB} = 0$. We use $\tilde{H}_A = e^{-T_A} H_A e^{T_A}$ and similarly for $\tilde{H}_B$ in a hopefully obvious notation.

Using that $T_{AB} = 0$, that operators working on different subsystems commute, and that excitation operators always commute, the Euler-Lagrange equations (E-L equations) for $l_{\mu^A}^{\text{A}}$, $l_{\mu^B}^{\text{B}}$, $s_{\mu^A}^{\text{A}}$, and $s_{\mu^B}^{\text{B}}$ yield the corresponding EOMs for the individual subsystems, as they should. Finally, we derive the EOMs for the $l_{\mu^A \mu^B}^{\text{AB}}$,

$$\begin{aligned} 0 &= \langle\Phi_{\text{tot}}| (1 + L_A + L_B + L_{AB}) e^{-(T_A + T_B)} [\hat{H}_A + \hat{H}_B, \tau_{\mu^A}^{\text{A}} \tau_{\mu^B}^{\text{B}}] \\ &\quad \times e^{T_A + T_B} |\Phi_{\text{tot}}\rangle + i l_{\mu^A \mu^B}^{\text{AB}} \\ &= \langle\Phi_{\text{tot}}| (L_B + L_{AB}) [\hat{H}_A, \tau_{\mu^A}^{\text{A}}] |\mu^B\rangle + \langle\Phi_{\text{tot}}| (L_A + L_{AB}) \\ &\quad \times [\hat{H}_B, \tau_{\mu^B}^{\text{B}}] |\mu^A\rangle + i l_{\mu^A \mu^B}^{\text{AB}}. \end{aligned} \quad (68)$$

Assume that at the given point in time, L_{AB} is the product $L_A L_B$. Then, we can proceed to write

$$\begin{aligned} i l_{\mu^A \mu^B}^{\text{AB}} &= i \langle\Phi_{\text{tot}}| L_B (1 + L_A) [\hat{H}_A, \tau_{\mu^A}^{\text{A}}] |\mu^B\rangle \\ &\quad + i \langle\Phi_{\text{tot}}| L_A (1 + L_B) [\hat{H}_B, \tau_{\mu^B}^{\text{B}}] |\mu^A\rangle \\ &= i \langle\Phi_A| (1 + L_A) [\hat{H}_A, \tau_{\mu^A}^{\text{A}}] |\Phi_A\rangle l_{\mu^B}^{\text{B}} \\ &\quad + i l_{\mu^A}^{\text{A}} \langle\Phi_B| (1 + L_B) [\hat{H}_B, \tau_{\mu^B}^{\text{B}}] |\Phi_B\rangle \\ &= i l_{\mu^A}^{\text{A}} l_{\mu^B}^{\text{B}} + l_{\mu^A}^{\text{A}} l_{\mu^B}^{\text{B}} = \frac{d}{dt} (l_{\mu^A \mu^B}^{\text{AB}}). \end{aligned} \quad (69)$$

This means that for the initial product state $\langle\Lambda_{\text{tot}}|$, the L_{AB} term will at all times evolve equivalently to the product $L_A L_B$. This evolution is, in turn, completely governed by that of L_A and L_B separately. So even though the product $\langle\Lambda_{\text{tot}}|$ is not representable within the same (truncated) TDVCC[k] as was used for the subsystems, all the necessary EOMs are retained.

3. Expectation value separability

Finally, we look at expectation values for the product states

$$|\Psi_{\text{tot}}^k\rangle = e^{T_A + T_B} |\Phi_{\text{tot}}\rangle, \quad (70)$$

$$\langle\tilde{\Lambda}_{\text{tot}}^k| = \langle\Phi_{\text{tot}}| (1 + L_A + L_B) e^{-(T_A + T_B)} \quad (71)$$

such as they are represented at the truncated TDVCC[k] level and thus without the L_{AB} term. We have excluded the phase factors which cancel each other out for spatial operators, but the results are easily verified to be equivalent if including them. For the additively separable operator $\hat{A}$, we have

$$\begin{aligned} \langle\hat{A}\rangle &= \langle\Phi_{\text{tot}}| (1 + L_A + L_B) (\hat{A}_A + \hat{A}_B) |\Phi_{\text{tot}}\rangle \\ &= \langle\tilde{\Lambda}_A| \hat{A}_A |\tilde{\Psi}_A\rangle + \langle\tilde{\Lambda}_B| \hat{A}_B |\tilde{\Psi}_B\rangle, \end{aligned} \quad (72)$$

using that $L_B \hat{A}_A |\Phi_{\text{tot}}\rangle = 0$, since the de-excitation operator in L_B will give zero when applied to the B reference state. Thus, additive separability is obtained as desired. However, for the multiplicatively separable operator $\hat{M}$, we get

$$\begin{aligned} \langle\hat{M}\rangle &= \langle\Phi_{\text{tot}}| (1 + L_A + L_B) \tilde{M}_A \tilde{M}_B |\Phi_{\text{tot}}\rangle \\ &= \langle\Phi_{\text{tot}}| ((1 + L_A)(1 + L_B) - L_A L_B) \tilde{M}_A \tilde{M}_B |\Phi_{\text{tot}}\rangle \\ &= \langle\Phi_A| (1 + L_A) \tilde{M}_A |\Phi_A\rangle \langle\Phi_B| (1 + L_B) \tilde{M}_B |\Phi_B\rangle \\ &\quad - \langle\Phi_A| L_A \tilde{M}_A |\Phi_A\rangle \langle\Phi_B| L_B \tilde{M}_B |\Phi_B\rangle \\ &= \langle\tilde{\Lambda}_A| \hat{M}_A |\tilde{\Psi}_A\rangle \langle\tilde{\Lambda}_B| \hat{M}_B |\tilde{\Psi}_B\rangle - \langle\Phi_A| L_A \tilde{M}_A |\Phi_A\rangle \langle\Phi_B| L_B \tilde{M}_B |\Phi_B\rangle, \end{aligned} \quad (73)$$

where the last term breaks the multiplicative separability.

4. Separability summary

In summary, we have shown the following curious but important features of TDVCC theory:

- The $|\Psi\rangle$ state is multiplicatively separable, whereas the $\langle\Lambda|$ state is *not*.
- All EOMs decouple into those of the separate subsystems, i.e., no undue correlation is induced by the EOMs even though the functional form of the $\langle\Lambda|$ state allows for it.
- Expectation values of additively separable operators are correctly additively separable, but those of multiplicatively separable operators are generally *not* multiplicatively separable.

Many operators of interest (not just the Hamiltonian) are indeed additively separable in the limit that the subsystems are not interacting, and we are thus quite satisfied with the results, given that a time-dependent calculation often has the implied purpose of computing the evolution of expectation values throughout the simulation. As alluded to in Sec. II F, one important product separable operator, namely, the time evolution operator $\hat{U}(t, t')$, deserves special attention since the autocorrelation function is indirectly its expectation value. Of particular interest is the choice between calculating it as one of $\langle\Lambda(0)|\Psi(t)\rangle$, $\langle\Lambda(t)|\Psi(0)\rangle^*$ or their average. The discussion in Sec. II F is mostly in favor of using their average value, but from the separability analysis above, we see the merits of the former in preserving exact separability, since it evolves in time according to the $|\Psi\rangle$ state, as opposed to $\langle\Lambda|$.

A subtle point, which has not been made explicit in the derivations above, is that if the $L_A(0)$ and $L_B(0)$ of the initial state have excitation levels of k_A and k_B , with $k_A + k_B \leq k$, then $L_{AB}(0) = L_A(0)L_B(0)$ is representable within the chosen TDVCC[k] method. When the system evolves in time, this attribute will not be preserved, but again, we see that it is still sufficient for $\langle\Lambda_{\text{tot}}^k(0)|\Psi_{\text{tot}}^k(t)\rangle$ to give the correct result. A special case of this is $L_A = L_B = 0$, corresponding to the initial states being the reference state for the cluster expansion. In the general case, the contributions from the last terms of Eq. (73) can break the exact separability.

H. Imaginary time propagation

As is well-known, for variational states (including the exact limit), propagation in imaginary time, the initial quantum state will decay into the lowest-energy eigenstate with which it has a nonzero overlap. Here, we will talk about both *forwards* (τ_+) and *backwards* (τ_-) imaginary time, with the following relations to the real time t :

$$\tau_{\pm} = \pm it, \quad (74)$$

$$\frac{\partial}{\partial \tau_{\pm}} = \frac{\partial}{\partial t} \frac{\partial t}{\partial \tau_{\pm}} = \mp i \frac{\partial}{\partial t}. \quad (75)$$

Expanding the initial state in the eigenstates of the (time-independent) Hamiltonian and then evolving it in imaginary time using the time evolution operator $e^{-i\hat{H}t} = e^{-\hat{H}\tau_+}$,

$$|\alpha(\tau_+)\rangle = e^{-\hat{H}\tau_+} \sum_i c_i |\alpha_i\rangle = e^{-E_0\tau_+} \sum_i c_i e^{-(E_i-E_0)\tau_+} |\alpha_i\rangle, \quad (76)$$

which goes toward $e^{-E_0\tau_+} c_0 |\alpha_0\rangle$, provided that c_0 is nonzero and $|\alpha_0\rangle$ is the lowest-energy state having weight in the initial state (for simplicity assumed nondegenerate). Similarly, the expectation value of the energy goes toward E_0 . While this is generally not a computationally efficient way of obtaining the ground state and its energy (because dedicated solvers for the TISE are capable of much better convergence acceleration), it does provide a neat confirmation that the implementation is correct because the EOMs are identical up to a factor, but the result can be directly validated against solutions from the time-independent implementation. However, also in this context, the different structure of CC theory could raise issues. Indeed Kvaal has, for example, raised significant concerns,⁴¹ while on the other hand Sato *et al.*⁴⁴ were able to use imaginary time propagation to find the electronic ground state of time-dependent optimized coupled-cluster. We accordingly find it worth to first investigate the situation theoretically and later confirm that numerical studies gives understandable and good results.

Taking the adjoint of the TDSE and its imaginary time equivalent, we see that

$$i \frac{\partial}{\partial t} |\alpha\rangle = \hat{H} |\alpha\rangle \Rightarrow -\frac{\partial}{\partial \tau_+} |\alpha\rangle = \hat{H} |\alpha\rangle, \quad (77)$$

$$-i \frac{\partial}{\partial t} \langle\alpha| = \langle\alpha| \hat{H} \Rightarrow -\frac{\partial}{\partial \tau_-} \langle\alpha| = \langle\alpha| \hat{H}, \quad (78)$$

i.e., the bra state can be thought of as propagating in *backwards* imaginary time [as is not unreasonable since $(it)^* = -it]$. This was discussed in Ref. 41 in relation to electronic CC theory; the notation there is slightly different but reflects the same ideas. For the fixed orbital limit of the orbital adaptive time-dependent coupled cluster (OATDCC) model (in which case it is analogous to TDVCC), Kvaal remarked that one can propagate the $|\Psi\rangle$ state in (forwards) imaginary time, through the s_μ EOMs, until reaching a stationary point. This is possible because the s_μ EOMs are independent of other parameters. It is, however, unfeasible to propagate the $\langle\Lambda|$ in (backwards) imaginary time because it contains both s_μ and l_μ parameters to be propagated forwards and backwards, respectively.

In this section, we refrain from discussing the theoretical interpretation of a $\langle\Lambda|$ containing both forwards and backwards propagated parameters and instead take the pragmatic approach of showing that if the s_μ and l_μ EOMs are propagated in forwards and backwards imaginary time, respectively, then the initial $|\Psi\rangle$ and $\langle\Lambda|$ states will evolve into the bra and ket ground states of the system (as found by VCC), under suitable conditions, and with a convergence that can be understood. In other words, what we mean by the state $\langle\Lambda|$ at some imaginary time τ is actually the construct $\langle\Lambda(s_\mu(\tau_+), l_\mu(\tau_-))|$.

Let $T^{\text{gs}} = \sum_\mu s_\mu^{\text{gs}} \tau_\mu$ and $L^{\text{gs}} = \sum_\mu l_\mu^{\text{gs}} \tau_\mu^\dagger$ be solutions to the time-independent VCC ground state Lagrangian equations, i.e., for all μ ,

$$0 = \langle\mu| e^{-T^{\text{gs}}} \hat{H} e^{T^{\text{gs}}} |\Phi\rangle = e_\mu, \quad (79)$$

$$0 = \langle\Phi| (1 + L^{\text{gs}}) e^{-T^{\text{gs}}} [\hat{H}, \tau_\mu] e^{T^{\text{gs}}} |\Phi\rangle = \eta_\mu + \sum_\nu l_\nu A_{\nu\mu}. \quad (80)$$

Assume now that our initial state has parameters s_μ and l_μ that deviate from the ground state parameters by $\Delta s_\mu = s_\mu - s_\mu^{\text{gs}}$ and

$\Delta l_\mu = l_\mu - l_\mu^{\text{gs}}$. If the Δs_μ and Δl_μ go toward zero when propagating in imaginary time, then it must mean that $s_\mu \rightarrow s_\mu^{\text{gs}}$ and $l_\mu \rightarrow l_\mu^{\text{gs}}$ and hence that the initial state evolves into the ground state.

Collecting the parameters into the *column* vectors $\mathbf{s}$, $\Delta\mathbf{s}$, and the *row* vectors $\mathbf{l}$, $\Delta\mathbf{l}$, we can look at how the vector norms squared of the deviations change. For $\Delta\mathbf{s}$ and $\tau = \tau_+ = +it$, we have

$$\frac{\partial}{\partial \tau} \|\Delta\mathbf{s}\|^2 = 2 \operatorname{Re} \left[-i \Delta\mathbf{s}^\dagger \frac{\partial \Delta\mathbf{s}}{\partial t} \right] = 2 \operatorname{Re} [-i \Delta\mathbf{s}^\dagger \dot{\mathbf{s}}] = -2 \operatorname{Re} [\Delta\mathbf{s}^\dagger \mathbf{e}]. \quad (81)$$

Defining that $\tilde{H}^{\text{gs}} \equiv e^{-T^{\text{gs}}} \hat{H} e^{T^{\text{gs}}}$, we can rewrite

$$e_\mu = \langle \mu | e^{-T^{\text{gs}} - \Delta T} \hat{H} e^{T^{\text{gs}} + \Delta T} | \Phi \rangle = \langle \mu | \tilde{H}^{\text{gs}} + [\tilde{H}^{\text{gs}}, \Delta T] + \mathcal{O}(\Delta T^2) | \Phi \rangle. \quad (82)$$

The first term on the right-hand side is zero from the ground state equations. If we assume that $\Delta\mathbf{s}$, and hence ΔT , are small deviations, the last term is negligible. The remaining term contains the Jacobian matrix $\mathbf{A}^{\text{gs}}$ of the VCC error vector for the ground state amplitudes, with elements $A_{\mu\nu}^{\text{gs}} \equiv \langle \mu | [\tilde{H}^{\text{gs}}, \tau_\nu] | \Phi \rangle$, right-multiplied by the $\Delta\mathbf{s}$ vector. We therefore have

$$\begin{aligned} \frac{\partial}{\partial \tau} \|\Delta\mathbf{s}\|^2 &\approx -2 \operatorname{Re} [\Delta\mathbf{s}^\dagger \mathbf{A}^{\text{gs}} \Delta\mathbf{s}] \\ &= -\Delta\mathbf{s}^\dagger (\mathbf{A}^{\text{gs}} + \mathbf{A}^{\text{gs}\dagger}) \Delta\mathbf{s} \\ &\equiv -2\Delta\mathbf{s}^\dagger \mathbf{A}_H^{\text{gs}} \Delta\mathbf{s}, \end{aligned} \quad (83)$$

where the H subscript here denotes the Hermitian part of the matrix. Thus, if $\mathbf{A}_H^{\text{gs}}$ is positive definite (or equivalently, if its eigenvalues are all positive), then $\|\Delta\mathbf{s}\|^2$ decreases monotonically. In itself this is not a guarantee that it decreases to zero, though, but if we single out its smallest eigenvalue, $\omega_{\min}(\mathbf{A}_H^{\text{gs}})$ (still assumed >0), we may write

$$\frac{\partial}{\partial \tau} \|\Delta\mathbf{s}\|^2 \leq -2\omega_{\min}(\mathbf{A}_H^{\text{gs}}) \|\Delta\mathbf{s}\|^2, \quad (84)$$

meaning that $\|\Delta\mathbf{s}\|^2$ will at least decay exponentially fast with decay constant $2\omega_{\min}$, so it *will* go to zero.

For the derivation for $\Delta\mathbf{l}$, we first observe that since the s_μ EOMs are independent of the l_μ , $s_\mu \rightarrow s_\mu^{\text{gs}}$, regardless of how the l_μ evolve in the meantime. We can therefore do the derivation for $\Delta\mathbf{l}$ from a point where $T = T^{\text{gs}} + \mathcal{O}(\Delta T) \approx T^{\text{gs}}$ and remark that since the EOMs are linear in the l_μ we need not assume $\Delta\mathbf{l}$ to be small as we had to for $\Delta\mathbf{s}$. Following the same arguments, but now with $\tau = \tau_- = -it$, we obtain

$$\begin{aligned} \frac{\partial}{\partial \tau} \|\Delta\mathbf{l}\|^2 &= -2 \operatorname{Re} [(\boldsymbol{\eta} + \mathbf{lA}) \Delta\mathbf{l}^\dagger] \\ &\approx -2 \operatorname{Re} [(\boldsymbol{\eta}^{\text{gs}} + (\mathbf{l}^{\text{gs}} + \Delta\mathbf{l}) \mathbf{A}^{\text{gs}}) \Delta\mathbf{l}^\dagger] \\ &= -2 \operatorname{Re} [\Delta\mathbf{lA}^{\text{gs}} \Delta\mathbf{l}^\dagger] \\ &= -2\Delta\mathbf{lA}_H^{\text{gs}} \Delta\mathbf{l}^\dagger \\ &\leq -2\omega_{\min}(\mathbf{A}_H^{\text{gs}}) \|\Delta\mathbf{l}\|^2, \end{aligned} \quad (85)$$

showing that $\|\Delta\mathbf{l}\|^2$ will also decay at least exponentially fast, with decay constant $2\omega_{\min}$, toward zero.

To summarize, we have shown that *if* the initial state has cluster amplitudes s_μ that deviate sufficiently little from those of the ground state solution, and *if* the Jacobian of the ground state VCC error vector has a positive definite Hermitian part, with

its smallest eigenvalue being $\omega_{\min}(\mathbf{A}_H^{\text{gs}})$, *then* propagating the s_μ and l_μ EOMs in forwards and backwards imaginary time, respectively, will evolve the initial state into the VCC ground state solution.

The only remaining question is then under which conditions $\mathbf{A}_H^{\text{gs}}$ is positive definite. The vibrational and electronic CC community has solid experience in dealing with the real CC error vector Jacobian ($\mathbf{A}^{\text{gs}}$), since it occurs in CC response theory. Here, (the real part of) its eigenvalues can be interpreted as the excitation energies. These should be inherently *positive* as long as the ground state is used as reference and it is nondegenerate. Indeed, the experience is that the eigenvalues of $\mathbf{A}^{\text{gs}}$ are usually purely real for the lowest lying states and/or well-separated states for which convergence of the CC equations corresponds to a correct physical description of the states. In these cases, the cluster amplitudes are often not too large and the Jacobian is dominated by the Hermitian part that will be positive definite for a physically correct ground state reference description.

While we are not aware of any relations between the eigenvalues of a general matrix and its Hermitian part that are directly useful in our case, there exist *some* characterizations.⁶⁰ One of these is the relation

$$\omega_{\min}(\mathbf{A}_H^{\text{gs}}) = \min_{\|\mathbf{v}\|=1} \mathbf{v}^\dagger \mathbf{A}_H^{\text{gs}} \mathbf{v} = \min_{\|\mathbf{v}\|=1} \operatorname{Re} [\mathbf{v}^\dagger \mathbf{A}^{\text{gs}} \mathbf{v}], \quad (86)$$

where the first equality is the variational principle. Taking $\mathbf{v}$ to be the eigenvector of $\mathbf{A}^{\text{gs}}$ with the smallest eigenvalue, we obtain the relation $\omega_{\min}(\mathbf{A}_H^{\text{gs}}) \leq \operatorname{Re}[\omega_{\min}(\mathbf{A}^{\text{gs}})]$. This *upper* bound obviously does little good in establishing whether $\omega_{\min}(\mathbf{A}_H^{\text{gs}}) > 0$, but based on the aforementioned experience of diagonally dominant Jacobians with purely real eigenvalues, it is tempting to speculate that the two eigenvalues are actually approximately equal, $\omega_{\min}(\mathbf{A}_H^{\text{gs}}) \approx \omega_{\min}(\mathbf{A}^{\text{gs}})$, for cases with physically relevant converged cluster amplitudes (as will be somewhat supported by the results in Sec. IV B).

Of course, this is not a strict mathematical proof, but rather a conjecture that for well-behaved molecular systems $\mathbf{A}_H^{\text{gs}}$ will be positive definite with a smallest eigenvalue similar to that of $\mathbf{A}^{\text{gs}}$. The propagation in imaginary time will accordingly be convergent, and in the final phase of convergence, the behavior will be dictated, to a reasonable approximation, by the lowest root of the Jacobian of the converged VCC error vector.

III. IMPLEMENTATION

The TDVCC method has been implemented in the Molecular Interactions, Dynamics And Simulations Chemistry Program Package (MidasCpp)⁶¹ for the special case of VCC[2]/H2. Note that the right-hand sides of the EOMs [Eqs. (26) and (27)] contain the exact same expressions as that occur in time-independent VCC ground state calculations, except for the fact that all quantities can be taken to be real in the time-independent case, while they need to be complex in the time-dependent one. The detailed VCC[2]/H2 ground state amplitude and multiplier equations have been published before (see Refs. 62 and 63). A key component of the implementation was to generalize the original implementation to accommodate complex numbers including complex integrals and parameters, but otherwise follows the strategy of the previous

work with respect to intermediates, etc. We will accordingly spare those details and refer to these original works^{62,63} for evaluation of the relevant energies and expectation values, and only note that the key computational bottleneck derives from the operations described there. Altogether, from Refs. 62 and 63, we conclude the EOM contributions for TDVCC[2] (and TDVCI[2]) have a computational cost with leading terms increasing like $\mathcal{O}(M^3N^2)$

and $\mathcal{O}(M^2N^3)$ with the number of modes M and the number of modals per mode N_m (here assumed identical to N for all modes).

The evaluation of the autocorrelation function has not been discussed before, but is fairly easy to achieve in the 2M case. We will here describe briefly how to compute Eq. (53) (the other forms proceed analogously),

$$\begin{aligned}\langle \Lambda(t') | CC(t) \rangle &= \langle \Phi | (1 + L(t')) \exp(-T(t')) \exp(T(t)) | \Phi \rangle \exp(i(\epsilon(t') - \epsilon(t))) \\ &= \langle \Phi | (1 + L(t')) \exp(T(t) - T(t')) | \Phi \rangle \exp(i(\epsilon(t') - \epsilon(t))) \\ &= (1 + \langle \Phi | (L(t')) \exp(T'(t, t')) | \Phi \rangle) \exp(i(\epsilon(t') - \epsilon(t))) \\ &= \left(1 + \sum_v \langle \Phi | L(t') | v \rangle \langle v | \exp(T'(t, t')) | \Phi \rangle \right) \exp(i(\epsilon(t') - \epsilon(t))) \\ &= \left(1 + \sum_v L_v C'_v(t, t') \right) \exp(i(\epsilon(t') - \epsilon(t))).\end{aligned}\quad (87)$$

Here, $T(t) - T(t') = T'(t, t')$ and C is the CI-expansion amplitude of the corresponding VCC state if it was expanded into a linear form

$$C'_v(t, t') = \langle v | \exp(T'(t, t')) | \Phi \rangle. \quad (88)$$

In the case of two-mode couplings, these CC to CI transforms are particularly easy to compute ($c_{a^{m_1}}^{m_1} = t_{a^{m_1}}^{m_1}$, $c_{a^{m_1}a^{m_2}}^{m_1m_2} = t_{a^{m_1}a^{m_2}}^{m_1m_2} + t_{a^{m_1}}^{m_1}t_{a^{m_2}}^{m_2}$).

The TDVCC module was implemented to interact with the rest of MidasCpp such that it can obtain and run with the modals from any prior VSCF calculation, and its initial state can be either the corresponding VSCF state (which corresponds to setting all parameters to zero in the TDVCC *ansatz*) or the ground state of a prior VCC calculation.

For assessing the performance of TDVCC, a TDVCI module was similarly implemented, using a linear parameterization,

$$|VCI(t)\rangle \equiv \sum_{\mu} c_{\mu}(t) \tau_{\mu} | \Phi \rangle \equiv \sum_{j=0}^k C_j(t) | \Phi \rangle, \quad (89)$$

where $C_j(t)$ consists of all terms exciting in j modes. From the TDSE, one comparatively trivially obtains the EOMs, $\dot{c}_{\mu}(t) = \langle \mu | \hat{H} | VCI(t) \rangle$. In the untruncated limit, where k equals the number of modes, the full Hartree-product space is spanned, making the TDVCI[k] model exact within the chosen modal basis, as was also mentioned in Sec. I. In this limit, we shall refer to the state as $|FVCI(t)\rangle$ and to the model as time-dependent full vibrational configuration interaction (TDFVCI).

The ordinary differential equation (ODE) integration reuses the general-purpose routines introduced by Madsen *et al.* in Ref. 14 for integrating the TDH equations, which can easily be tailored to handle the various TDVCC EOMs. As in Ref. 14, we use the Dormand-Prince 8(5,3) explicit Runge-Kutta method. It is possible to run with both fixed and adaptive step-size, the latter meaning that we at the onset define an integration tolerance, and the ODE driver then adaptively determines a suitable step length based

on the error estimate from the stepper method. This ODE tolerance is defined as in Ref. 64, and both absolute and relative tolerances can be used. The ODE module is also able to interpolate points in between the actual steps, yielding equidistant points as required for using the fast Fourier transform (FFT) for obtaining spectra from autocorrelation functions. At each step (actual or interpolated), it is an option to compute and save expectation values of arbitrary operators (e.g., for the Hamiltonian, dipole, position, and/or momentum operators), autocorrelation functions, and details about the norms of the vibrational state parameters, their difference with the initial ones or with a precalculated VCC ground state.

IV. RESULTS

A. Computational details

We have tested the TDVCC on various molecular systems, ranging from 2 to 156 modes.

For directly comparing the TDVCC method with TDFVCI, we are restricted to studying 2-dimensional systems. For this purpose, we have used a 2-dimensional Henon-Heiles (2D-HH) potential; the M -mode Henon-Heiles (HH) Hamiltonian operator takes the form

$$\hat{H} = -\frac{1}{2} \sum_{m=1}^M \frac{\partial^2}{\partial q_m^2} + \frac{1}{2} \sum_{m=1}^M q_m^2 + \lambda \sum_{m=1}^{M-1} \left(q_m^2 q_{m+1} - \frac{1}{3} q_{m+1}^3 \right), \quad (90)$$

where we used $\Lambda = 0.111803$, as has also been done in Ref. 14 where further discussion and references are given for HH potentials.

For small, yet physically relevant, molecular systems, we have performed calculations on water and formaldehyde. The corresponding potential energy surfaces (PESs) are some of those computed in Ref. 65. The chosen functional form is a sum-over-products of polynomial terms containing at most two different modes, thus resulting in a 2-mode coupled operator suitable for our current

TDVCC implementation. Each term in the fit was allowed to have a polynomial order of up to 10 (included).

For studying the scaling of TDVCC with respect to the number of modes, we have performed calculations on a series of PAHs, described in Ref. 66.

All calculations employ a primitive B-spline basis, which are then used in a VSCF calculation for generating the (time-independent) modal basis to be used in the time-dependent calculations. In most cases, the initial state is the resulting VSCF reference state, except for Sec. IV F where we use the ground state of an ensuing VCC calculation.

In most calculations (except for the ones in Sec. IV E), we have used adaptive step-size control, with the relative and absolute ODE tolerances being equal to each other.

B. Propagation in imaginary time

In order to validate the implementation as well as to study the theoretical points made in Sec. II H, we have simulated imaginary time propagation for the water, formaldehyde, benzene (PAH1), and naphthalene (PAH2) molecules, as well as for the 2-dimensional Henon-Heiles potential.

In all cases, the VSCF was first used to find a suitable modal basis and an initial state for the systems. Then, the time-independent VCC equations were solved, both for ground state and response, in order to obtain the target s_μ and l_μ parameters that we theoretically should obtain. We used 6 VSCF-modals per mode as the modal basis in the VCC and TDVCC calculations. The VSCF and VCC equations were tightly converged to $1.00 \cdot 10^{-15}$ (around machine precision) for the VSCF energy change, the VCC error vector norm, and the VCC response residual norm.

Having set up the modal basis, initial state, and the target VCC ground state (for comparison), a TDVCC[2] was run in imaginary time with an ODE tolerance of $1.00 \cdot 10^{-16}$. The simulation was then set to terminate when the combined derivative norm $[(\|\dot{\mathbf{s}}\|^2 + \|\dot{\mathbf{l}}\|^2)^{1/2}]$ would fall below $1.00 \cdot 10^{-15}$. At each time step, the energy E_V was stored, as well as the norms of the deviations of the current parameters from the target VCC ground state parameters, $\|\Delta \mathbf{s}\|$ and $\|\Delta \mathbf{l}\|$.

Figure 1 shows the convergence of $|\Delta E_V| = |E_V - E_V^{\text{gs}}|$, $\|\Delta \mathbf{s}\| = \|\mathbf{s} - \mathbf{s}^{\text{gs}}\|$, and $\|\Delta \mathbf{l}\| = \|\mathbf{l} - \mathbf{l}^{\text{gs}}\|$ toward zero for formaldehyde. Convergence for 2D-HH, water, and the PAHs is seen in the supplementary material. We observe that in all cases the parameter

FIG. 1. Convergence of TDVCC parameters toward VCC ground state solutions, when propagating the EOMs in imaginary time, for formaldehyde. The dotted lines are $\exp(-k_x \tau)$ fits. See the [supplementary material](#) for 2D-HH, water, PAH1, and PAH2 results.

convergences are very systematic and at some point enter a region where they decay exponentially (linearly on the logarithmic scale plots). First of all, this is a confirmation that the implementation works as intended—we are indeed able to obtain the VCC ground state solution through propagation in imaginary time. As a consequence of the convergence of the s_μ and l_μ parameters, the energy naturally converges to the VCC ground state energy as well.

Furthermore, the fact that we in the last part of the simulations observe pure exponential decay is in agreement with the derivations in Sec. IV B. Taking the analysis a step further, we have for each system fitted an exponential decay function $\|\Delta \mathbf{x}\|(\tau) \propto \exp(-k_x \tau)$ ($\mathbf{x} = \mathbf{s}, \mathbf{l}$) to the data for the *last* half of the time period, where all systems have entered the final exponential decay region (based on visual inspection of the plots).

This allowed us to extract the decay constants k_x , which from our derivations should equal the minimum eigenvalue of the Hermitian part of the Jacobian matrices, of which the initial state has a nonzero component. The last remark is important, since for a symmetric molecule, we may start out with a symmetric initial VSCF state, meaning that the eigenvalue determining the decay constant will be the one for the lowest totally symmetric excitation.

Table I shows our findings; the fitted decay constants and the minimum eigenvalues are in good agreement, generally to within

TABLE I. Comparison of exponential decay constants, k , and smallest excitation energies for totally symmetric transitions, $\omega_{\min}^{A_1}$ (except for the PAHs where it is the lowest of any symmetry). Decay constants are obtained from a $\|\Delta \mathbf{x}\| \propto \exp(-k_x \tau)$ fit (with $\mathbf{x} = \mathbf{s}, \mathbf{l}$) to the *last* half of the time period. Excitation energies are shown for the Jacobian $\mathbf{A}^{\text{gs}}$ and for its Hermitian part $\mathbf{A}_H^{\text{gs}}$ where it was feasible to calculate. Relative deviations are with respect to the excitation energy of $\mathbf{A}_H^{\text{gs}}$ in the latter case, otherwise with respect to those of $\mathbf{A}^{\text{gs}}$.

System	$\omega_{\min}^{A_1}(\mathbf{A}^{\text{gs}})/\text{a.u.}$	$\omega_{\min}^{A_1}(\mathbf{A}_H^{\text{gs}})/\text{a.u.}$	$k_s/\text{a.u.}$	$k_l/\text{a.u.}$	$\Delta_{\text{rel}} k_s/\%$	$\Delta_{\text{rel}} k_l/\%$
2D-HH	$9.914\,83 \times 10^{-1}$	$9.914\,82 \times 10^{-1}$	$9.914\,84 \times 10^{-1}$	$9.890\,63 \times 10^{-1}$	0.0002	−0.2440
H ₂ O	$7.235\,44 \times 10^{-3}$	$7.235\,41 \times 10^{-3}$	$7.235\,44 \times 10^{-3}$	$7.235\,07 \times 10^{-3}$	0.0004	−0.0047
H ₂ CO	$6.849\,51 \times 10^{-3}$	...	$6.849\,60 \times 10^{-3}$	$6.843\,02 \times 10^{-3}$	0.0013	−0.0947
PAH1	$1.682\,79 \times 10^{-3}$	...	$1.684\,70 \times 10^{-3}$	$1.683\,12 \times 10^{-3}$	0.1135	0.0197
PAH2	$8.031\,09 \times 10^{-4}$	...	$8.092\,49 \times 10^{-4}$	$8.084\,05 \times 10^{-4}$	0.7645	0.6595

1% in relative deviation, and better yet for most cases. For formaldehyde (H_2CO), the reported $\omega_{\min}^{\text{AI}}$ is actually the third-lowest excitation energy—this signifies that the initial state had no nontotally symmetric components. For the PAHs, the decay constant is in agreement with the lowest-lying eigenvalue, which is, however, *not* for a totally symmetric excitation—this is due to a small amount of symmetry-breaking noise in the PES.

We also observe that the decay constants can be slightly smaller than those allowed by theory. Based on an in-depth inspection of the evolution of the parameters, we ascribe this to numerical difficulties in the final parts of the ODE integration; as the integrator approaches convergence, it has to make increasingly smaller corrections to the parameters (of finite size), meaning that round-off errors become increasingly problematic, slowing down the convergence. Similarly, difference norm computations involve differences of increasingly similar nonzero numbers, meaning that increasingly more precision is lost to round-off errors.

In summary, we have seen that the propagation of the TDVCC EOMs in imaginary time is a feasible method for obtaining the VCC ground state of the given system. Additionally, the exponential decay constants are in good agreement with the lowest excitation energies of the molecular systems. Both of these observations are as predicted by our theoretical derivations. We have not mentioned computational timings, but it should be noted that the convergence is generally computationally *slow*, especially for the larger molecules, where the low-lying excitation energies are predominant and lead to small decay constants—so the convergence-accelerated methods of time-independent VCC are still much preferable.⁶⁷

C. Comparison with the exact limit in a 2-mode system

With the results from propagation in imaginary time reassuring us that the implementation works as intended, we next set out to study the correspondence between FVCI and TDVCC[k] in the FVCI limit, i.e., where $k = M$ and the TDVCC[k] is thus untruncated. Given the very different parameterizations and EOMs for TDVCC and FVCI, it is by no means trivial that the two should describe the same time evolution. However, they both span the same space (provided that the state has a nonzero overlap with the reference state), and their EOMs are derivable from the same time-dependent (bi)variational principle, so from theory we do expect them to be equivalent. This is what we confirm numerically in this subsection.

With our current implementation only being able to handle $k \leq 2$, we restrict ourselves to the 2D-HH system. The HH potentials are generally unbounded due to the odd-order polynomial terms, but we have restricted our primitive B-spline basis to $(q_0, q_1) \in [-7.50; 7.50] \times [-6.00; 9.00]$. In practice, this amounts to inserting infinitely steep walls at these boundaries, which approximately correspond to where the saddle-points of the 2D-HH potential are located. Figure 2 illustrates the part of the potential that is within the boundaries. For generating an initial state, we have solved for the VSCF ground state for a similar PES containing *only* the harmonic contributions and whose equilibrium point is displaced by (0.50, 0.50). The modal from this calculation is then used as the modal basis in the following TDVCC time evolution. Effectively, this

FIG. 2. Contour plot of the 2D-HH PES. Thin and thick contour lines are $0.10 E_h$ and $1.00 E_h$ apart, respectively. The entire plotted region corresponds to our chosen primitive basis boundaries and approximately extends to the saddle-points of the PES. The extent of our chosen modal basis (10 modals per mode) is shown by the shaded region; its borders are at the classical turning points of the highest-lying modal of each mode. The dot indicates the center of the Gaussian wavepacket used as the initial state, while the radius of the enclosing circle equals the classical turning point of the Gaussian.

means that the initial state is (to a very good approximation) a Gaussian wavepacket, displaced by (0.50, 0.50) from the minimum of the PES used for time evolution, and that the TDVCC state is propagated using a modal basis consisting of the corresponding one-mode eigenstates that are very good approximations to harmonic oscillator eigenfunctions. Obviously, the modal basis is therefore displaced with respect to the PES minimum, as also illustrated in Fig. 2. Note that this is suboptimal in that it provides uneven descriptions of the state depending on its position relative to the minimum. Using a time-evolving basis could obviously be a more accurate and economical approach, but this topic is deferred to a later work. In any case, the modal basis consists of 10 modals per mode—as is shown in Fig. 2, the extent of the modal basis should be adequate for spanning the region in which the wavepacket moves. Furthermore, for the present purpose of comparing TDVCC against FVCI, this is not an issue, since both models evolve in the same fairly reasonable modal basis.

The initial state was integrated for a time period of 1000 a.u., using ODE tolerances ranging from $1.00 \cdot 10^{-4}$ (loose) to $1.00 \cdot 10^{-15}$ (tight). For comparison, the simulations were carried out using both TDVCC[2] and time-dependent VCI[2]. The latter is of course FVCI, but we will here reserve the FVCI label for the VCI[2] calculation with the tightest tolerance ($1.00 \cdot 10^{-15}$), which we will then take to be the (near-exact) reference for comparisons. At each time step of the simulation properties such as energy, autocorrelation function, position, and momentum, expectation values were saved. Additionally, the $|\Psi\rangle$ and $\langle A \rangle$ state parameters were converted to FVCI parameterizations, allowing for direct comparisons with the FVCI solution at each point in time, as

well as for monitoring the norm $N_\Psi = \|\Psi\| = \langle \Psi | \Psi \rangle^{1/2}$ discussed in Sec. II E.

From the theoretical derivations, we expect energy to be conserved generally (for a time-independent operator) and the norms (squared) to be conserved in the FVCI limit studied here. For assessing the degree of conservation, we look at the maximal deviation of the given property A between any two points in time during the simulation,

$$\Delta_{\max} A \equiv \max_t A - \min_t A. \quad (91)$$

For assessing the equivalence between some state $|\alpha\rangle$ and the |FVCI⟩ state, we normalize the two and then look at the norm of their difference,

$$|\Delta_{\text{FVCI}}\alpha(t)\rangle \equiv \frac{1}{\sqrt{\langle \alpha(t) | \alpha(t) \rangle}} |\alpha(t)\rangle - \frac{1}{\sqrt{\langle \text{FVCI}(t) | \text{FVCI}(t) \rangle}} |\text{FVCI}(t)\rangle, \quad (92)$$

$$\|\Delta_{\text{FVCI}}\alpha(t)\| = \sqrt{\langle \Delta_{\text{FVCI}}\alpha(t) | \Delta_{\text{FVCI}}\alpha(t) \rangle}, \quad (93)$$

where $|\alpha(t)\rangle$ is either of the VCC states $|\Psi(t)\rangle$ or $|\Lambda(t)\rangle$, or $|\text{VCI}(t)\rangle$, the latter, in principle, also being FVCI but from a calculation with a looser ODE tolerance. The reason we choose to normalize is that we already look at conservation of the $\langle \alpha | \alpha \rangle^{1/2}$ norms separately; hence, this comparison is purely regarding the orientations of $|\alpha(t)\rangle$ in the FVCI vector space. We then condense the difference norms from the entire simulation down to the single number $\Delta_{\max} \|\Delta_{\text{FVCI}}\alpha\|$ as prescribed by Eq. (91).

Figures 3–5 show $\Delta_{\max} E_V$, $\Delta_{\max} \|\alpha\|^2$, and maximum and average values of $\|\Delta_{\text{FVCI}}\alpha\|$, respectively, for $|\alpha\rangle = |\Psi\rangle$, $|\Lambda\rangle$, $|\text{VCI}\rangle$, and different choices of ODE tolerance. For the energy, both the maximal real and imaginary deviations are shown. We observe that the energy and $\langle \Psi | \Psi \rangle^{1/2}$ norm are increasingly better conserved when tightening the ODE tolerance and that the conservation errors are generally on the same order of magnitude as those of the VCI calculations. We are therefore rather confident that conservation errors are due to the expected inaccuracies in the numerical integration of the EOMs, not due to flaws in the theory or implementation.

FIG. 3. The maximal deviation in (real and imaginary) energy expectation values throughout TDVCC and TDVCI simulations. Note that the VCI expectation value is real by construction.

FIG. 4. The maximal deviation in norms squared throughout TDVCC and TDVCI simulations.

The same conclusions apply to the deviations from the tightly integrated FVCI state, meaning that in the FVCI limit $\langle \Lambda |$ and $|\Psi\rangle$ does indeed evolve as $\langle \text{FVCI} |$ and $|\text{FVCI}\rangle$ despite the very different EOMs.

Having demonstrated the possibility of error control through the choice of ODE tolerance, we only look at the most tightly integrated TDVCC calculation for the remainder of this section, in order to study the time evolution in greater detail.

Figure 6 shows the deviation of the energy from its initial value over time. The imaginary part remains comparatively close to its initial value of zero, as it should, while there is a rather systematic gradual loss of the real part of the energy through the entire integration. This is, of course, principally undesirable, and we note here that the use of a symplectic integration scheme could remedy this, such as proposed in, e.g., Ref. 46. As demonstrated above, however, we have error control even when using our nonsymplectic integrator, and given that an energy loss on the order of 10^{-14} is very modest

FIG. 5. The maximal and average deviations from the FVCI state throughout the simulation, as measured by the norm of the difference between the states and the FVCI state. For the latter, the VCI calculation with the tightest ODE tolerance ($1.00 \cdot 10^{-15}$) is used. Note that the $|\Psi\rangle$ and $|\Lambda\rangle$ are nearly on top of each other.

FIG. 6. Energy expectation values relative to the initial value $E_V(0) = 1.26 E_h$. TDVCC[2] on 2D-HH potential with ODE tolerance $1.00 \cdot 10^{-15}$.

compared to the initial energy $1.26 E_h$, we are not concerned by this.

Figure 7 shows the evolution of the norms of the TDVCC parameters over time. They are initially zero and then oscillate in magnitude with an oscillation period of about 6 a.u. Looking at the contour plot in Fig. 2, we would indeed expect the state to oscillate back and forth across the minimum, periodically getting close to its initial state, but not exactly due to the anharmonicities of the PES. The observed oscillation period is in good agreement with the oscillations being dominated by the lowest excitation energy gap which is at about $1 E_h$, giving an oscillation period of around 2π a.u. ≈ 6 a.u. Obviously, other energy differences are important as well, as is seen by the long-term changes in the parameter norms. Note that the parameter norms of magnitude 1 in this calculation are actually rather large compared to what is obtained in time-independent VCC ground state calculations, where the cluster amplitude norms are usually orders of magnitude smaller than 1. It is positive to see the TDVCC nevertheless being able to handle the time evolution even when the VSCF reference is *not* a dominating contribution to the state.

FIG. 7. Norms of parameter vectors, $\mathbf{s}$ and $\mathbf{l}$. TDVCC[2] on 2D-HH potential with ODE tolerance $1.00 \cdot 10^{-15}$. See the [supplementary material](#) for entire time period.

FIG. 8. Magnitude and real and imaginary parts of the TDVCC[2] autocorrelation function $\frac{1}{2}(\langle \Lambda(0) | \Psi(t) \rangle + \langle \Lambda(t) | \Psi(0) \rangle^*)$. Both terms are practically equal. See the [supplementary material](#) for entire time period and difference between the terms.

Finally, we turn to the autocorrelation function, part of which is plotted in Fig. 8. Not surprisingly, we see oscillations similar to those for the parameter norms. Of particular interest is whether the two terms $\langle \Lambda(0) | \Psi(t) \rangle$ and $\langle \Lambda(t) | \Psi(0) \rangle^*$ are equal, such as they should be in the FVCI limit, as we discussed in Sec. II F. As seen in the [supplementary material](#), the largest discrepancies are of order 10^{-14} (see the [supplementary material](#)), so we conclude that this is indeed the case.

In short, we have established the equivalence of the TDVCC-parameterized $|\Psi\rangle$ and $\langle \Lambda|$ states with the FVCI state in the FVCI limit, as well as demonstrated the possibility of obtaining increasingly good energy and $\langle \Psi | \Psi \rangle^{1/2}$ norm conservation by adjusting the ODE tolerance.

D. Separability

In this subsection, we seek to illustrate the theoretical predictions set forth in Sec. II G. For allowing a direct comparison with the FVCI solution, we perform calculations on two *uncoupled* 2D-HH potentials equal to the ones used in Sec. IV C. The Hamiltonian is then additively separable, and since each subsystem only contains 2 modes, we expect the TDVCC[2] and FVCI solutions to be in agreement to the extent described in Sec. II G.

The computational setup is as in Sec. IV C, with the initial state having its center at (0.50, 0.50) in both subsystems. The modal basis also generally contains 10 modals per mode, the only exception being for the calculations in which we measure FVCI norms and compare $|\Psi\rangle$ and $\langle \Lambda|$ with the FVCI state. The reason for this is that the conversions of the former two to FVCI parametrization at *each* time step is *very* slow, since it is affected by the curse of dimensionality. Such conversions are not necessary in standard computations, but we are here interested in looking at wave functions in some detail to compare with the theory. As also remarked in Sec. IV C, the size of the modal basis does not have any impact with regard to the FVCI comparisons, since all methods evolve using the same basis. The simulation time is also reduced to 100 a.u. in these calculations.

FIG. 9. The maximal and average deviations from the FVCI state throughout the simulation, as measured by the norm of the difference between the states and the FVCI state (5 modals per mode, 100 a.u. simulation time).

For the FVCI state, we have evolved a time-dependent VCI[4] state with ODE tolerance $1.00 \cdot 10^{-15}$. In addition to the TDVCC[2] calculations, we have also evolved VCI[2] states under the same conditions, in order to illustrate the shortcomings of VCI.

Figure 9 shows the maximum and average values of $\|\Delta_{\text{FVCI}}\alpha\|$ for the different wave functions $|\alpha\rangle = |\Psi\rangle, |\Lambda\rangle, |\text{VCI}\rangle$ and different choices of ODE tolerance, in the same manner as in Fig. 5. In contrast to Fig. 5, we now see that only $|\Psi\rangle$ is equivalent to $|\text{FVCI}\rangle$ throughout the simulation, which is, however, in agreement with our derivations in Sec. II G 1. As in Sec. IV C, we again see that the agreement with FVCI is systematically controllable through the choice of ODE tolerance, and we therefore restrict ourselves to looking at the calculations with tight $1.00 \cdot 10^{-15}$ ODE tolerance for the remainder of this subsection.

In Fig. 10, we show how the respective $\|\Delta_{\text{FVCI}}\alpha\|$ evolve over time. They all start out at zero, all states being equal to the initial VSCF state, and then quickly diverge in the case of the $|\text{VCI}\rangle$ and $|\Lambda\rangle$

FIG. 10. The evolution of the deviation from the FVCI state throughout the simulation, as measured by the norm of the difference between the states and the FVCI state (5 modals per mode, 100 a.u. simulation time, ODE tolerance $1.00 \cdot 10^{-15}$).

states. Both of these show some oscillatory behavior, especially for $\langle\Lambda\rangle$, which we will also revisit when discussing the autocorrelation functions. For $|\Psi\rangle$, the divergence increases but remains small, as theoretically expected.

The discussion so far confirms our statements about the product separability for $|\Psi\rangle$ and the lack thereof for $\langle\Lambda\rangle$ (and $|\text{VCI}\rangle$). We then turn to the important point of calculating expectation values. Figure 11 shows the time evolution of $\langle q_0 \rangle$, $\langle q_0 + q_2 \rangle$, and $\langle q_0 q_2 \rangle$ as calculated by the TDFVCI, TDVCI[2], and TDVCC[2] methods.

FIG. 11. TDFVCI, TDVCI[2], and TDVCC[2] expectation values for q_0 (top), $q_0 + q_2$ (middle), and $q_0 q_2$ (bottom). Note that the TDVCC[2] expectation values lie on top of the FVCI ones in the upper two plots.

FIG. 12. FVCI, VCI[2], and TDVCC[2] autocorrelation functions; real and imaginary parts marked with solid and dashed lines, respectively. The subscripts A and B denote the two terms in the TDVCC autocorrelation functions, with A being $\langle \Lambda(0) | \Psi(t) \rangle$ and B being $\langle \Lambda(t) | \Psi(0) \rangle^*$. Note that the former is on top of the FVCI one. See the [supplementary material](#) for entire time period.

In agreement with our derivations, we see that the TDVCC[2] are indeed able to reproduce the TDFVCI results for the additively separable operators, *despite* the $\langle \Lambda |$ not being product separable. As expected, it is *not* able to reproduce the results for the multiplicatively separable $q_0 q_2$ operator, though. The VCI[2] state (also not product separable) produces completely wrong results, both in terms of oscillation magnitude and frequency, not only for $\langle q_0 + q_2 \rangle$ and $\langle q_0 q_2 \rangle$ but also for the single subsystem operator q_0 .

Finally, we turn to the autocorrelation functions, which are shown in Fig. 12. We see that the one from VCI[2] is generally wrong compared to FVCI, while the $\langle \Lambda(0) | \Psi(t) \rangle$ term from TDVCC[2] is correct, as also predicted in Sec. II G 4, since our initial state has $L_A = L_B = 0$.

The $\langle \Lambda(t) | \Psi(0) \rangle^*$ is generally incorrect, also as expected, although it has the interesting feature that it recovers every period, when the state comes close to the initial VSCF state. It is, however, uncertain whether this behavior will generally be observed or whether it is just a consequence of the present choice of system and initial state. As such, $\langle \Lambda(t) | \Psi(0) \rangle^*$, and hence also the average in Eq. (57), suffer from significant problems due to $\langle \Lambda |$ not being product separable. This points out to $\langle \Lambda(0) | \Psi(t) \rangle$ as the more natural choice for the TDVCC autocorrelation function, but an elaborate study is required to completely settle this.

To summarize, we have confirmed our theoretical predictions that $|\Psi\rangle$ is product separable while $\langle \Lambda |$ is not, but that additively separable expectation values are calculated correctly. Furthermore, VCI is seen to fail dramatically in both regards.

E. Computational scaling

While we have so far looked at low-dimensional systems, our implementation can handle much larger systems, which we now demonstrate in a study of the computational scalings of TDVCC[2] for computations on the series of PAHs.

As discussed in Sec. III, the TDVCC[2] and the TDVCI[2] implementations are expected to have computational costs with leading terms scaling as $\mathcal{O}(M^3 N^2)$ and $\mathcal{O}(M^2 N^3)$ with respect to the number of modes M and the number of modals per mode N_m .

The computational timings for computations on different systems and setups are obviously proportional to the cost of computing such a full set of contributions to the EOMs, but also the number of times such computations are required as dictated by the ODE integrator is a factor, and in the adaptive case, this could vary. We have therefore here chosen to integrate with a fixed step-size, in order to achieve a cleaner comparison of timings across TDVCC and TDVCI and different choices of M and N_m . A fixed step-size of 3.0 a.u. was picked since adaptive step-size computations on PAH1-3 with tight ODE tolerance ($1.00 \cdot 10^{-15}$) gave averaged step-sizes for TDVCC[2] and TDVCI[2] of about 3.5 a.u. and 1.0 a.u., respectively. The potentially larger step-size for TDVCC is noteworthy. It is interesting from a pragmatic point of view as it can be used for saving steps and thereby time. Furthermore, it showcases that it is apparently numerically easier to solve the EOMs for the complicated nonlinear TDVCC parameterization in a stable fashion than it is for a more standard linear TDVCI parameterization. The [supplementary material](#) has more to this point.

FIG. 13. Computational timings of entire ODE integration, varying the number of modes M , i.e., for different PAH-molecules (6 modals per mode).

The initial states of all PAH systems were generated as the VSCF state from purely harmonic parts of the relevant PESs, as in Ref. 14. For the series of different PAH molecules, 6 modals per mode were used. For examining scaling with respect to the number of modals, the PAH1 (benzene) PES was used. Each system was evolved for 100 steps (300 a.u.), each step requiring 12 derivative calculations with the employed Dormand-Prince 8(5,3) explicit Runge-Kutta method. For the largest systems, this is quite an impressive feat, given the number of wave function parameters and operator terms. For the largest system, PAH12 with 156 modes, the TDVCC[2] state contains 606 063 parameters and the operator consists of 799 812 terms.

Computational timings with respect to the number of modes M are reported in Fig. 13. We observe a clear $\mathcal{O}(M^3)$ scaling as expected. While this shows a significant increase in computational cost with increasing size of the systems, one must recall that it is very far from the dramatic, exponential scaling cost of FVCI and MCTDH.

The N_m scaling can be seen in the [supplementary material](#); fits of the computational times give scalings of $\mathcal{O}(N_m^{2.224})$ for TDVCI[2] and $\mathcal{O}(N_m^{2.737})$ for TDVCC[2]. The $\mathcal{O}(N_m^3)$ scaling is thus less evident, but we ascribe this to the $\mathcal{O}(M^3 N_m^2)$ terms

simply being dominating already for benzene with $M = 30$. Unsurprisingly, the TDVCI[2] computations are about an order of magnitude faster than the TDVCC[2] ones. This is also observed in time-independent calculations and simply derives from TDVCC[2] having more terms. The potential gains from a longer step-length of TDVCC[2] are not likely to regain this fully. In any case, the perspective here is the expectation that TDVCC[2] generally provides higher accuracy than TDVCI[2] as well as satisfactory behavior with respect to separability. To obtain similar behavior, it is anticipated that a much higher level TDVCI is needed or other methods.

F. Dynamics with time-dependent Hamiltonian

Until now, we have for the initial state used a converged state from another PES, which can, e.g., simulate instantaneous excitation from one surface to another. Another natural choice is to use the VCC ground state from the effective PES; this is, however, in itself uninteresting because the ground state is stationary as seen by the EOMs. Therefore, we introduce a time-dependent contribution to the Hamiltonian, which can, e.g., simulate the physically very relevant case of a ground state molecule being hit by a laser pulse.

FIG. 14. The actual energy expectation values during simulation, as well as the ones *predicted* by integrating the energy time-derivative. $E_V(0) = 2.12241 \cdot 10^{-2}$ a.u. and $2.12238 \cdot 10^{-2}$ a.u. for VCC[2] and FVCI, respectively. Left: TDVCC[2]. Right: TDVCI[3] (FVCI). Top: Real part of energy. Bottom: Imaginary part of energy. Notice that the actual and predicted energies appear on top of each other; their values are indicated by the left y axes. Their discrepancies are several orders of magnitude smaller and are indicated by the right y axes.

In the present case, the molecule stays in the same electronic state, while the case of motion on coupled surfaces is beyond the scope of this work.

For its simplicity, we look at a water molecule (3 modes, 16 modals per mode) being hit by a Gaussian-profiled pulse that (only) interacts with the q_0 mode (the symmetric bend). The Hamiltonian thus takes the form

$$\hat{H} = \hat{H}_0 + c(t)\hat{H}_1, \quad (94)$$

where $\hat{H}_0$ is the usual time-independent PES and kinetic energy operators of the water molecule, $\hat{H}_1 = \hat{q}_0$ is the interaction operator, and $c(t)$ is the Gaussian pulse,

$$c(t) = A \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right) \cos(\omega(t-t_0) - \phi). \quad (95)$$

Admittedly, the physically relevant choice would be to use a dipole operator, but we choose the q_0 interaction because of its simplistic interpretation; the pulse itself can only interact with the q_0 mode, and any other motion will then happen due to mode correlation. For comparison, we have performed similar calculations using both TDVCC[2], TDVCI[2] and TDVCI[3]

(i.e., TDFVCI), both integrated with a tight ODE tolerance of $1.00 \cdot 10^{-15}$.

In both cases, the simulation time was 2.0×10^5 a.u. (≈ 4.8378 ps) and the pulse peaks at $t_0 = 2.0 \times 10^4$ a.u. (≈ 483.78 ps) and has an amplitude of 8.68×10^{-6} a.u. and a phase shift $\phi = 0$. The angular frequency was chosen to match the fundamental q_0 excitation energy as obtained from VCC[2], VCI[2], and VCI[3] response theory; these were $7.2354 \cdot 10^{-3}$ a.u., $7.3210 \cdot 10^{-3}$ a.u., and $7.2302 \cdot 10^{-3}$ a.u., respectively. The σ of the Gaussian were then chosen so that the full width at half maximum (FWHM) would be 10 times the oscillation period, $\tau_{\text{per}} = 2\pi/\omega$, using the relation $\text{FWHM} = 2\sqrt{2 \cdot \ln 2} \sigma$ for Gaussian profiles. The pulses used are thus not completely identical, but are identically tuned to match each their q_0 transition.

In Sec. IV C, we have focused much on energy conservation, but with a time-dependent Hamiltonian, the energy is no longer conserved. Instead, we obtain, from Eq. (37), that

$$\frac{d}{dt} E_V = \dot{c}(t) \langle \Lambda(t) | H_1 | \Psi(t) \rangle, \quad (96)$$

meaning that by storing $\dot{c}(t)$ and $\langle \Lambda(t) | H_1 | \Psi(t) \rangle$ at each ODE integration point, we can approximately predict the energy evolution through a simple trapezoidal quadrature

FIG. 15. Change in the position expectation values when the water molecule is hit by the q_0 pulse. Left: TDVCC[2]. Middle: TDVCI[3] (TDFVCI). Right: TDVCI[2]. Top: $\langle q_0 \rangle$, $\langle q_1 \rangle$ (relative to values at $t = 0$). Bottom: Amplitude of the pulse. Note the different y axis ranges. $\langle q_2 \rangle \lesssim 2 \times 10^{-10}$ a.u. at all times.

FIG. 16. Change in the position expectation values when the water molecule is hit by the q_0 pulse, full time period. Left: TDVCC[2]. Middle: TDVCI[3] (TDFVCI). Right: TDVCI[2]. Note the different y axis ranges. See the [supplementary material](#) for higher resolution versions of the same plots.

$$E_V^{\text{pred}}(t) - E_V(0) = \int_0^t \dot{c}(t') \langle H_1(t') \rangle dt' \\ \approx \sum_{i=1}^{N_{\text{step}}} \frac{1}{2} \left(\dot{c}(t_{i-1}) \langle H_1(t_{i-1}) \rangle + \dot{c}(t_i) \langle H_1(t_i) \rangle \right) \Delta t_i, \quad (97)$$

a formula that actually also applies to the TDFVCI calculation.

Using Eq. (97), we do indeed observe the energy to evolve as expected when the pulse hits. This is seen in Fig. 14, where the actual and predicted energy changes are shown for both real and imaginary parts of the energy for both methods. The TDVCC energy attains an imaginary component, also in agreement with the predicted change, but which remains comparatively small in any case. It is reassuring to see that the TDVCC method not only conserves energy when it should but that the energy also evolves correctly for the time-dependent Hamiltonians.

Figure 15 shows how the position expectation values change when the pulse hits the molecule. As expected, they are constantly zero in the initial time period and then $\langle q_0 \rangle$ starts oscillating when the pulse arrives. Some oscillations also appear in $\langle q_1 \rangle$ (symmetric stretch), while $\langle q_2 \rangle$ (antisymmetric stretch) remains ≈ 0 at all times (apart from small numerical noise). The onset of oscillation in $\langle q_1 \rangle$ (but not in $\langle q_2 \rangle$), although not directly affected by the pulse, is physically reasonable because the motions in the symmetric bend and stretch are able to correlate, since both are totally symmetric vibrations, whereas the antisymmetric stretch is not. After the pulse turns off, the oscillations remain in agreement with the molecule having absorbed energy from the pulse; it is no longer in the ground state.

Let us finally compare the methods in slightly more detail. We see that very similar time-dependent expectation values are predicted in the TDVCC[2] compared to TDFVCI while simultaneously TDVCI[2] is deviating more. This can be seen already in the

short time evolution of the expectation values in Fig. 15, but even clearer for longer times as shown in Fig. 16 where there is a substantial difference between TDVCI[2] on the one hand and TDVCC[2] and TDFVCI on the other hand, where the latter two stay very close qualitatively and quantitatively.

To summarize, we have established the correct energy evolution in TDVCC, also for time-dependent Hamiltonians, and we have illustrated the capability of the method to describe physically motivated laser pulse experiments. Furthermore, the close qualitative agreement between TDVCC[2] and the FVCI calculation regarding the time evolution of both energy and position expectation value operators is remarkable. The latter hints that the efficiency of the parameterization and the associated implicit accuracy of the spectrum, as is well-known in time-independent theory, as well as the size-consistency of the TDVCC[2] approach is more important for accurate time-dependent predictions than the preservation of the exact variational property and features derived from that.

V. SUMMARY AND OUTLOOK

Although time-dependent coupled cluster theory is not without peculiarities, deriving from its nonvariational nature, we hope to have convincingly shown that it holds potential as a realistic and interesting approach for studying quantum molecular dynamics. Detailed summaries of our findings have been given on the way, and the overall summary can be simply stated as follows: (i) working equations can be derived covering both time-dependent and time-independent Hamiltonians; (ii) a corresponding efficient implementation can be obtained for the special case of at most two-mode couplings in the cluster expansion and in the Hamiltonian, facilitating the treatment of systems with many modes; (iii) the behavior with respect to evolution of norm, energy, and expectation values can be understood and the appropriate limits

are obtained in theory and numerical computations; (iv) separability with respect to systems consisting of noninteracting subsystems (in the spirit of time-independent size-consistency analysis) can be studied in a time-dependent context giving insightful and nontrivial theoretical results that can be numerically verified; (v) it was found that the nonlinearly, nonvariationally parameterized coupled cluster theory gave higher accuracy than a standard linear variational wave function parameterization at equivalent levels of approximation.

The potential of TDVCC theory will be further studied and developed in subsequent work. This includes addressing two of the principal limitations of the presented theory and implementation, namely, (i) the use of time-independent modals and (ii) the limitation to two-mode couplings of the implementation. Regarding the first, we note that the use of variational time-dependent one-mode basis functions is the core behind the success of the MCTDH approach in quantum molecular dynamics. It is an obvious question whether time-dependent modals can further expand the application range of TDVCC. There has been work on using time-dependent orbitals in electronic coupled cluster theory.^{41,44} As we will return to in a later work, the issue is generally nontrivial and the implementation in the nuclear dynamics case includes new categories of terms compared to the case with time-independent modals. Extension to higher coupling levels in both the Hamiltonian and wave function, still using time-independent modals, is in its general aspects more clear-cut. In practical terms, these higher-level vibrational coupled cluster theories are extremely involved with thousands of terms, etc., but automatized procedures for deriving, analyzing, and implementing the equations have been developed.^{25,68} It is therefore our hope that it will be a realistic undertaking to combine these with the setup of this work to obtain a more open-ended TDVCC method. This paves the way for more detailed convergence studies on the potential gains of the TDVCC parameterization, as well as further insight into the consequences of its peculiarities.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional numerical results.

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