

Many-body theory for systems with particle conversion: Extending the multiconfigurational time-dependent Hartree method

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We derive a multiconfigurational time-dependent Hartree theory for systems with particle conversion. In such systems particles of one kind can convert to another kind and the total number of particles varies in time. The theory thus extends the scope of the available and successful multiconfigurational time-dependent Hartree methods—which were solely formulated for and applied to systems with a fixed number of particles—to a broader class of physical systems and problems. As a guiding example we treat explicitly a system where bosonic atoms can combine to form bosonic molecules and vice versa. In the theory for particle conversion, the time-dependent many-particle wave function is written as a sum of configurations made of a different number of particles, and assembled from sets of atomic and molecular orbitals. Both the expansion coefficients and the orbitals forming the configurations are time-dependent quantities that are fully determined according to the Dirac-Frenkel time-dependent variational principle. By employing the Lagrangian formulation of the Dirac-Frenkel variational principle we arrive at two sets of coupled equations of motion, one for the atomic and molecular orbitals and one for the expansion coefficients. The first set is comprised of first-order differential equations in time and nonlinear integrodifferential equations in position space, whereas the second set consists of first-order differential equations with coefficients forming a time-dependent Hermitian matrix. Particular attention is paid to the reduced density matrices of the many-particle wave function that appear in the theory and enter the equations of motion. There are two kinds of reduced density matrices: particle-conserving reduced density matrices which directly only couple configurations with the same number of atoms and molecules, and particle nonconserving reduced density matrices which couple configurations with a different number of atoms and molecules. Closed-form and compact equations of motion are derived for contact as well as general two-body interactions, and their properties are analyzed and discussed.

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I. INTRODUCTION

The exploration of quantum dynamics of many-particle systems is a fundamental and ongoing challenge of many branches in physics [1–6]. The equation of motion governing the evolution of quantum particles is, in many cases, the well-known time-dependent Schrödinger equation. Solving the time-dependent Schrödinger equation for many-particle systems can rarely be made analytically or exactly, which renders efficient approximations a must.

The multiconfigurational time-dependent Hartree method (MCTDH) [7,8], which has been developed in the past two decades, is considered at present the most efficient wave-packet propagation approach [9] and has successfully and routinely been used for multidimensional dynamical systems consisting of distinguishable degrees of freedom, such as molecular vibrations, see Refs. [10–19]. The main idea behind the MCTDH method is to expand the time-dependent many-body wave function of distinguishable particles by *time-dependent* configurations that are assembled from *time-dependent* orbitals (one-body functions) and optimized according to the Dirac-Frenkel variational principle [20,21]. In this way, a much larger effective subspace of the many-

particle Hilbert space can be spanned in practice in comparison to multiconfigurational expansions with *stationary* configurations. By grouping several “elementary” degrees of freedom together and treating them as “generalized” particles, the efficiency of the MCTDH algorithm increases [10,11]. Choosing to use MCTDH itself to propagate multidimensional “generalized” particles has led to the idea of cascading [13]. Finally, expanding the time-dependent orbitals of the “generalized” particles themselves by other time-dependent orbitals, and so on, putting the resulting time-dependent expansion under the Dirac-Frenkel variational principle, leads to the multilayer formulation of the MCTDH theory [22] which further increases the efficiency of the MCTDH method for larger, complex systems. The MCTDH can be applied to systems of identical particles. In this direction, we would like to mention that the MCTDH approach has very successfully been employed in unveiling fundamental physics of few-boson systems [23–28] on the numerically exact many-body level.

A new branch of MCTDH-based methods has emerged after it had been realized that, to effectively treat the dynamics of more than a handful *identical* particles, it is essential to use their quantum statistics, Fermi-Dirac or Bose-Einstein, to eliminate the large amount of redundancies of coefficients in the distinguishable particle multiconfigurational expansion of the MCTDH wave function. First, taking explicitly the antisymmetry of the many-fermion wave function to permutations of any two particles into account, the fermionic version

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of MCTDH—MCTDHF—was independently developed by several groups [29–31]. Shortly after, the bosonic version of MCTDH—MCTDHB—was developed in [32,33]. This advancement is in particular valuable since very many bosons can reside in only a small number of orbitals owing to Bose-Einstein statistics, thereby allowing the successful and quantitative attack of the dynamics of a much larger number of bosons with the MCTDHB theory. For applications of MCTDHF to the many-body dynamics of at present few-fermion systems with or without external laser field, see Refs. [34–40], and for applications of MCTDHB for the many-body dynamics of repulsive and attractive bosonic systems, Refs. [32,41–43]. We mention that Ref. [43] has combined optimal control theory with MCTDHB.

Five decades ago, in his seminal paper, Löwdin defined the reduced density matrices of many-fermion wave functions [44]. Since then, reduced density matrices and, in particular, reduced two-body density matrices is a fruitful and vivid research area including theory and applications in electronic structure of molecules, quantum phase transitions, and ground-state nuclear motion [45–51]. In the present context, reduced one- and two-body density matrices were used to derive the stationary many-body states within the general variational theory with complete self-consistency for trapped bosonic systems—the multiconfigurational Hartree for bosons (MCHB) [52]. Later on, the MCTDHF and MCTDHB were formulated in a unified manner, making use of the reduced one- and two-body density matrices of the time-dependent many-body wave function [53]. Finally, treating mixtures of two kinds of identical particles in a unified manner, and utilizing the reduced one- and two-body density matrices of the mixture’s wave function, a multiconfigurational time-dependent Hartree method for Fermi-Fermi (MCTDH-FF), Bose-Bose (MCTDH-BB), and Bose-Fermi (MCTDH-BF) mixtures has been derived [54].

The multiconfigurational time-dependent Hartree method and its versions specified for identical particles and mixtures are *particle-conserving* many-body propagation theories. Namely, they were solely formulated for and applied to systems with a fixed number of particles. Conceptually, they aim at describing systems of coupled degrees of freedom or interacting particles which have first-quantization Hamiltonian. This brings us to the theme of the present work, which is to derive a multiconfigurational time-dependent Hartree theory for systems with *particle conversion*. In such systems particles of one kind can convert to another kind and the total number of particles varies in time. Hence, they are generally represented by a phenomenological second-quantized Hamiltonian which includes a *conversion term*. Doing so, we extend the scope of the available and successful multiconfigurational time-dependent Hartree method and its versions specified for identical particles and mixtures to new physical systems and problems. We abbreviate the multiconfigurational time-dependent Hartree theory for systems with particle conversion by MCTDH-*conversion*.

As a concrete and guiding example for a many-body system with particle conversion and without loss of generality, we consider explicitly the conversion of bosonic atoms (a) to bosonic molecules (m) via the “reaction” $2a \rightleftharpoons m$, which has been a system of tremendous theoretical and experimental interest in quantum-gas physics [55–85].

An effective quantum-field-theory-based Hamiltonian for atomic and molecular Bose-Einstein condensates (BECs) coupled by conversion was put forward by Drummond *et al.* in [55]. In [56], a proposition that a molecular BEC could be produced by coherent photoassociation was made and a phenomenological two-mode Hamiltonian to describe this process was suggested. A microscopic theory to derive the many-body Hamiltonian of bosonic atoms and molecules with conversion and the respective Gross-Pitaevskii theory with conversion were put forward in [57], also see [59]. In [58], a coupled system of Gross-Pitaevskii equations with conversion and deactivation-rate (dissipation) terms has been derived. The validity of the two-mode approach for conversion, at least in the homogeneous system, was questioned in [62], where dissociation of molecules to other than the ground atomic mode signifies that one needs to go beyond the two-mode approximation. The importance of pair correlations in the dynamics of resonantly-coupled atomic and molecular BECs, leading to significant deviations from the respective Gross-Pitaevskii theory, was put forward in [63]. That even in the perfect two-mode limit the mean-field theory with conversion can fail, because of strong particle-particle entanglement near the dynamically unstable molecular mode, was reported in [65]. A proposition to create a molecule BEC from an atomic Mott-insulator phase with exactly two bosons per lattice site was made in [68]. A full microscopic theory to derive the Hamiltonian of atoms and molecules with the conversion term from the microscopic particle-conserving Hamiltonian of a homogeneous gas of identical bosonic atoms with two internal states was given in [69], also see [74]. Quantum phase transitions and effects of rotations in homogeneous systems of atomic and molecular BECs with conversion have been discovered in [75,77] and [76], respectively. Finally, in a (harmonic) trap, confinement effects on the stimulated dissociation (effective conversion rate) of a molecular to an atomic BEC were recently found in [83], and unique phases (vortex configurations) of rotating interacting atomic-molecular BECs in [85].

Molecules were first produced from and identified in an ^{87}Rb BEC by Wynar *et al.* [60]. Soon after, photoassociation of ultracold sodium molecules in an atomic BEC was made [66]. Atomic-molecular coherence in a BEC [made of ^{85}Rb atoms] was achieved in [67]. A pure molecular quantum gas produced from an atomic cesium BEC was reported in [71], and a quantum-degenerate gas of sodium molecules in [72]. More recently, with ^{87}Rb atoms in the Mott phase of optical lattices, state-selective conversion of atoms to molecules [78], following the theoretical proposition in [68], and atom-molecule Rabi oscillations [84] have been observed.

Finally, systems with particle conversion can involve, of course, fermions; in the cold-atom world—see the reviews [82,86] and references therein—and beyond it. In the latter context, it is gratifying to mention the Friedberg-Lee model of superconductivity, describing the conversion of two electrons to a single Cooper pair and vice versa by a boson-fermion Hamiltonian with a phenomenological conversion term [87,88]. We would also like to mention that other approaches for describing systems with particle conversion and composite particles have been pursued, see, e.g., [89,90].

Let us return now to MCTDH-*conversion*, and put it in

the particular context of interacting atomic and molecular BECs with conversion. For the explicit scenario of the conversion “reaction” $2a \rightleftharpoons m$ dealt with throughout this work, the theory shall be referred to as MCTDH- $[2a \rightleftharpoons m]$. MCTDH- $[2a \rightleftharpoons m]$, as its particle-conserving predecessors [7,8,12,29–33,53,54], is intended for systems with a finite number of interacting particles, typically trapped in an external potential. As a first step, we extend or “merge” two theoretical approaches much in use in the literature: the Gross-Pitaevskii theory with conversion and the two-mode approximation, see, e.g., Refs. [57,59,61,64,81,85] and Refs. [56,65,80], respectively. This results in a fully variational theory where the two modes—the atomic and molecular orbitals—and each and every expansion coefficient in the two-mode many-body wave function are fully optimized—the orbitals in time and space and the expansion coefficients in time—according to the Dirac-Frenkel variational principle [20,21]. Our main aim is to go beyond any two-mode description of the atomic-molecular coupled system and present a fully variational multiconfigurational time-dependent many-body theory for bosonic atoms and molecules coupled by conversion—the MCTDH- $[2a \rightleftharpoons m]$ theory.

The structure of the paper is as follows. We open in Sec. II with the many-body Hamiltonian of the system of atoms and molecules with conversion. In Sec. III we consider as mentioned above a specific case of interest, the fully variational theory where there are one atomic and one molecular orbitals. This specific theory will be referred to as *conversion mean field*. Next, Sec. IV is devoted to the general theory. Both time-dependent as well as time-independent theories are presented. Finally, in Sec. V we put forward a summary and concluding remarks. Complementary derivations and relevant matrix elements are deferred to and collected in Appendixes A and B, respectively.

II. THE MANY-BODY HAMILTONIAN OF INTERACTING ATOMS AND MOLECULES WITH CONVERSION

As a concrete example for a many-body system with particle conversion and without loss of generality, we consider a system of bosons which will be referred to as atoms (a) and their conversion to another type of bosons which will be referred to as molecules (m) via the “reaction” $2a \rightleftharpoons m$. The many-body Hamiltonian of the coupled atom-molecule system is taken from the literature of cold-atom physics [55,57,69,76] and is written for our needs as a sum of four terms,

$$\hat{H}^{(2a \rightleftharpoons m)} = \hat{H}^{(am)} + \hat{W}^{(2a \rightleftharpoons m)} = \hat{H}^{(a)} + \hat{H}^{(m)} + \hat{W}^{(am)} + \hat{W}^{(2a \rightleftharpoons m)}. \quad (1)$$

The first three terms are particle-conserving terms and together describe a mixture of two kinds of interacting bosonic particles; a (atoms) and m (molecules),

$$\begin{aligned} \hat{H}^{(a)} &= \hat{h}^{(a)} + \hat{W}^{(a)} \\ &= \int d\mathbf{r} \left[\hat{\Psi}_a^\dagger(\mathbf{r}) \hat{h}^{(a)}(\mathbf{r}) \hat{\Psi}_a(\mathbf{r}) \right. \\ &\quad \left. + \frac{1}{2} \int d\mathbf{r}' \hat{\Psi}_a^\dagger(\mathbf{r}) \hat{\Psi}_a^\dagger(\mathbf{r}') \hat{W}^{(a)}(\mathbf{r}, \mathbf{r}') \hat{\Psi}_a(\mathbf{r}') \hat{\Psi}_a(\mathbf{r}) \right], \end{aligned}$$

$$\begin{aligned} \hat{H}^{(m)} &= \hat{h}^{(m)} + \hat{W}^{(m)} \\ &= \int d\mathbf{r} \left[\hat{\Psi}_m^\dagger(\mathbf{r}) \hat{h}^{(m)}(\mathbf{r}) \hat{\Psi}_m(\mathbf{r}) \right. \\ &\quad \left. + \frac{1}{2} \int d\mathbf{r}' \hat{\Psi}_m^\dagger(\mathbf{r}) \hat{\Psi}_m^\dagger(\mathbf{r}') \hat{W}^{(m)}(\mathbf{r}, \mathbf{r}') \hat{\Psi}_m(\mathbf{r}') \hat{\Psi}_m(\mathbf{r}) \right], \end{aligned}$$

$$\hat{W}^{(am)} = \int d\mathbf{r} \int d\mathbf{r}' \hat{\Psi}_a^\dagger(\mathbf{r}) \hat{\Psi}_m^\dagger(\mathbf{r}') \hat{W}^{(am)}(\mathbf{r}, \mathbf{r}') \hat{\Psi}_m(\mathbf{r}') \hat{\Psi}_a(\mathbf{r}). \quad (2)$$

The last term describes the conversion of atoms to molecules and vice versa and is given by [55,57,69,76]

$$\begin{aligned} \hat{W}^{(2a \rightleftharpoons m)} &= \hat{W}^{(2a \rightarrow m)} + \hat{W}^{(m \rightarrow 2a)} \\ &= \frac{1}{\sqrt{2}} \int d\mathbf{r} \int d\mathbf{r}' \left[\hat{\Psi}_m^\dagger \left(\frac{\mathbf{r} + \mathbf{r}'}{2} \right) \right. \\ &\quad \times \hat{W}^{(2a \rightarrow m)}(\mathbf{r}, \mathbf{r}') \hat{\Psi}_a(\mathbf{r}) \hat{\Psi}_a(\mathbf{r}') + \hat{\Psi}_a^\dagger(\mathbf{r}') \hat{\Psi}_a^\dagger(\mathbf{r}) \\ &\quad \left. \times \hat{W}^{(m \rightarrow 2a)}(\mathbf{r}, \mathbf{r}') \hat{\Psi}_m \left(\frac{\mathbf{r} + \mathbf{r}'}{2} \right) \right], \end{aligned} \quad (3)$$

The coordinates entering the field operators in Eq. (3) represent the annihilation (creation) of two atoms, one at position \mathbf{r} and the second at position \mathbf{r}' , and the creation (annihilation) of a molecule at the center-of-mass coordinate $\mathbf{R} = \frac{\mathbf{r} + \mathbf{r}'}{2}$. The atomic and molecular field operators satisfy the usual commutation relations for bosons, $[\hat{\Psi}_a(\mathbf{r}), \hat{\Psi}_a^\dagger(\mathbf{r}')] = [\hat{\Psi}_m(\mathbf{r}), \hat{\Psi}_m^\dagger(\mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}')$ and $[\hat{\Psi}_a(\mathbf{r}), \hat{\Psi}_m(\mathbf{r}')] = [\hat{\Psi}_m(\mathbf{r}), \hat{\Psi}_a(\mathbf{r}')] = 0$. Since the atoms and molecules are distinguishable (different) particles, their mutual field operators commute, $[\hat{\Psi}_a(\mathbf{r}), \hat{\Psi}_m^\dagger(\mathbf{r}')] = [\hat{\Psi}_m(\mathbf{r}), \hat{\Psi}_a^\dagger(\mathbf{r}')] = 0$. Finally, we note that the interaction terms appearing in the Hamiltonian [Eqs. (1)–(3)] are symmetric, i.e., $\hat{W}^{(a)}(\mathbf{r}, \mathbf{r}') = \hat{W}^{(a)}(\mathbf{r}', \mathbf{r}), \dots, \hat{W}^{(m \rightarrow 2a)}(\mathbf{r}, \mathbf{r}') = \hat{W}^{(m \rightarrow 2a)}(\mathbf{r}', \mathbf{r})$, because the Hamiltonian is symmetric to the exchange of position of any two particles of the same kind.

The Hamiltonian [Eqs. (1)–(3)] commutes with the following particle-number operator:

$$\hat{N} = \hat{N}_a + 2\hat{N}_m = \int d\mathbf{r} [\hat{\Psi}_a^\dagger(\mathbf{r})\hat{\Psi}_a(\mathbf{r}) + 2\hat{\Psi}_m^\dagger(\mathbf{r})\hat{\Psi}_m(\mathbf{r})], \quad (4)$$

reflecting a conservation law in presence of particle conversion. Accordingly, the Hilbert space of the problem is a direct sum of Hilbert subspaces with a different number of atoms and molecules, $\{N \text{ atoms}; 0 \text{ molecules}\} \oplus \{N-2 \text{ atoms}; 1 \text{ molecule}\} \oplus \{N-4 \text{ atoms}; 2 \text{ molecules}\} \oplus \dots \oplus \{N-2\lfloor \frac{N}{2} \rfloor \text{ atoms}; \lfloor \frac{N}{2} \rfloor \text{ molecules}\}$, where $\lfloor j \rfloor$ means the greatest integer not exceeding j .

The purpose of this work is to treat the many-body Hamiltonian with atom-molecule conversion [Eqs. (1)–(3)] multiconfigurationaly. To this end, we expand the atomic $\hat{\Psi}_a(\mathbf{r})$ and molecular $\hat{\Psi}_m(\mathbf{r})$ field operators by two complete sets of *time-dependent* orbitals,

$$\hat{\Psi}_a(\mathbf{r}) = \sum_k \hat{b}_k(t) \phi_k(\mathbf{r}, t), \quad \hat{\Psi}_m(\mathbf{r}) = \sum_{k'} \hat{c}_{k'}(t) \psi_{k'}(\mathbf{r}, t). \quad (5)$$

The sets of atomic $\{\phi_k(\mathbf{r}, t)\}$ and molecular $\{\psi_{k'}(\mathbf{r}, t)\}$ orbitals span the *time-dependent* Hilbert space in which the system is to be propagated. The advantages of time-dependent multiconfigurational expansions, see the Introduction, is the employment of *time-dependent* orbitals which change in time according to a time-dependent variational principle. This allows one to use in practical computations a smaller number of time-dependent orbitals than the number of time-independent orbitals that would have been required otherwise. A general multiconfigurational expansion, see Sec. IV, employs M orbitals for the bosonic atoms and M' orbitals for the bosonic molecules. In particular, even if only one orbital is available for the bosonic atoms and another one for the bosonic molecules, the resulting theory *goes beyond* the Gross-Pitaevskii mean-field theory for this system [57], see subsequent Sec. III.

Finally, it is convenient to derive the relevant results first for the popular contact interaction,

$$\hat{W}^{(a)}(\mathbf{r}, \mathbf{r}') = \lambda_a \delta(\mathbf{r} - \mathbf{r}'), \quad \hat{W}^{(m)}(\mathbf{r}, \mathbf{r}') = \lambda_m \delta(\mathbf{r} - \mathbf{r}'),$$

$$\hat{W}^{(am)}(\mathbf{r}, \mathbf{r}') = \lambda_{am} \delta(\mathbf{r} - \mathbf{r}'),$$

$$\hat{W}^{(2a \rightarrow m)}(\mathbf{r}, \mathbf{r}') = \hat{W}^{(m \rightarrow 2a)}(\mathbf{r}, \mathbf{r}') = \lambda_{con} \delta(\mathbf{r} - \mathbf{r}'). \quad (6)$$

Thus, substituting Eqs. (5) and (6) into the generic Hamiltonian [Eqs. (1)–(3)] we obtain

$$\begin{aligned} \hat{H}^{(2a \rightarrow m)} = & \sum_{k,q} \langle \phi_k | \hat{h}^{(a)} | \phi_q \rangle \hat{b}_k^\dagger \hat{b}_q + \frac{\lambda_a}{2} \sum_{k,s,l,q} \langle \phi_k \phi_s | \phi_q \phi_l \rangle \hat{b}_k^\dagger \hat{b}_s^\dagger \hat{b}_l \hat{b}_q \\ & + \sum_{k',q'} \langle \psi_{k'} | \hat{h}^{(m)} | \psi_{q'} \rangle \hat{c}_{k'}^\dagger \hat{c}_{q'} \\ & + \frac{\lambda_m}{2} \sum_{k',s',l',q'} \langle \phi_{k'} \phi_{s'} | \phi_{q'} \phi_{l'} \rangle \hat{c}_{k'}^\dagger \hat{c}_{s'}^\dagger \hat{c}_{l'} \hat{c}_{q'} \end{aligned}$$

$$\begin{aligned} & + \lambda_{am} \sum_{k,k',q,q'} \langle \phi_k \psi_{k'} | \phi_q \psi_{q'} \rangle \hat{b}_k^\dagger \hat{b}_q \hat{c}_{k'}^\dagger \hat{c}_{q'} \\ & + \frac{\lambda_{con}}{\sqrt{2}} \sum_{k',k,q} [\langle \psi_{k'} | \phi_k \phi_q \rangle \hat{c}_{k'}^\dagger \hat{b}_k \hat{b}_q \\ & + \langle \phi_q \phi_k | \psi_{k'} \rangle \hat{b}_q^\dagger \hat{b}_k^\dagger \hat{c}_{k'}]. \end{aligned} \quad (7)$$

Here and hereafter, the dependence of quantities on time is not shown explicitly whenever unambiguous. Below, we will work throughout Secs. III and IV A with the contact-interaction Hamiltonian (7) and handle the case of general interactions [Eqs. (1)–(3)] thereafter, in Sec. IV B.

III. THE SIMPLEST CASE OF ATOM-MOLECULE CONVERSION: CONVERSION MEAN FIELD (FULLY VARIATIONAL TWO-MODE APPROXIMATION)

A. The multiconfigurational ansatz

To introduce the nomenclature in the first stage of this work and, independently, as an interesting and relevant problem for itself, we consider the resulting theory when there is only one orbital available for the (bosonic) atoms and one orbital available for the (bosonic) molecules. The atomic orbital will be denoted by $\phi_1(\mathbf{r}, t) \equiv \phi_a(\mathbf{r}, t)$ and the molecular orbital by $\psi_1(\mathbf{r}, t) \equiv \psi_m(\mathbf{r}, t)$. The corresponding creation operators are denoted by $\hat{b}_1^\dagger(t) \equiv \hat{b}_a^\dagger(t)$ and $\hat{c}_1^\dagger(t) \equiv \hat{c}_m^\dagger(t)$. The atomic and molecular creation, annihilation operators obey the bosonic commutation relations corresponding to the field operators.

The problem we wish to solve may now be formulated. In the present section we would like to derive a multiconfigurational theory for atom-molecule conversion which is exact in the smallest Hilbert subspace possible for bosonic species, namely, the Hilbert space spanned by the *single* molecular orbital $\psi_m(\mathbf{r}, t)$ and *single* atomic orbital $\phi_a(\mathbf{r}, t)$. We term this specific case of the general theory: *conversion mean field*. More technically, this theory is a fully variational extension of the literature two-mode approximation [56,65] and, of course, of the Gross-Pitaevskii theory with conversion [57].

The multiconfigurational wave function takes on the following form:

$$|\Psi(t)\rangle = \sum_{p=0}^{\lfloor N/2 \rfloor} C_p(t) |N-2p, p; t\rangle,$$

$$|N-2p, p; t\rangle = \frac{1}{\sqrt{(N-2p)! p!}} [\hat{b}_a^\dagger(t)]^{N-2p} [\hat{c}_m^\dagger(t)]^p |\text{vac}\rangle, \quad (8)$$

where $|\text{vac}\rangle$ is a *common* vacuum of no atoms and no molecules. The index p enumerates the number of bosonic molecules in the system. The corresponding number of atoms is $N-2p$. N is the maximal number of atoms in the system which is obtained when there are no molecules. Obviously, $|\Psi(t)\rangle$ is an eigenfunction of the particle-number operator \hat{N} , Eq. (4), with the eigenvalue N . The atomic and molecular number operators in the relevant Hilbert space boil down to

$\hat{N}_a = \hat{b}_a^\dagger \hat{b}_a$ and $\hat{N}_m = \hat{c}_m^\dagger \hat{c}_m$, respectively. The size of this Hilbert space is $\lfloor \frac{N}{2} \rfloor + 1$.

B. The functional action S of the time-dependent Schrödinger equation and its evaluation

Solving the time-dependent Schrödinger equation with the Hamiltonian (7) and the multiconfigurational ansatz (8) means finding the equations governing the time evolution of the atomic and molecular orbitals, $\phi_a(\mathbf{r}, t)$ and $\psi_m(\mathbf{r}, t)$, and of the expansion coefficients $\{C_p(t)\}$. The derivation of these equations of motion for $\phi_a(\mathbf{r}, t)$, $\psi_m(\mathbf{r}, t)$, and $\{C_p(t)\}$ requires a time-dependent variational principle. We employ the Lagrangian formulation of the (Dirac-Frenkel) time-dependent variational principle [91,92], also see Refs. [33,53,54], and write the functional action of the time-dependent Schrödinger equation which takes on the form

$$\begin{aligned} S[\{C_p(t)\}, \phi_a(\mathbf{r}, t), \psi_m(\mathbf{r}, t)] &= \int dt \left\{ \left\langle \Psi(t) \left| \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} \right| \Psi(t) \right\rangle \right. \\ &\quad - \mu_a(t) [\langle \phi_a(\mathbf{r}, t) | \phi_a(\mathbf{r}, t) \rangle - 1] \\ &\quad - \mu_m(t) [\langle \psi_m(\mathbf{r}, t) | \psi_m(\mathbf{r}, t) \rangle - 1] \\ &\quad \left. - \varepsilon(t) \left[\sum_{p=0}^{\lfloor N/2 \rfloor} |C_p(t)|^2 - 1 \right] \right\}. \end{aligned} \quad (9)$$

The time-dependent Lagrange multipliers $\mu_a(t)$, $\mu_m(t)$, and $\varepsilon(t)$ are introduced to ensure normalization of the atomic $\phi_a(\mathbf{r}, t)$ and molecular $\psi_m(\mathbf{r}, t)$ orbitals and of the expansion coefficients $\{C_p(t)\}$ at all times. $\mu_a(t)$ and $\mu_m(t)$ also serve another role. They exactly “compensate” for those terms appearing within the Dirac-Frenkel formulation of the variational principle $\langle \delta \Psi(t) | \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} | \Psi(t) \rangle$ [20,21], i.e., when the variation of $\Psi(t)$ is performed before the expectation value $\langle \Psi(t) | \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} | \Psi(t) \rangle$ is evaluated; see in this context [33,92]. We shall see below and more elaborately in Appendix A 1 that these Lagrange multipliers can be eliminated from the resulting equations of motion by making use of the normalization of the orbitals in combination with unitary transformations.

The expectation value of the Hamiltonian in Eq. (9) can be expressed in two equivalent forms. The first form depends explicitly on the orbitals $\phi_a(\mathbf{r}, t)$, $\psi_m(\mathbf{r}, t)$ and the second on the expansion coefficients $\{C_p(t)\}$. The two forms are needed to derive the respective equations of motion for the orbitals and expansion coefficients.

1. Orbital-explicit expression of S

Utilizing the multiconfigurational expansion (8) and the individual terms of the many-body Hamiltonian (7), the first form of the expectation value of $\hat{H}^{(a=m)} - i \frac{\partial}{\partial t}$ reads

$$\begin{aligned} &\left\langle \Psi(t) \left| \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} \right| \Psi(t) \right\rangle \\ &= \langle \hat{N}_a \rangle \left\langle \phi_a \left| \hat{h}^{(a)} - i \frac{\partial}{\partial t} \right| \phi_a \right\rangle + \frac{\lambda_a}{2} \langle \hat{N}_a (\hat{N}_a - 1) \rangle \langle \phi_a^2 | \phi_a^2 \rangle \\ &\quad + \langle \hat{N}_m \rangle \left\langle \psi_m \left| \hat{h}^{(m)} - i \frac{\partial}{\partial t} \right| \psi_m \right\rangle \\ &\quad + \frac{\lambda_m}{2} \langle \hat{N}_m (\hat{N}_m - 1) \rangle \langle \psi_m^2 | \psi_m^2 \rangle \\ &\quad + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle \langle \phi_a \psi_m | \phi_a \psi_m \rangle + \frac{\lambda_{con}}{\sqrt{2}} [\langle \hat{c}_m^\dagger \hat{b}_a \hat{b}_a \rangle \langle \psi_m | \phi_a^2 \rangle \\ &\quad + \langle \hat{b}_a^\dagger \hat{b}_a \hat{c}_m \rangle \langle \phi_a^2 | \psi_m \rangle] - i \sum_{p=0}^{\lfloor N/2 \rfloor} C_p^* \frac{\partial C_p}{\partial t}. \end{aligned} \quad (10)$$

In Eq. (10) and hereafter we use the shorthand notation for expectation values of operators with respect to $\Psi(t)$: $\langle \hat{N}_a \rangle \equiv \langle \Psi(t) | \hat{N}_a | \Psi(t) \rangle$, $\langle \hat{b}_a^\dagger \hat{b}_a \hat{c}_m \rangle \equiv \langle \Psi(t) | \hat{b}_a^\dagger \hat{b}_a \hat{c}_m | \Psi(t) \rangle$, etc. We can indeed see that expression (10) depends explicitly on the orbitals $\phi_a(\mathbf{r}, t)$ and $\psi_m(\mathbf{r}, t)$ through integrals over one-body terms, two-body interaction terms, and the conversion term, $\langle \phi_a | \hat{h}^{(a)} - i \frac{\partial}{\partial t} | \phi_a \rangle$, $\langle \phi_a \psi_m | \phi_a \psi_m \rangle$, etc.

Making use of the multiconfigurational expansion (8), we can express the above expectation values $\langle \Psi(t) | \dots | \Psi(t) \rangle$ in a closed form. The expectation values of particle-conserving operators, such as the number operators \hat{N}_a and \hat{N}_m , with respect to $\Psi(t)$ read

$$\begin{aligned} \langle \hat{N}_a \rangle &= \sum_{p=0}^{\lfloor N/2 \rfloor} (N - 2p) |C_p(t)|^2, \quad \langle \hat{N}_m \rangle = \sum_{p=0}^{\lfloor N/2 \rfloor} p |C_p(t)|^2, \\ \langle \hat{N}_a (\hat{N}_a - 1) \rangle &= \sum_{p=0}^{\lfloor N/2 \rfloor} (N - 2p)(N - 2p - 1) |C_p(t)|^2, \\ \langle \hat{N}_m (\hat{N}_m - 1) \rangle &= \sum_{p=0}^{\lfloor N/2 \rfloor} p(p - 1) |C_p(t)|^2, \\ \langle \hat{N}_a \hat{N}_m \rangle &= \sum_{p=0}^{\lfloor N/2 \rfloor} p(N - 2p) |C_p(t)|^2. \end{aligned} \quad (11)$$

We see that the dependence of the expectation values (11) on the expansion coefficients is only through weighted sums $\sum_{p=0}^{\lfloor N/2 \rfloor} |C_p(t)|^2$, i.e., that configurations of a different number p of molecules are not directly coupled. The expectation values of particle nonconserving operators, originating from the conversion of particles, are given by

$$\begin{aligned} \langle \hat{c}_m^\dagger \hat{b}_a \hat{b}_a \rangle &= \sum_{p=1}^{\lfloor N/2 \rfloor} \sqrt{p(N - 2p + 1)(N - 2p + 2)} C_p^*(t) C_{p-1}(t), \\ \langle \hat{b}_a^\dagger \hat{b}_a \hat{c}_m \rangle &= \{ \langle \hat{c}_m^\dagger \hat{b}_a \hat{b}_a \rangle \}^*, \end{aligned} \quad (12)$$

and seen to couple directly configurations with a different number of p and $p - 1$ molecules.

2. Expansion-coefficient-explicit expression of S

Utilizing the multiconfigurational expansion (8) and the many-body Hamiltonian (7) as a whole, we can express the expectation value of $\hat{H}^{(2a \rightleftharpoons m)} - i \frac{\partial}{\partial t}$ in the functional action (9) as an explicit function of the expansion coefficients $\{C_p(t)\}$. One readily finds

$$\begin{aligned} & \left\langle \Psi(t) \left| \hat{H}^{(2a \rightleftharpoons m)} - i \frac{\partial}{\partial t} \right| \Psi(t) \right\rangle \\ &= \sum_{p=0}^{[N/2]} C_p^* \left[\sum_{p'=0}^{[N/2]} \left\langle N-2p, p; t \left| \hat{H}^{(2a \rightleftharpoons m)} \right. \right. \\ & \quad \left. \left. - i \frac{\partial}{\partial t} \right| N-2p', p'; t \right\rangle C_{p'} - i \frac{\partial C_p}{\partial t} \right]. \end{aligned} \quad (13)$$

Equation (13) contains yet another type of matrix elements, which are the representation of $\hat{H}^{(2a \rightleftharpoons m)} - i \frac{\partial}{\partial t}$ in the subspace of configurations $\{|N-2p, p; t\rangle\}$. These matrix elements can be evaluated explicitly. We divide them into two types, recalling that the Hamiltonian is expressed as a sum of particle-conserving and particle-nonconserving parts, $\hat{H}^{(2a \rightleftharpoons m)} = \hat{H}^{(am)} + \hat{W}^{(2a \rightleftharpoons m)}$. The diagonal or particle-conserving matrix elements read

$$\begin{aligned} & \left\langle N-2p, p; t \left| \hat{H}^{(am)} - i \frac{\partial}{\partial t} \right| N-2p, p; t \right\rangle \\ &= (N-2p) \left\langle \phi_a \left| \hat{h}^{(a)} - i \frac{\partial}{\partial t} \right| \phi_a \right\rangle \\ & \quad + \frac{\lambda_a}{2} (N-2p)(N-2p-1) \langle \phi_a^2 | \phi_a^2 \rangle \\ & \quad + p \left\langle \phi_m \left| \hat{h}^{(m)} - i \frac{\partial}{\partial t} \right| \phi_m \right\rangle + \frac{\lambda_m}{2} p(p-1) \langle \phi_m^2 | \phi_m^2 \rangle \\ & \quad + \lambda_{am} p(N-2p) \langle \phi_a \phi_m | \phi_a \phi_m \rangle, \quad p=0, \dots, [N/2]. \end{aligned} \quad (14)$$

The off-diagonal, particle-nonconserving matrix elements, originating from the conversion term $\hat{W}^{(2a \rightleftharpoons m)} = \hat{W}^{(2a \rightarrow m)} + \hat{W}^{(m \rightarrow 2a)}$, take on the following form:

$$\begin{aligned} & \langle N-2p, p; t | \hat{W}^{(2a \rightarrow m)} | N-2(p-1), p-1; t \rangle \\ &= \frac{\lambda_{con}}{\sqrt{2}} \sqrt{p(N-2p+1)(N-2p+2)} \langle \phi_m | \phi_a^2 \rangle, \\ & \quad p=1, \dots, [N/2], \\ & \langle N-2(p-1), p-1; t | \hat{W}^{(m \rightarrow 2a)} | N-2p, p; t \rangle \\ &= \{ \langle N-2p, p; t | \hat{W}^{(2a \rightarrow m)} | N-2(p-1), p-1; t \rangle \}^*, \\ & \quad p=1, \dots, [N/2]. \end{aligned} \quad (15)$$

All other matrix elements of $\hat{H}^{(2a \rightleftharpoons m)} - i \frac{\partial}{\partial t}$ in the subspace of configurations $\{|N-2p, p; t\rangle\}$ vanish. With explicit expres-

sions of the functional action (9) we can now proceed and derive the equations of motion of $\Psi(t)$.

C. The equations of motion for $\Psi(t)$

We perform the variation of the action functional [Eqs. (9), (10), and (13)] with respect to the orbitals and coefficients. Equating the variation of $S[\{C_p(t)\}, \phi_a(\mathbf{r}, t), \psi_m(\mathbf{r}, t)]$ with respect to the orbitals [see Eqs. (9) and (10)] to zero, eliminating the Lagrange multipliers $\mu_a(t)$ and $\mu_m(t)$ from the resulting equations (see Appendix A 1 for details), and dividing the result by $\langle \hat{N}_a \rangle$ and $\langle \hat{N}_m \rangle$, respectively, we obtained the following equations of motion for the orbitals:

$$\begin{aligned} \hat{\mathbf{P}}^{(a)} i | \dot{\phi}_a \rangle &= \hat{\mathbf{P}}^{(a)} \{ [\hat{h}^{(a)} + \Lambda_a(t) | \phi_a \rangle^2 + \Lambda_{am}(t) | \psi_m \rangle^2] | \phi_a \rangle \\ & \quad + \sqrt{2} \Lambda_{con}(t) \phi_a^* | \psi_m \rangle \}, \\ \hat{\mathbf{P}}^{(m)} i | \dot{\psi}_m \rangle &= \hat{\mathbf{P}}^{(m)} \left\{ [\hat{h}^{(m)} + \Lambda_m(t) | \psi_m \rangle^2 + \Lambda_{ma}(t) | \phi_a \rangle^2] | \psi_m \rangle \right. \\ & \quad \left. + \frac{\Lambda'_{con}(t)}{\sqrt{2}} \phi_a | \phi_a \rangle \right\}, \end{aligned} \quad (16)$$

where the shorthand notation $\dot{\phi}_a \equiv \frac{\partial \phi_a}{\partial t}$, $\dot{\psi}_m \equiv \frac{\partial \psi_m}{\partial t}$ is used here and hereafter. The ‘‘interaction strengths’’ are given by

$$\begin{aligned} \Lambda_a(t) &= \lambda_a \frac{\langle \hat{N}_a (\hat{N}_a - 1) \rangle}{\langle \hat{N}_a \rangle}, & \Lambda_{am}(t) &= \lambda_{am} \frac{\langle \hat{N}_a \hat{N}_m \rangle}{\langle \hat{N}_a \rangle}, \\ \Lambda_{con}(t) &= \lambda_{con} \frac{\langle \hat{b}_a^\dagger \hat{b}_a^\dagger \hat{c}_m \rangle}{\langle \hat{N}_a \rangle}, \\ \Lambda_m(t) &= \lambda_m \frac{\langle \hat{N}_m (\hat{N}_m - 1) \rangle}{\langle \hat{N}_m \rangle}, & \Lambda_{ma}(t) &= \lambda_{am} \frac{\langle \hat{N}_a \hat{N}_m \rangle}{\langle \hat{N}_m \rangle}, \\ \Lambda'_{con}(t) &= \lambda_{con} \frac{\langle \hat{c}_m^\dagger \hat{b}_a \hat{b}_a \rangle}{\langle \hat{N}_m \rangle}, \end{aligned} \quad (17)$$

and vary in time due to the conversion of atoms to molecules and vice versa.

The quantities appearing on both the right- and left-hand sides of equations of motion (16) are projection operators and given by

$$\hat{\mathbf{P}}^{(a)} = 1 - | \phi_a \rangle \langle \phi_a |, \quad \hat{\mathbf{P}}^{(m)} = 1 - | \psi_m \rangle \langle \psi_m |. \quad (18)$$

When acting on one-body functions in the atomic and molecular spaces, $\hat{\mathbf{P}}^{(a)}$ and $\hat{\mathbf{P}}^{(m)}$ project these functions onto the subspaces orthogonal to the orbitals $\phi_a(\mathbf{r}, t)$ and $\psi_m(\mathbf{r}, t)$, respectively. The projection operators $\hat{\mathbf{P}}^{(a)}$, $\hat{\mathbf{P}}^{(m)}$ emerge when one eliminates the Lagrange multipliers $\mu_a(t)$, $\mu_m(t)$ from the equations of motion, see Appendix A 1.

The appearance of the projection operator on both the left- and right-hand sides of Eq. (16) makes Eq. (16) a cumbersome set of two coupled integrodifferential nonlinear

equations. Can one simplify the matters? The answer is positive.

To this end, we invoke the invariance properties of the many-particle wave function $\Psi(t)$. Specifically, we can multiply the atomic $\phi_a(\mathbf{r}, t)$ and molecular $\psi_m(\mathbf{r}, t)$ orbitals by time-dependent phase factors to give transformed orbitals $\bar{\phi}_a(\mathbf{r}, t)$ and $\bar{\psi}_m(\mathbf{r}, t)$, and from the latter assemble transformed configurations $|N-2p, p; t\rangle \rightarrow |\bar{N}-2p, p; t\rangle$. Then, we can compensate for transforming the orbitals by the “reverse” transformation of the expansion coefficients $\{C_p(t)\} \rightarrow \{\bar{C}_p(t)\}$. Overall, we write this invariance of the many-body wave function as follows:

$$|\Psi(t)\rangle = \sum_{p=0}^{[N/2]} C_p(t) |N-2p, p; t\rangle = \sum_{p=0}^{[N/2]} \bar{C}_p(t) \overline{|N-2p, p; t\rangle}. \quad (19)$$

Clearly, unitary transformations of the orbitals and the respective transformation of the expansion coefficients neither change the size of the Hilbert space nor couple configurations with a different number of molecules. To express these properties we use the same summation index p in both the middle part and right-hand side of Eq. (19).

We can now make use of the invariance relation (19) to simplify Eq. (16). Specifically, there exists one unitary transformation that eliminates the projection operators acting on the time-derivatives (left-hand sides) in Eq. (16), without introducing any further constraint into the equations of motion; see Appendix A 1 for more details. The equations of motion for the atomic and molecular orbitals thus finally read

$$\begin{aligned} i|\dot{\phi}_a\rangle &= \hat{\mathbf{P}}^{(a)} \{ [\hat{h}^{(a)} + \Lambda_a(t)|\phi_a|^2 + \Lambda_{am}(t)|\psi_m|^2] |\phi_a\rangle \\ &\quad + \sqrt{2}\Lambda_{con}(t)\phi_a^* |\psi_m\rangle\}, \\ i|\dot{\psi}_m\rangle &= \hat{\mathbf{P}}^{(m)} \left\{ [\hat{h}^{(m)} + \Lambda_m(t)|\psi_m|^2 + \Lambda_{ma}(t)|\phi_a|^2] |\psi_m\rangle \right. \\ &\quad \left. + \frac{\Lambda'_{con}(t)}{\sqrt{2}} \phi_a |\phi_a\rangle \right\}. \end{aligned} \quad (20)$$

Equation (20) has the following property. Operating from the left with $\langle\phi_a|$ and $\langle\psi_m|$, respectively, we obtain the relations

$$\langle\phi_a|\dot{\phi}_a\rangle = 0, \quad \langle\psi_m|\dot{\psi}_m\rangle = 0, \quad (21)$$

clearly ensuring that initially-normalized orbitals remain normalized for all times. We can see the meaning of the unitary transformation carrying Eq. (16) to Eq. (20). This unitary transformation takes normalized time-dependent orbitals, $\langle\phi_a|\phi_a\rangle=1$ and $\langle\psi_m|\psi_m\rangle=1$, which therefore satisfy the general relations $\frac{\partial\langle\phi_a|\phi_a\rangle}{\partial t} = \langle\dot{\phi}_a|\phi_a\rangle + \langle\phi_a|\dot{\phi}_a\rangle = 0$ and $\frac{\partial\langle\psi_m|\psi_m\rangle}{\partial t} = \langle\dot{\psi}_m|\psi_m\rangle + \langle\psi_m|\dot{\psi}_m\rangle = 0$, and transforms them to time-dependent orbitals satisfying the specific differential condition (21).

Before we move to the corresponding working equations for the expansion coefficients $\{C_p(t)\}$, it is instructive to enquire whether we could further simplify the equations of motion (20), by eliminating the projection operators $\hat{\mathbf{P}}^{(a)}$, $\hat{\mathbf{P}}^{(m)}$

also from the right-hand sides. The answer is in general negative. If we could eliminate the projection operators remaining on the right-hand sides, it means that conditions (21) are not satisfied any more. What would then guarantee that the atomic and molecular orbitals remain normalized at all times? It turns out that the condition for that is $\text{Im}\{\lambda_{con}\langle c_m^\dagger b_a b_a\rangle\langle\psi_m|\phi_a\phi_a\rangle\} = 0$ for all times. In turn, even if this condition is satisfied at $t=0$, it is not in general guaranteed that it remains so for all times. Thus, the *presence of particle conversion* does not allow one to eliminate the projection operators $\hat{\mathbf{P}}^{(a)}$, $\hat{\mathbf{P}}^{(m)}$ also from the right-hand sides of the equations of motion (20). Alternatively speaking, in the absence of particle conversion, it is possible to eliminate the projection operators completely from Eq. (20), see in this context [93].

To derive the equations of motion of $\{C_p(t)\}$, we equate the variation of the action functional [Eqs. (9) and (13)] with respect to the expansion coefficients to zero and eliminate the Lagrange multiplier $\varepsilon(t)$ (see for details Appendix A 1). The following equations of motion are obtained:

$$\begin{aligned} \mathcal{H}^{(2a\rightleftharpoons m)}(t)\mathbf{C}(t) &= i\frac{\partial\mathbf{C}(t)}{\partial t}, \\ \mathcal{H}_{p,p'}^{(2a\rightleftharpoons m)}(t) &= \left\langle N-2p, p; t \left| \hat{H}^{(2a\rightleftharpoons m)} - i\frac{\partial}{\partial t} \right| N-2p', p'; t \right\rangle, \end{aligned} \quad (22)$$

where the vector $\mathbf{C}(t)$ collects the expansion coefficients $\{C_p(t)\}$. Equation (22) is a set of coupled first-order differential equations with time-dependent coefficients, and preserves the norm of an initially normalized vector of coefficients $\mathbf{C}(0)$. The time-dependent coefficients $\mathcal{H}_{p,p'}^{(2a\rightleftharpoons m)}(t)$, being the matrix representation of $\hat{H}^{(2a\rightleftharpoons m)} - i\frac{\partial}{\partial t}$ in the subspace of configurations $\{|N-2p, p; t\rangle\}$ and hence depending on the atomic $\phi_a(\mathbf{r}, t)$ and molecular $\psi_m(\mathbf{r}, t)$ orbitals, are prescribed in the previous section, Sec. III B.

Next, we make use of the invariance of the multiconfigurational wave function to unitary transformations (19). Explicitly, the unitary transformation responsible for transforming Eq. (16) for the orbitals to Eq. (20), transforms equations of motion (22) for the expansion coefficients to the final form:

$$\mathbf{H}^{(2a\rightleftharpoons m)}(t)\mathbf{C}(t) = i\frac{\partial\mathbf{C}(t)}{\partial t},$$

$$H_{p,p'}^{(2a\rightleftharpoons m)}(t) = \langle N-2p, p; t | \hat{H}^{(2a\rightleftharpoons m)} | N-2p', p'; t \rangle. \quad (23)$$

Equivalently, Eq. (23) can be obtained from Eq. (22) by substituting into the latter the differential condition (21).

The coupled sets of equations of motion for the atomic $\phi(\mathbf{r}, t)$ and molecular $\psi_m(\mathbf{r}, t)$ orbitals and expansion coefficients $\{C_p(t)\}$, Eqs. (16) and (22) or, respectively, Eqs. (20) and (23) constitute the *conversion mean field theory* (fully variational two-mode approximation) for the interacting atomic-molecular system with conversion.

D. The stationary self-consistent coherent mean field (time-independent fully variational two-mode approximation)

The theory presented above is a time-dependent many-body theory. It is certainly interesting to enquire what are the corresponding stationary many-body states of the atomic-molecular Hamiltonian [Eqs. (1)–(3)]? In other words, what are the self-consistent solutions that minimize (extremize) the expectation value $\langle \Psi | \hat{H}^{(2a=m)} | \Psi \rangle$ for a given time-independent multiconfigurational ansatz $|\Psi\rangle = \sum_{p=0}^{[N/2]} C_p |N-2p, p\rangle$ assembled from time-independent atomic $\phi_a(\mathbf{r})$ and molecular orbitals $\psi_m(\mathbf{r})$? To obtain this stationary self-consistent coherent mean field (time-independent fully variational two-mode approximation), we resort to imaginary time propagation and set $t \rightarrow -it$ in the corresponding equations of motion.

Setting $t \rightarrow -it$ in (the left-hand side of) either Eq. (16) or (20), the left-hand side decays to zero in time and the equation becomes time independent. Then, by multiplying the result, respectively, by $\langle \hat{N}_a \rangle$ and $\langle \hat{N}_m \rangle$, and translating back the projection operators $\hat{\mathbf{P}}^{(a)}$ and $\hat{\mathbf{P}}^{(b)}$ to the corresponding Lagrange multipliers μ_a and μ_b (see Appendix A 1), we obtain the multiconfigurational self-consistent (time-independent) equations for the atomic and molecular orbitals:

$$\begin{aligned} & [\langle \hat{N}_a \rangle \hat{h}^{(a)} + \lambda_a \langle \hat{N}_a (\hat{N}_a - 1) \rangle |\phi_a|^2 + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle |\psi_m|^2] |\phi_a\rangle \\ & + \sqrt{2} \lambda_{con} \langle \hat{b}_a^\dagger \hat{b}_a^\dagger \hat{c}_m \rangle \phi_a^* |\psi_m\rangle = \mu_a |\phi_a\rangle, \\ & [\langle \hat{N}_m \rangle \hat{h}^{(m)} + \lambda_m \langle \hat{N}_m (\hat{N}_m - 1) \rangle |\psi_m|^2 + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle |\phi_a|^2] |\psi_m\rangle \\ & + \frac{\lambda_{con}}{\sqrt{2}} \langle \hat{c}_m^\dagger \hat{b}_a^\dagger \hat{b}_a \rangle \phi_a |\phi_a\rangle = \mu_m |\psi_m\rangle. \end{aligned} \quad (24)$$

Similarly, restoring the Lagrange multiplier $\varepsilon(t)$ into either Eq. (22) or (23), see in this respect Appendix A 1, and setting $t \rightarrow -it$ therein, we obtain the stationary (self-consistent) eigenvalue equation

$$\mathbf{H}^{(2a=m)} \mathbf{C} = \varepsilon \mathbf{C},$$

$$H_{p,p'}^{(2a=m)} = \langle N-2p, p | \hat{H}^{(2a=m)} | N-2p', p' \rangle \quad (25)$$

for the expansion coefficients. We see that the (redundant) time-dependent Lagrange multiplier $\varepsilon(t)$ of the time-dependent theory has emerged as the eigenenergy $\varepsilon = \langle \Psi | \hat{H}^{(2a=m)} | \Psi \rangle$ of the stationary theory.

The theory “distilled” into Eqs. (24) and (25) is a fully variational stationary theory for the interacting atomic-molecular system in presence of conversion, where a single orbital is allowed for the atoms and a single orbital to the molecules. It is a system of coupled eigenvalue-like equations for the orbitals and eigenvalue equation for the coefficients, thought nonlinear and integrodifferential ones.

IV. THE GENERAL MULTICONFIGURATIONAL THEORY WITH ATOM-MOLECULE CONVERSION

In this section we develop a general many-body theory for atom-molecule conversion, by allowing the atoms and mol-

ecules to occupy more orbitals. Section IV A builds the theory for the popular contact interaction, whereas the case of generic noncontact interactions is presented in Sec. IV B.

A. Formulation for contact interactions

1. The multiconfigurational ansatz for the wave function

The multiconfigurational expansion mixes atomic-molecular states with different numbers of particles which are eigenfunctions of the particle-number operator [Eq. (4)] $\hat{N} |\Psi(t)\rangle = N |\Psi(t)\rangle$,

$$\begin{aligned} |\Psi(t)\rangle &= \sum_{p=0}^{[N/2]} \sum_{\vec{n}^p, \vec{m}^p} C_{\vec{n}^p \vec{m}^p}(t) |\vec{n}^p, \vec{m}^p; t\rangle, \\ |\vec{n}^p, \vec{m}^p; t\rangle &\equiv \frac{1}{\sqrt{n_1^p \cdots n_M^p! m_1^p! \cdots m_{M'}^p!}} [\hat{b}_1^\dagger(t)]^{n_1^p} \cdots \\ &\quad \times [\hat{b}_M^\dagger(t)]^{n_M^p} [\hat{c}_1^\dagger(t)]^{m_1^p} \cdots [\hat{c}_{M'}^\dagger(t)]^{m_{M'}^p} |\text{vac}\rangle. \end{aligned} \quad (26)$$

We collect the individual occupations in the vectors $\vec{n}^p = (n_1^p, \dots, n_M^p)$, $\vec{m}^p = (m_1, \dots, m_{M'}^p)$. The number of bosonic atoms $|\vec{n}^p| \equiv n_1^p + \dots + n_M^p = N-2p$ and molecules $|\vec{m}^p| \equiv m_1^p + \dots + m_{M'}^p = p$ of each configuration $|\vec{n}^p, \vec{m}^p; t\rangle$ satisfies the particle-conservation law $|\vec{n}^p| + 2|\vec{m}^p| = N$. Observe that the number of molecules p serves as an index to the occupation numbers \vec{n}^p and \vec{m}^p . This simply reflects the fact that, for a given number of $N-2p$ atoms and p molecules, the possible occupation numbers which the configurations can assume depend on p itself. The index p together with the occupation numbers \vec{n}^p, \vec{m}^p make a unique representation of each configuration. The atomic and molecular number operators in the corresponding Hilbert space boil down to $\hat{N}_a = \sum_{k=1}^M \hat{b}_k^\dagger \hat{b}_k$ and $\hat{N}_m = \sum_{k'=1}^{M'} \hat{c}_{k'}^\dagger \hat{c}_{k'}$, respectively. The size of the resulting Hilbert space is given by $\sum_{p=0}^{[N/2]} \binom{N-2p+M-1}{M-1} \binom{p+M'-1}{M'-1}$, i.e., by the sum of products of the sizes of the respective Hilbert subspaces for $N-2p$ bosonic atoms with M orbitals and p bosonic molecules with M' orbitals.

2. Reduced density matrices for systems with particle conversion

As part of the variational derivation we will need the expectation value of $\hat{H}^{(2a=m)} - i \frac{\partial}{\partial t}$ with respect to $\Psi(t)$. To this end, it will be proved valuable to define and employ the reduced density matrices of $\Psi(t)$. We remind that Löwdin has introduced the concept of reduced density matrices for systems of a fixed number of particles (identical fermions) [44]. Nevertheless and although $\Psi(t)$ is not comprised of a fixed number of atoms or a fixed number of molecules, it is possible to define the reduced density matrices of a mixture of atoms and molecules *with conversion*.

Having at hand the normalized many-body wave function $\Psi(t)$, the reduced one-body density matrices of the atoms and molecules are defined by

$$\begin{aligned}
\rho^{(a)}(\mathbf{r}_1|\mathbf{r}_2;t) &= \langle \hat{\Psi}_a^\dagger(\mathbf{r}_2)\hat{\Psi}_a(\mathbf{r}_1) \rangle \\
&= \sum_{k,q=1}^M \rho_{kq}^{(a)}(t) \phi_k^*(\mathbf{r}_2,t) \phi_q(\mathbf{r}_1,t), \\
\rho^{(m)}(\mathbf{r}_1|\mathbf{r}_2;t) &= \langle \hat{\Psi}_m^\dagger(\mathbf{r}_2)\hat{\Psi}_m(\mathbf{r}_1) \rangle \\
&= \sum_{k',q'=1}^{M'} \rho_{k'q'}^{(m)}(t) \psi_{k'}^*(\mathbf{r}_2,t) \psi_{q'}(\mathbf{r}_1,t), \quad (27)
\end{aligned}$$

where the matrix elements $\rho_{kq}^{(a)}(t) = \langle \hat{b}_k^\dagger \hat{b}_q \rangle$ and $\rho_{k'q'}^{(m)}(t) = \langle \hat{c}_{k'}^\dagger \hat{c}_{q'} \rangle$ are prescribed in Appendix B. We collect these matrix elements as $\boldsymbol{\rho}^{(a)}(t) = \{\rho_{kq}^{(a)}(t)\}$ and $\boldsymbol{\rho}^{(m)}(t) = \{\rho_{k'q'}^{(m)}(t)\}$. Similarly, the reduced two-body density matrices of the atoms and molecules are defined by

$$\begin{aligned}
\rho^{(a)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3, \mathbf{r}_4;t) &= \langle \hat{\Psi}_a^\dagger(\mathbf{r}_3)\hat{\Psi}_a^\dagger(\mathbf{r}_4)\hat{\Psi}_a(\mathbf{r}_2)\hat{\Psi}_a(\mathbf{r}_1) \rangle \\
&= \sum_{k,s,l,q=1}^M \rho_{kslq}^{(a)}(t) \phi_k^*(\mathbf{r}_3,t) \\
&\quad \times \phi_s^*(\mathbf{r}_4,t) \phi_l(\mathbf{r}_2,t) \phi_q(\mathbf{r}_1,t), \\
\rho^{(m)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3, \mathbf{r}_4;t) &= \langle \hat{\Psi}_m^\dagger(\mathbf{r}_3)\hat{\Psi}_m^\dagger(\mathbf{r}_4)\hat{\Psi}_m(\mathbf{r}_2)\hat{\Psi}_m(\mathbf{r}_1) \rangle \\
&= \sum_{k',s',l',q'=1}^{M'} \rho_{k's'l'q'}^{(m)}(t) \psi_{k'}^*(\mathbf{r}_3,t) \\
&\quad \times \psi_{s'}^*(\mathbf{r}_4,t) \psi_{l'}(\mathbf{r}_2,t) \psi_{q'}(\mathbf{r}_1,t), \\
\rho^{(am)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3, \mathbf{r}_4;t) &= \langle \hat{\Psi}_a^\dagger(\mathbf{r}_3)\hat{\Psi}_a(\mathbf{r}_1)\hat{\Psi}_m^\dagger(\mathbf{r}_4)\hat{\Psi}_m(\mathbf{r}_2) \rangle \\
&= \sum_{k,q=1}^M \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)}(t) \phi_k^*(\mathbf{r}_3,t) \\
&\quad \times \phi_q(\mathbf{r}_1,t) \psi_{k'}^*(\mathbf{r}_4,t) \psi_{q'}(\mathbf{r}_2,t), \quad (28)
\end{aligned}$$

where the matrix elements $\rho_{kslq}^{(a)}(t) = \langle \hat{b}_k^\dagger \hat{b}_s^\dagger \hat{b}_l \hat{b}_q \rangle$, $\rho_{k's'l'q'}^{(m)}(t) = \langle \hat{c}_{k'}^\dagger \hat{c}_{s'}^\dagger \hat{c}_{l'} \hat{c}_{q'} \rangle$, and $\rho_{kk'qq'}^{(am)}(t) = \langle \hat{b}_k^\dagger \hat{b}_{q'} \hat{c}_{k'}^\dagger \hat{c}_{q'} \rangle$ are prescribed in Appendix B. Because the reduced density matrices (27) and (28) directly only couple configurations with the same number of atoms and molecules, we will refer to them as *particle-conserving* reduced density matrices. In this context, $\rho^{(am)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3, \mathbf{r}_4;t)$ is the lowest-order *interspecies* particle-conserving reduced density matrix.

From the above discussion it is anticipated that, due to the conversion term (3) in the Hamiltonian, another kind of reduced density matrices appears in the theory. Specifically, we define the *particle nonconserving* reduced density matrices as follows:

$$\begin{aligned}
\rho^{(2a \rightarrow m)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3;t) &= \langle \hat{\Psi}_m^\dagger(\mathbf{r}_3)\hat{\Psi}_a(\mathbf{r}_2)\hat{\Psi}_a(\mathbf{r}_1) \rangle \\
&= \sum_{k'=1}^{M'} \sum_{k,q=1}^M \rho_{k'kq}^{(2a \rightarrow m)}(t) \\
&\quad \times \psi_{k'}^*(\mathbf{r}_3,t) \phi_k(\mathbf{r}_2,t) \phi_q(\mathbf{r}_1,t), \\
\rho^{(m \rightarrow 2a)}(\mathbf{r}_3|\mathbf{r}_2, \mathbf{r}_1;t) &= \langle \hat{\Psi}_a^\dagger(\mathbf{r}_1)\hat{\Psi}_a^\dagger(\mathbf{r}_2)\hat{\Psi}_m(\mathbf{r}_3) \rangle \\
&= \sum_{k'=1}^{M'} \sum_{k,q=1}^M \rho_{qkk'}^{(m \rightarrow 2a)}(t) \phi_q^*(\mathbf{r}_1,t) \\
&\quad \times \phi_k^*(\mathbf{r}_2,t) \psi_{k'}(\mathbf{r}_3,t), \\
\rho^{(m \rightarrow 2a)}(\mathbf{r}_3|\mathbf{r}_2, \mathbf{r}_1;t) &= \{\rho^{(2a \rightarrow m)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3;t)\}^*,
\end{aligned}$$

$$\rho_{qkk'}^{(m \rightarrow 2a)}(t) = \{\rho_{k'kq}^{(2a \rightarrow m)}(t)\}^*. \quad (29)$$

The matrix elements $\rho_{k'kq}^{(2a \rightarrow m)} = \langle \hat{c}_{k'}^\dagger \hat{b}_k \hat{b}_q \rangle$ are given in Appendix B.

3. The functional action S and its evaluation

We start from the functional action of the time-dependent Schrödinger equation which in the general multiconfigurational case takes on the form

$$\begin{aligned}
S[\{C_{\bar{n}\bar{p}\bar{m}\bar{p}}(t)\}, \{\phi_k(\mathbf{r},t)\}, \{\psi_{k'}(\mathbf{r},t)\}] \\
= \int dt \left\{ \left\langle \Psi(t) \left| \hat{H}^{(2a \rightarrow m)} - i \frac{\partial}{\partial t} \right| \Psi(t) \right\rangle \right. \\
- \sum_{k,j=1}^M \mu_{kj}^{(a)}(t) [\langle \phi_k(\mathbf{r},t) | \phi_j(\mathbf{r},t) \rangle - \delta_{kj}] \\
- \sum_{k',j'=1}^{M'} \mu_{k'j'}^{(m)}(t) [\langle \psi_{k'}(\mathbf{r},t) | \psi_{j'}(\mathbf{r},t) \rangle - \delta_{k'j'}] \\
\left. - \varepsilon(t) \left[\sum_{\rho=0}^{\lfloor N/2 \rfloor} \sum_{\bar{n}\bar{p}, \bar{m}\bar{p}} |C_{\bar{n}\bar{p}\bar{m}\bar{p}}(t)|^2 - 1 \right] \right\}. \quad (30)
\end{aligned}$$

The time-dependent Lagrange multipliers $\{\mu_{kj}^{(a)}(t)\}$, $\{\mu_{k'j'}^{(m)}(t)\}$, and $\varepsilon(t)$ are introduced to ensure orthonormalization of the atomic $\{\phi_k(\mathbf{r},t)\}$ and molecular $\{\psi_{k'}(\mathbf{r},t)\}$ orbital sets and normalization of the expansion coefficients $\{C_{\bar{n}\bar{p}\bar{m}\bar{p}}(t)\}$.

To derive the equations of motion for the atomic-molecular multiconfigurational wave function (26), the expectation value of $\hat{H}^{(2a \rightarrow m)} - i \frac{\partial}{\partial t}$ with respect to $\Psi(t)$ is needed, where $\hat{H}^{(2a \rightarrow m)}$ is given in Eq. (7). The expectation value of $\hat{H}^{(2a \rightarrow m)} - i \frac{\partial}{\partial t}$ is expressed by two equivalent forms, as done in Sec. III B. The first form, where the dependence of Eq. (30) on the atomic and molecular orbitals is explicit, reads

$$\begin{aligned}
\left\langle \Psi(t) \left| \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} \right| \Psi(t) \right\rangle &= \sum_{k,q=1}^M \rho_{kq}^{(a)} \left\langle \phi_k \left| h^{(a)} - i \frac{\partial}{\partial t} \right| \phi_q \right\rangle + \frac{\lambda_a}{2} \sum_{k,s,l,q=1}^M \rho_{kslq}^{(a)} \langle \phi_k \phi_s | \phi_q \phi_l \rangle + \sum_{k',q'=1}^{M'} \rho_{k'q'}^{(m)} \left\langle \psi_{k'} \left| h^{(m)} - i \frac{\partial}{\partial t} \right| \psi_{q'} \right\rangle \\
&+ \frac{\lambda_m}{2} \sum_{k',s',l',q'=1}^{M'} \rho_{k's'l'q'}^{(m)} \langle \phi_{k'} \phi_{s'} | \phi_{q'} \phi_{l'} \rangle + \lambda_{am} \sum_{k,q=1}^M \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)} \langle \phi_k \psi_{k'} | \phi_q \psi_{q'} \rangle \\
&+ \frac{\lambda_{con}}{\sqrt{2}} \sum_{k,q=1}^M \sum_{k'=1}^{M'} [\rho_{k'kq}^{(2a \rightarrow m)} \langle \psi_{k'} | \phi_k \phi_q \rangle + \rho_{qkk'}^{(m \rightarrow 2a)} \langle \phi_q \phi_k | \psi_{k'} \rangle] - i \sum_{p=0}^{[N/2]} \sum_{\vec{n}^p, \vec{m}^p} C_{\vec{n}^p \vec{m}^p}^* \frac{\partial C_{\vec{n}^p \vec{m}^p}}{\partial t}. \quad (31)
\end{aligned}$$

We see in Eq. (31) the appearance of the particle-conserving and particle-nonconserving reduced density matrices introduced in the previous Sec. IV A 2. Equation (31) is to be used to derive the equations of motion of $\{\phi_k(\mathbf{r}, t)\}$ and $\{\psi_{k'}(\mathbf{r}, t)\}$.

The second form of the expectation value of $\hat{H}^{(2a=m)} - i \frac{\partial}{\partial t}$ in the functional action (30),

$$\left\langle \Psi(t) \left| \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} \right| \Psi(t) \right\rangle = \sum_{p=0}^{[N/2]} \sum_{\vec{n}^p, \vec{m}^p} C_{\vec{n}^p \vec{m}^p}^* \left[\sum_{p'=0}^{[N/2]} \sum_{\vec{n}'^p, \vec{m}'^p} \left\langle \vec{n}^p, \vec{m}^p; t \left| \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} \right| \vec{n}'^p, \vec{m}'^p; t \right\rangle C_{\vec{n}'^p, \vec{m}'^p} - i \frac{\partial C_{\vec{n}^p \vec{m}^p}}{\partial t} \right], \quad (32)$$

displays its explicit dependence on the expansion coefficients, and therefore will be employed to derive the equations of motion of $\{C_{\vec{n}^p \vec{m}^p}(t)\}$. Finally, it is deductive to compare the structure of Eqs. (10) and (13) in the conversion mean field (fully variational two-mode) problem to that of Eqs. (31) and (32) of the general problem.

4. The equations of motion for $\Psi(t)$

Collecting the above ingredients, we are ready to perform the variation of the functional action $S[\{C_{\vec{n}^p \vec{m}^p}(t)\}, \{\phi_k(\mathbf{r}, t)\}, \{\psi_{k'}(\mathbf{r}, t)\}]$ and arrive at the equations of motion of $\Psi(t)$. Equating the variation of the functional action [Eqs. (30) and (31)] with respect to the orbitals to zero and eliminating the Lagrange multipliers $\{\mu_{kj}^{(a)}(t)\}, \{\mu_{k'j'}^{(m)}(t)\}$ (see Appendix A 2), we obtain the following result, $j=1, \dots, M, j'=1, \dots, M'$:

$$\begin{aligned}
\hat{\mathbf{P}}^{(a)} i |\dot{\phi}_j\rangle &= \hat{\mathbf{P}}^{(a)} \left[\hat{h}^{(a)} |\phi_j\rangle + \sum_{k=1}^M \{\rho^{(a)}(t)\}_{jk}^{-1} \right. \\
&\times \sum_{q=1}^M \left(\{\rho_2(\phi^2, \psi^2)\}_{kq}^{(a)} |\phi_q\rangle \right. \\
&\left. \left. + \sqrt{2} \lambda_{con} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m \rightarrow 2a)} \phi_q^* |\psi_{k'}\rangle \right) \right], \\
\hat{\mathbf{P}}^{(m)} i |\dot{\psi}_{j'}\rangle &= \hat{\mathbf{P}}^{(m)} \left[\hat{h}^{(m)} |\psi_{j'}\rangle + \sum_{k'=1}^{M'} \{\rho^{(m)}(t)\}_{j'k'}^{-1} \right. \\
&\times \left(\sum_{q'=1}^{M'} \{\rho_2(\psi^2, \phi^2)\}_{k'q'}^{(m)} |\psi_{q'}\rangle \right. \\
&\left. \left. + \frac{\lambda_{con}}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a \rightarrow m)} \phi_k |\phi_q\rangle \right) \right], \quad (33)
\end{aligned}$$

where terms with products of reduced two-body density matrices times orbital pairs are collected together and denoted for brevity as

$$\begin{aligned}
\{\rho_2(\phi^2, \psi^2)\}_{kq}^{(a)} &\equiv \lambda_a \sum_{s,l=1}^M \rho_{kslq}^{(a)} (\phi_s^* \phi_l) + \lambda_{am} \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)} (\psi_{k'}^* \psi_{q'}), \\
\{\rho_2(\psi^2, \phi^2)\}_{k'q'}^{(m)} &\equiv \lambda_m \sum_{s',l'=1}^{M'} \rho_{k's'l'q'}^{(m)} (\psi_{s'}^* \psi_{l'}) + \lambda_{am} \sum_{k,q=1}^M \rho_{kk'qq'}^{(am)} (\phi_k^* \phi_q), \quad (34)
\end{aligned}$$

and

$$\hat{\mathbf{P}}^{(a)} = 1 - \sum_{u=1}^M |\phi_u\rangle \langle \phi_u|, \quad \hat{\mathbf{P}}^{(m)} = 1 - \sum_{u'=1}^{M'} |\psi_{u'}\rangle \langle \psi_{u'}|, \quad (35)$$

are projection operators. When acting on one-body functions in the atomic and molecular spaces, $\hat{\mathbf{P}}^{(a)}$ and $\hat{\mathbf{P}}^{(m)}$ project them onto the subspaces orthogonal to those spanned by the orbitals $\{\phi_k(\mathbf{r}, t)\}$ and $\{\psi_{k'}(\mathbf{r}, t)\}$, respectively. These projection operators emerge when one eliminates the Lagrange multipliers $\{\mu_{kj}^{(a)}(t)\}$ and $\{\mu_{k'j'}^{(m)}(t)\}$ from the equations of motion, see Appendix A 2. To remind, we use the shorthand notation $\dot{\phi}_j \equiv \frac{\partial \phi_j}{\partial t}$, $\dot{\psi}_{j'} \equiv \frac{\partial \psi_{j'}}{\partial t}$ in the equations of motion for the orbitals.

The appearance of the projection operators on both the left- and right-hand sides of Eq. (33) makes the system (33) a cumbersome system of integrodifferential nonlinear equations. This situation can be simplified by generalizing the treatment of Sec. III C, namely, exploiting the invariance properties of the many-particle wave function $\Psi(t)$. Specifi-

cally, we perform independent unitary transformations on the atomic $\{\phi_k(\mathbf{r}, t)\} \rightarrow \{\bar{\phi}_k(\mathbf{r}, t)\}$ and molecular $\{\psi_{k'}(\mathbf{r}, t)\} \rightarrow \{\bar{\psi}_{k'}(\mathbf{r}, t)\}$ orbitals, which results in transformed configurations $|\vec{n}^p, \vec{m}^p; t\rangle \rightarrow |\bar{n}^p, \bar{m}^p; t\rangle$. Then, we can compensate for the transformations of the orbital sets by the “reverse” transformation of the expansion coefficients $\{C_{\vec{n}^p, \vec{m}^p}(t)\} \rightarrow \{\bar{C}_{\bar{n}^p, \bar{m}^p}(t)\}$. We represent this invariance by the following equality:

$$\begin{aligned} |\Psi(t)\rangle &= \sum_{p=0}^{[N/2]} \sum_{\vec{n}^p, \vec{m}^p} C_{\vec{n}^p, \vec{m}^p}(t) |\vec{n}^p, \vec{m}^p; t\rangle \\ &= \sum_{p=0}^{[N/2]} \sum_{\bar{n}^p, \bar{m}^p} \bar{C}_{\bar{n}^p, \bar{m}^p}(t) |\bar{n}^p, \bar{m}^p; t\rangle. \end{aligned} \quad (36)$$

The transformations of the orbital sets and expansion coefficients do not change the size of the Hilbert space, or couple systems with different numbers of atoms and/or molecules. We remark that transformations which intermix atomic and molecular orbitals are not required for our needs. To represent these properties, the same occupation numbers \vec{n}^p , \vec{m}^p and summation index p of the number of molecules are used for both multiconfigurational expansions of $\Psi(t)$ in Eq. (36).

We can now make use of the invariance (36) to simplify the equations of motion (33), without introducing further constraints into the equations of motion. We utilize a specific unitary transformation of the many-particle wave function that eliminates the projection operators acting on the time derivatives (left-hand sides) in Eq. (33); see Appendix A 2 for more details. The final result for the equations of motion for the atomic $\{\phi_k(\mathbf{r}, t)\}$ and molecular $\{\psi_{k'}(\mathbf{r}, t)\}$ orbitals thus takes on the form, $j=1, \dots, M$, $j'=1, \dots, M'$:

$$\begin{aligned} i|\dot{\phi}_j\rangle &= \hat{\mathbf{P}}^{(a)} \left[\hat{h}^{(a)}|\phi_j\rangle + \sum_{k=1}^M \{\rho^{(a)}(t)\}_{jk}^{-1} \right. \\ &\quad \times \sum_{q=1}^M \left(\{\rho_2(\phi^2, \psi^2)\}_{kq}^{(a)} |\phi_q\rangle \right. \\ &\quad \left. \left. + \sqrt{2}\lambda_{con} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m \rightarrow 2a)} \phi_q^* |\psi_{k'}\rangle \right) \right], \\ i|\dot{\psi}_{j'}\rangle &= \hat{\mathbf{P}}^{(m)} \left[\hat{h}^{(m)}|\psi_{j'}\rangle + \sum_{k'=1}^{M'} \{\rho^{(m)}(t)\}_{j'k'}^{-1} \right. \\ &\quad \times \left(\sum_{q'=1}^{M'} \{\rho_2(\psi^2, \phi^2)\}_{k'q'}^{(m)} |\psi_{q'}\rangle \right. \\ &\quad \left. \left. + \frac{\lambda_{con}}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a \rightarrow m)} \phi_k |\phi_q\rangle \right) \right], \end{aligned} \quad (37)$$

with the projection operators $\hat{\mathbf{P}}^{(a)}$ and $\hat{\mathbf{P}}^{(m)}$ appearing now on the right-hand sides only.

Now, taking the respective scalar products of Eq. (37) with $\{\langle\phi_k|\}$ and $\{\langle\psi_{k'}|\}$, we obtain the following differential conditions:

$$\begin{aligned} \langle\phi_k|\dot{\phi}_q\rangle &= 0, \quad k, q = 1, \dots, M, \\ \langle\psi_{k'}|\dot{\psi}_{q'}\rangle &= 0, \quad k', q' = 1, \dots, M'. \end{aligned} \quad (38)$$

It is instructive to mention that these differential conditions have been introduced originally by the MCTDH developers [7,8], and used thereafter in particle-conserving multiconfigurational theories for identical particles and mixtures [29–33,53,54].

The differential conditions (38) ensure that initially orthonormalized orbital sets $\{\phi_k(\mathbf{r}, t)\}$, $\{\psi_{k'}(\mathbf{r}, t)\}$ remain orthonormalized at all times. The meaning of the unitary transformation carrying equations of motion (33) to equations of motion (37) can now be seen. This unitary transformation takes orthonormal time-dependent orbitals, $\langle\phi_k|\phi_q\rangle = \delta_{kq}$ and $\langle\psi_{k'}|\psi_{q'}\rangle = \delta_{k'q'}$ [δ_{kq} , $\delta_{k'q'}$ is the Kronecker δ function], which therefore satisfy the general relations $\frac{\partial\langle\phi_k|\phi_q\rangle}{\partial t} = \langle\dot{\phi}_k|\phi_q\rangle + \langle\phi_k|\dot{\phi}_q\rangle = 0$ and $\frac{\partial\langle\psi_{k'}|\psi_{q'}\rangle}{\partial t} = \langle\dot{\psi}_{k'}|\psi_{q'}\rangle + \langle\psi_{k'}|\dot{\psi}_{q'}\rangle = 0$, and transforms them to time-dependent orbitals satisfying the specific differential conditions (38).

Moving to the equations of motion for the coefficients $\{C_{\vec{n}^p, \vec{m}^p}(t)\}$, we equate the variation of the functional action [Eqs. (30) and (32)] with respect to the expansion coefficients to zero. Eliminating the Lagrange multiplier $\varepsilon(t)$ by a respective phase transformation of the coefficients, we arrive at the form

$$\mathcal{H}^{(2a \rightarrow m)}(t) \mathbf{C}(t) = i \frac{\partial \mathbf{C}(t)}{\partial t},$$

$$\mathcal{H}_{\vec{n}^p, \vec{m}^p, \bar{n}^p, \bar{m}^p}^{(2a \rightarrow m)}(t) = \left\langle \vec{n}^p, \vec{m}^p; t \left| \hat{H}^{(2a \rightarrow m)} - i \frac{\partial}{\partial t} \right| \bar{n}^p, \bar{m}^p; t \right\rangle. \quad (39)$$

Equation (39) has exactly the same form as Eq. (22) in the specific theory of Sec. III C, and constitutes a set of coupled first-order differential equations with time-dependent coefficients that preserve the norm of an initially normalized vector of coefficients $\mathbf{C}(0)$. The matrix elements of $\hat{H}^{(2a \rightarrow m)} - i \frac{\partial}{\partial t}$ with respect to two general configurations, $\mathcal{H}_{\vec{n}^p, \vec{m}^p, \bar{n}^p, \bar{m}^p}^{(2a \rightarrow m)}(t)$, are prescribed in Appendix B.

Now, to arrive at the final form of the equations of motion for the coefficients, we make use of the invariance of $\Psi(t)$ to unitary transformations (36). Specifically, the unitary transformation carrying Eq. (33) for the orbitals to Eq. (37), casts Eq. (39) for the expansion coefficients into the final result,

$$\mathbf{H}^{(2a \rightarrow m)}(t) \mathbf{C}(t) = i \frac{\partial \mathbf{C}(t)}{\partial t},$$

$$H_{\vec{n}^p, \vec{m}^p, \bar{n}^p, \bar{m}^p}^{(2a \rightarrow m)}(t) = \langle \vec{n}^p, \vec{m}^p; t | \hat{H}^{(2a \rightarrow m)} | \bar{n}^p, \bar{m}^p; t \rangle. \quad (40)$$

Equation (40) has exactly the same form as Eq. (23) in the specific case of Sec. III C. Of course, there are much more

expansion coefficients in the general case. Finally and equivalently, we note that the result (40) can be obtained from Eq. (39) when the differential condition (38) is substituted into the latter.

Let us pause for a moment and summarize. We have started from the functional action (30) and arrived at the equations of motion for $\Psi(t)$. Equation (33) for the orbitals $\{\phi_k(\mathbf{r}, t)\}$, $\{\psi_{k'}(\mathbf{r}, t)\}$ and Eq. (39) for the expansion coefficients $\{C_{\vec{n}^p, \vec{m}^p}(t)\}$, or, respectively, Eqs. (37) and (40) constitute the multiconfigurational time-dependent Hartree theory for systems with particle conversion; here specifically the theory for bosonic atoms and bosonic molecules with conversion.

5. The stationary self-consistent general multiconfigurational theory with conversion

The theory presented above is a time-dependent many-body theory and, as done in the previous Sec. III, it is relevant to put forward the corresponding stationary general theory. Consider the multiconfigurational expansion $|\Psi\rangle = \sum_{p=0}^{[N/2]} \sum_{\vec{n}^p, \vec{m}^p} C_{\vec{n}^p, \vec{m}^p} |\vec{n}^p, \vec{m}^p\rangle$, where the expansion coefficients $\{C_{\vec{n}^p, \vec{m}^p}\}$ and orbitals $\{\phi_k(\mathbf{r})\}$, $\{\psi_{k'}(\mathbf{r})\}$ assembling the configurations $\{|\vec{n}^p, \vec{m}^p\rangle\}$ are time-independent quantities. What are then the self-consistent solutions that minimize (extremize) the expectation value $\langle \Psi | \hat{H}^{(2a=m)} | \Psi \rangle$?

The working equations of the stationary theory can be obtained by resorting to imaginary time propagation and setting $t \rightarrow -it$ in either equations of motion (33) and (39) or equations of motion (37) and (40), after the time-dependent Lagrange multiplier $\varepsilon(t)$ has been reinstated. Then, by translating the projection operators $\hat{\mathbf{P}}^{(a)}$, $\hat{\mathbf{P}}^{(m)}$ to the respective Lagrange multipliers $\{\mu_{kj}^{(a)}\}$, $\{\mu_{k'j'}^{(m)}\}$, the resulting working equations take on the form

$$\begin{aligned} & \sum_{q=1}^M \left\{ \left[\rho_{kq}^{(a)} \hat{h}^{(a)} + \{\rho_2(\phi^2, \psi^2)\}_{kq}^{(a)} \right] |\phi_q\rangle \right. \\ & \quad \left. + \sqrt{2} \lambda_{con} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m-2a)} \phi_q^* |\psi_{k'}\rangle \right\} \\ & = \sum_{j=1}^M \mu_{kj}^{(a)} |\phi_j\rangle, \quad k = 1, \dots, M, \\ & \sum_{q'=1}^{M'} \left[\rho_{k'q'}^{(m)} \hat{h}^{(m)} + \{\rho_2(\psi^2, \phi^2)\}_{k'q'}^{(m)} \right] |\psi_{q'}\rangle \\ & \quad + \frac{\lambda_{con}}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a-m)} \phi_k |\phi_q\rangle \\ & = \sum_{j'=1}^{M'} \mu_{k'j'}^{(m)} |\psi_{j'}\rangle, \quad k' = 1, \dots, M' \end{aligned} \quad (41)$$

for the orbitals, and

$$\mathbf{H}^{(2a=m)} \mathbf{C} = \varepsilon \mathbf{C},$$

$$H_{\vec{n}^p, \vec{m}^p, \vec{n}'^p, \vec{m}'^p}^{(2a=m)} = \langle \vec{n}^p, \vec{m}^p | \hat{H}^{(2a=m)} | \vec{n}'^p, \vec{m}'^p \rangle \quad (42)$$

for the expansion coefficients. As seen in Sec. III, the time-dependent Lagrange multiplier $\varepsilon(t)$ emerges in the time-independent theory as the eigenenergy of the coupled atom-molecule system with $\varepsilon = \langle \Psi | \hat{H}^{(2a=m)} | \Psi \rangle$.

The stationary equations for the orbitals (41) can be further simplified. The stationary wave function Ψ , as its time-dependent counterpart, is invariant to independent unitary transformations of the orbital sets $\{\phi_k(\mathbf{r})\}$, $\{\psi_{k'}(\mathbf{r})\}$ and the “inverse” transformation of the expansion coefficients $\{C_{\vec{n}^p, \vec{m}^p}\}$. We can use the unitary matrices which diagonalize the matrices of Lagrange multipliers $\{\mu_{kj}^{(a)}\}$, $\{\mu_{k'j'}^{(m)}\}$. We note that the matrices of Lagrange multipliers are Hermitian matrices for stationary states. As a result of this transformation, we obtain a set of coupled equations for the orbitals that look just as Eq. (41), except for the right-hand sides being diagonal,

$$\begin{aligned} & \sum_{q=1}^M \left\{ \left[\rho_{kq}^{(a)} \hat{h}^{(a)} + \{\rho_2(\phi^2, \psi^2)\}_{kq}^{(a)} \right] |\phi_q\rangle \right. \\ & \quad \left. + \sqrt{2} \lambda_{con} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m-2a)} \phi_q^* |\psi_{k'}\rangle \right\} \\ & = \mu_k^{(a)} |\phi_k\rangle, \quad k = 1, \dots, M, \\ & \sum_{q'=1}^{M'} \left[\rho_{k'q'}^{(m)} \hat{h}^{(m)} + \{\rho_2(\psi^2, \phi^2)\}_{k'q'}^{(m)} \right] |\psi_{q'}\rangle \\ & \quad + \frac{\lambda_{con}}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a-m)} \phi_k |\phi_q\rangle \\ & = \mu_{k'}^{(m)} |\psi_{k'}\rangle, \quad k' = 1, \dots, M'. \end{aligned} \quad (43)$$

The form of the equation for the expansion coefficients (42) does not change. Thus, the final result for the stationary theory, Eqs. (42) and (43), is a coupled system of integrodifferential, nonlinear equations constituting eigenvalue equations for the orbitals and eigenvalue equation for the expansion coefficients; compare to Sec. III D. Generally, the transformation of the matrices of Lagrange multipliers to diagonal form would make the orbitals delocalized. Hence, in problems where working with localized orbitals is of advantage or relevance, for instance in lattices, it is the form (41) with the in general nondiagonal Lagrange multipliers which is to be preferred.

B. Formulation for general interactions

The last stage of the theory is to return to the case of generic noncontact interactions in the Hamiltonian [Eqs. (1)–(3)] and have the respective theory derived. The derivation of the equations of motion follows essentially the same steps taken in the previous Sec. IV A and there is obviously

no need to repeat it. The only extra care needed is when minimizing the conversion term in the functional action with respect to the molecular orbitals, where exchange of variables is used. This point and related derivations are discussed in Appendix A 2. Below, we report the final results of the time-dependent as well as the self-consistent time-independent theories.

The final form of the time-dependent equations of motion of the orbitals reads, $j=1, \dots, M, j'=1, \dots, M'$,

$$i|\dot{\phi}_j\rangle = \hat{\mathbf{P}}^{(a)} \left[\hat{h}^{(a)}|\phi_j\rangle + \sum_{k=1}^M \{\rho^{(a)}(t)\}_{jk}^{-1} \right. \\ \left. \times \sum_{q=1}^M \left(\{\rho_2 W\}_{kq}^{(a)}|\phi_q\rangle + \sqrt{2} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m-2a)} \hat{W}_{qk'}^{(m-2a)} \right) \right], \\ i|\dot{\psi}_{j'}\rangle = \hat{\mathbf{P}}^{(m)} \left[\hat{h}^{(m)}|\psi_{j'}\rangle + \sum_{k'=1}^{M'} \{\rho^{(m)}(t)\}_{j'k'}^{-1} \right. \\ \left. \times \left(\sum_{q'=1}^{M'} \{\rho_2 W\}_{k'q'}^{(m)}|\psi_{q'}\rangle + \frac{1}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a-m)} \hat{W}_{kq}^{(2a-m)} \right) \right], \quad (44)$$

where terms with products of reduced two-body density matrices times one-body potentials (see below) are collected together and denoted for brevity as

$$\{\rho_2 W\}_{kq}^{(a)} \equiv \sum_{s,l=1}^M \rho_{kslq}^{(a)} \hat{W}_{sl}^{(a)} + \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)} \hat{W}_{k'q'}^{(am)}, \\ \{\rho_2 W\}_{k'q'}^{(m)} \equiv \sum_{s',l'=1}^{M'} \rho_{k's'l'q'}^{(m)} \hat{W}_{s'l'}^{(m)} + \sum_{k,q=1}^M \rho_{kk'qq'}^{(am)} \hat{W}_{kq}^{(am)}. \quad (45)$$

Comparing Eq. (37) of the previous Sec. IV A to Eq. (44), we see that in the latter more general, time-dependent local potentials appear which are given explicitly by

$$\hat{W}_{sl}^{(a)}(\mathbf{r}, t) = \int \phi_s^*(\mathbf{r}', t) \hat{W}^{(a)}(\mathbf{r}, \mathbf{r}') \phi_l(\mathbf{r}', t) d\mathbf{r}', \\ \hat{W}_{s'l'}^{(m)}(\mathbf{r}, t) = \int \psi_{s'}^*(\mathbf{r}', t) \hat{W}^{(m)}(\mathbf{r}, \mathbf{r}') \psi_{l'}(\mathbf{r}', t) d\mathbf{r}', \\ \hat{W}_{k'q'}^{(am)}(\mathbf{r}, t) = \int \psi_{k'}^*(\mathbf{r}', t) \hat{W}^{(am)}(\mathbf{r}, \mathbf{r}') \psi_{q'}(\mathbf{r}', t) d\mathbf{r}', \\ \hat{W}_{kq}^{(ma)}(\mathbf{r}, t) = \int \phi_k^*(\mathbf{r}', t) \hat{W}^{(am)}(\mathbf{r}, \mathbf{r}') \phi_q(\mathbf{r}', t) d\mathbf{r}',$$

$$\hat{W}_{kq}^{(2a-m)}(\mathbf{r}, t) = \int d\mathbf{r}' \hat{W}^{(2a-m)}\left(\mathbf{r} + \frac{\mathbf{r}'}{2}, \mathbf{r} - \frac{\mathbf{r}'}{2}\right) \\ \times \phi_k\left(\mathbf{r} + \frac{\mathbf{r}'}{2}, t\right) \phi_q\left(\mathbf{r} - \frac{\mathbf{r}'}{2}, t\right),$$

$$\hat{W}_{qk'}^{(m-2a)}(\mathbf{r}, t) = \int d\mathbf{r}' \phi_q^*(\mathbf{r}', t) \hat{W}^{(m-2a)}(\mathbf{r}, \mathbf{r}') \psi_{k'}\left(\frac{\mathbf{r} + \mathbf{r}'}{2}, t\right). \quad (46)$$

These potentials derive from the interaction terms and conversion term in the Hamiltonian [Eqs. (1)–(3)] and, in the specific case of contact particle-particle interactions, boil down to products of orbitals, see for comparison Eqs. (34) and (37). The form of the equations of motion for the corresponding expansion coefficients,

$$\mathbf{H}^{(2a=m)}(t)\mathbf{C}(t) = i \frac{\partial \mathbf{C}(t)}{\partial t},$$

$$H_{\vec{n}^p \vec{m}^p, \vec{n}'^p \vec{m}'^p}^{(2a=m)}(t) = \langle \vec{n}^p, \vec{m}^p; t | \hat{H}^{(2a=m)} | \vec{n}'^p, \vec{m}'^p; t \rangle, \quad (47)$$

does not change for general interactions. Of course, the matrix elements $H_{\vec{n}^p \vec{m}^p, \vec{n}'^p \vec{m}'^p}^{(2a=m)}(t)$ do depend on the specific form of the particle-particle interactions.

Finally, the self-consistent, time-independent general theory is obtained from the time-dependent one by taking $t \rightarrow -it$. The stationary self-consistent equations for the orbitals read

$$\sum_{q=1}^M \left\{ [\rho_{kq}^{(a)} \hat{h}^{(a)} + \{\rho_2 W\}_{kq}^{(a)}] |\phi_q\rangle + \sqrt{2} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m-2a)} \hat{W}_{qk'}^{(m-2a)} \right\} \\ = \sum_{j=1}^M \mu_{kj}^{(a)} |\phi_j\rangle \rightarrow \mu_k^{(a)} |\phi_k\rangle, \quad k=1, \dots, M, \\ \sum_{q'=1}^{M'} [\rho_{k'q'}^{(m)} \hat{h}^{(m)} + \{\rho_2 W\}_{k'q'}^{(m)}] |\psi_{q'}\rangle + \frac{1}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a-m)} \hat{W}_{kq}^{(2a-m)} \\ = \sum_{j'=1}^{M'} \mu_{k'j'}^{(m)} |\psi_{j'}\rangle \rightarrow \mu_{k'}^{(m)} |\psi_{k'}\rangle, \quad k'=1, \dots, M', \quad (48)$$

where the arrows indicate the Lagrange multipliers in their diagonal form, as done in Eq. (43). Finally, the self-consistent eigenvalue form of the equation for the expansion coefficients,

$$\mathbf{H}^{(2a=m)}\mathbf{C} = \varepsilon\mathbf{C},$$

$$H_{\vec{n}^p \vec{m}^p, \vec{n}'^p \vec{m}'^p}^{(2a=m)} = \langle \vec{n}^p, \vec{m}^p | \hat{H}^{(2a=m)} | \vec{n}'^p, \vec{m}'^p \rangle, \quad (49)$$

remains unchanged for general interactions.

Equations (44) and (47) constitute a multiconfigurational *time-dependent* theory for systems of bosonic atoms and molecules with conversion (particle conversion in the generic case). Furthermore, Eqs. (48) and (49) constitute a mul-

ticonfigurational self-consistent *time-independent* theory for systems of bosonic atoms and molecules with conversion (particle conversion in the generic case). Both theories extend the scope of the successful multiconfigurational time-dependent Hartree method and its versions specified for systems of identical particles and mixtures to new physical systems and problems.

V. SUMMARY AND CONCLUDING REMARKS

In this work we have derived a many-body propagation theory for systems with particle conversion. The theory is intended for systems with a finite number of interacting particles, typically in a trap potential. The theory has been exemplified and working equations have been explicitly derived for systems of interacting structureless bosonic atoms and bosonic molecules undergoing the conversion “reaction” $2a \rightleftharpoons m$. In doing so, we have also extended the scope of the successful multiconfigurational time-dependent Hartree (MCTDH) method and its versions specified for systems of identical particles and mixtures to a broader class of physical systems and problems. We note that the MCTDH method is considered at present the most efficient wave-packet propagation approach for in general distinguishable coupled degrees of freedom, with no particle conversion, of course. The general multiconfigurational theory with particle conversion shall be referred to as MCTDH-*conversion* theory, whereas the explicit scenario derived throughout this work by MCTDH- $[2a \rightleftharpoons m]$ theory.

To treat systems with particle conversion, one has to work in second quantization formalism, where the Hamiltonian with particle-conversion terms can be represented. The next step is to define the configurations. In the presence of particle conversion configurations with different numbers of atoms and different numbers of molecules are coupled. For instance, consider the particular case of the conversion “reaction” $2a \rightleftharpoons m$. In this case, the subspace of coupled configurations can be easily obtained by starting from the configurations made of N atoms only, and operating repeatedly with the conversion operators in the Hamiltonian until configurations made of the maximal number $\lfloor \frac{N}{2} \rfloor$ of molecules are reached.

In the multiconfigurational theory for the “reaction” $2a \rightleftharpoons m$, there are M *time-dependent* orbitals $\{\phi_k(\mathbf{r}, t)\}$ available for the atoms and M' *time-dependent* orbitals $\{\psi_{k'}(\mathbf{r}, t)\}$ for the molecules. The multiconfigurational ansatz for the many-particle wave function $\Psi(t)$ is taken as linear combination with *time-dependent* coefficients $\{C_{\vec{n}\vec{m}^p}(t)\}$ of all possible configurations $\{|\vec{n}^p, \vec{m}^p; t\rangle\}$ assembled from p molecules and $N-2p$ atoms, $p=0, \dots, \lfloor \frac{N}{2} \rfloor$ —distributed over the M and M' respective orbitals—and coupled by the conversion term in the Hamiltonian.

The evolution of $\Psi(t)$ is then determined by the Dirac-Frenkel time-dependent variational principle. Utilizing the Lagrangian formulation of the Dirac-Frenkel variational principle, one arrives at two sets of coupled equations of motion: The first set is for the orbitals $\{\phi_k(\mathbf{r}, t)\}$ and $\{\psi_{k'}(\mathbf{r}, t)\}$, and the second for the expansion coefficients $\{C_{\vec{n}\vec{m}^p}(t)\}$. The first set is comprised of first-order differential

equations in time and nonlinear integrodifferential equations in position space. The second set consists of first-order differential equations with coefficients forming a time-dependent Hermitian matrix. Thus, equations of motion, Eqs. (33) and (39), or Eqs. (37) and (40) [Eqs. (44) and (47) for general interactions], constitute the time-dependent multiconfigurational theory for bosonic atoms and molecules with conversion—MCTDH- $[2a \rightleftharpoons m]$ theory.

The structure of the equations of motion for systems with particle conversion reminds of the structure of the equations of motion in multiconfigurational time-dependent theories for systems of identical particles and mixtures [32,33,53,54]: (i) There are projection operators on the right-hand sides of the equations of motion for the orbitals, ensuring that the respective orbitals remain normalized and orthogonal to one another for all times; (ii) the equations for the expansion coefficients are first-order differential equations with time-dependent coefficients; and (iii) the equations of motion for the orbitals are formulated in terms of reduced density matrices. This resemblance would allow one to transfer the effective numerical techniques that have been developed in the past almost 20 years for multiconfigurational time-dependent many-body systems *without* particle conversion [7,8,12,29–33,53,54] to the present theory for systems *with* particle conversion.

Particular attention has been paid to the reduced density matrices appearing in the theory. As the multiconfigurational expansion involves configurations with different numbers of atoms and molecules, two types of reduced density matrices are defined. There are *particle-conserving* reduced density matrices, $\rho^{(a)}(\mathbf{r}_1|\mathbf{r}_2; t)$, $\rho^{(m)}(\mathbf{r}_1|\mathbf{r}_2; t)$, $\rho^{(a)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3, \mathbf{r}_4; t)$, $\rho^{(m)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3, \mathbf{r}_4; t)$ and $\rho^{(am)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3, \mathbf{r}_4; t)$, which directly do not couple configurations with different numbers of atoms and molecules. Despite this property, the particle-conserving reduced density matrices, such as $\rho^{(a)}(\mathbf{r}_1|\mathbf{r}_2; t)$ and $\rho^{(a)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3, \mathbf{r}_4; t)$, are *not* the standard density matrices introduced by Löwdin [44] for many-particle systems *without* conversion. The second type of reduced density matrices that appear in the theory are *particle nonconserving* reduced density matrices, $\rho^{(2a \rightarrow m)}(\mathbf{r}_1, \mathbf{r}_2|\mathbf{r}_3; t)$ and $\rho^{(m \rightarrow 2a)}(\mathbf{r}_3|\mathbf{r}_2, \mathbf{r}_1; t)$, and originate from the conversion term in the Hamiltonian. They obviously have no analogs in systems without conversion. Here, it is of interest by itself to study properties of particle-conserving reduced density matrices and certainly of particle nonconserving reduced density matrices in systems *with* particle conversion.

The time-dependent multiconfigurational theory MCTDH- $[2a \rightleftharpoons m]$ readily admits the corresponding *stationary* theory. By resorting to imaginary time propagation, the equations of motion of the time-dependent theory boil down to the fully self-consistent time-independent multiconfigurational theory, Eqs. (48) and (49), for stationary states of the system $2a \rightleftharpoons m$, in presence of all particle-particle interactions, of course. With this result, available self-consistent multiconfigurational theories for systems *without* particle conversion, noticeably for fermions [94,95], distinguishable degrees of freedom [13], bosons [52], and mixtures [54], are taken a step further, to systems *with* particle conversion.

A specific case of interest for systems of bosonic atoms and molecules with conversion is the case of $M=1$ atomic

and $M'=1$ molecular orbitals, which is presented in Sec. III before the general MCTDH-[$2a \rightleftharpoons m$] theory is developed. For $M=1$ and $M'=1$, the corresponding multiconfigurational theory is the fully variational theory that results when the shape of the atomic $\phi_a(\mathbf{r}, t)$ and molecular $\psi_m(\mathbf{r}, t)$ orbitals and of each and every expansion coefficient $C_p(t)$ are optimized according to the variational principle. Being fully variational with respect to the shape of the orbitals $\phi_a(\mathbf{r}, t)$, $\psi_m(\mathbf{r}, t)$ and with respect to the expansion coefficients $\{C_p(t)\}$, the theory generalizes the literature Gross-Pitaevskii equation [57] and two-mode approximation [56,65] for bosonic atoms and molecules with conversion. We term this specific case of the general theory *conversion mean field*, as there is only one orbital available for the bosonic atoms and one for the molecules—the minimal number possible for bosonic species.

At the other end, in the limit where the number M of atomic orbitals and M' of molecular orbitals goes to infinity, the MCTDH-[$2a \rightleftharpoons m$] theory becomes an exact representation of the time-dependent many-particle Schrödinger equation with the particle-conversion Hamiltonian $\hat{H}^{(2a \rightleftharpoons m)}$ [Eqs. (1)–(3)]. In practice, one obviously has to limit M and M' . Here, the employment of *time-dependent* orbitals, which has been very successful for the MCTDH approach and its versions specified for identical particles and mixtures, is of great help and advantage. Of course, even with time-dependent orbitals the size of the Hilbert space grows rapidly with the size of the system and the number of orbitals M and M' employed. Consequently, with increasing system size and as the number of orbitals which one has to employ becomes larger, e.g., for stronger interactions, it is instructive to devise truncation schemes beyond the usage of *time-dependent* multiconfigurational expansions over *complete* Hilbert subspaces. We mention two such truncation strategies: (i) to truncate time-dependent multiconfigurational expansions to include parts of Hilbert subspaces, i.e., to include not all available configurations for a given system size and number of orbitals M, M' ; and (ii) to concentrate on the reduced density matrices, write equations of motion for them directly, and thereafter truncate the resulting hierarchy of equations of motion for higher-order reduced density matrices at some given order. The development of these truncation schemes for *time-dependent* multiconfigurational expansions in systems with particle conversion extends beyond the scope of the present work.

Finally, the explicit equations of motion presented in this work are for the specific “reaction” $2a \rightleftharpoons m$ where the atoms and molecules are structureless bosons—the MCTDH-[$2a \rightleftharpoons m$] theory. Several other systems come to mind: (i) Other “reactions” with bosonic atoms of the same kind, e.g., $3a \rightleftharpoons m$; (ii) “reactions” with bosonic atoms of a different kind, e.g., $a+a' \rightleftharpoons m$. In this case and for general particle-particle interactions, the center of mass coordinate is, of course, $\mathbf{R} = \frac{m_a \mathbf{r} + m_{a'} \mathbf{r}'}{m_a + m_{a'}}$, where m_a and $m_{a'}$ are the masses of the respective species; (iii) “reactions” including fermionic atoms, e.g., $a_f + a_b \rightleftharpoons m_f$ and $a_f + a_f \rightleftharpoons m_b$ where the subscript b, f stands for bosonic, fermionic species. In the latter case, a unified form of the respective equations of motion and those of the present work is anticipated; and (iv) a whole zoo of

“reactions” for particles with spin and/or internal structure. The extension of MCTDH-[$2a \rightleftharpoons m$] theory for the above concrete examples as well as for other systems with particle conversion can be done by following the theory and derivation steps of the present work.

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APPENDIX A: FURTHER DETAILS OF THE DERIVATION OF THE EQUATIONS OF MOTION

1. The specific case of the conversion mean field (fully variational two-mode approximation)

When the variations of the functional action (9) with respect to the orbitals and expansion coefficients are put to zero, the following equations of motion are obtained:

$$\begin{aligned} & \left[\langle \hat{N}_a \rangle \left(\hat{h}^{(a)} - i \frac{\partial}{\partial t} \right) + \lambda_a \langle \hat{N}_a (\hat{N}_a - 1) \rangle |\phi_a\rangle^2 \right. \\ & \quad \left. + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle |\psi_m\rangle^2 \right] |\phi_a\rangle \\ & \quad + \sqrt{2} \lambda_{con} \langle \hat{b}_a^\dagger \hat{b}_a^\dagger \hat{c}_m \rangle \phi_a^* |\psi_m\rangle = \mu_a(t) |\phi_a\rangle, \\ & \left[\langle \hat{N}_m \rangle \left(\hat{h}^{(m)} - i \frac{\partial}{\partial t} \right) + \lambda_m \langle \hat{N}_m (\hat{N}_m - 1) \rangle |\psi_m\rangle^2 \right. \\ & \quad \left. + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle |\phi_a\rangle^2 \right] |\psi_m\rangle \\ & \quad + \frac{\lambda_{con}}{\sqrt{2}} \langle \hat{c}_m^\dagger \hat{b}_a \hat{b}_a \rangle \phi_a |\phi_a\rangle = \mu_m(t) |\psi_m\rangle \end{aligned} \quad (\text{A1})$$

and

$$[\mathcal{H}^{(a \rightleftharpoons m)}(t) - \varepsilon(t) \cdot \mathbf{1}] \mathbf{C}(t) = i \frac{\partial \mathbf{C}(t)}{\partial t}. \quad (\text{A2})$$

The three time-dependent Lagrange multipliers $\mu_a(t)$, $\mu_m(t)$, and $\varepsilon(t)$ appear therein. How to eliminate them?

It is straightforward to eliminate $\varepsilon(t)$. This is done by transforming the expansion coefficients as follows:

$$\bar{\mathbf{C}}(t) = e^{-i \int^t \varepsilon(t') dt'} \mathbf{C}(t). \quad (\text{A3})$$

Substituting Eq. (A3) into Eq. (A2) and removing at the end the “bar” from all quantities we obtain

$$\mathcal{H}^{(a \rightleftharpoons m)}(t) \mathbf{C}(t) = i \frac{\partial \mathbf{C}(t)}{\partial t}. \quad (\text{A4})$$

From Eqs. (A2)–(A4) we see that the role of the Lagrange multiplier $\varepsilon(t)$ is that of a (redundant) global time-dependent phase of the many-particle wave function $\bar{\Psi}(t) = e^{-i \int^t \varepsilon(t') dt'} \Psi(t)$. We note that Eq. (A1) is not affected by the transformation (A3) because reduced density matrices are

“insensitive” to a global phase of the wave function, namely $\langle \bar{\Psi}(t) | \cdots | \bar{\Psi}(t) \rangle = \langle \Psi(t) | \cdots | \Psi(t) \rangle$.

The next step is to eliminate the remaining Lagrange multipliers $\mu_a(t)$ and $\mu_m(t)$. Making use of the orbitals being normalized and taking the respective scalar products of Eq. (A1) with $\langle \phi_a |$ and $\langle \psi_m |$, we obtain

$$\begin{aligned} \mu_a(t) &= \langle \hat{N}_a \rangle \left\langle \phi_a \left| \hat{h}^{(a)} - i \frac{\partial}{\partial t} \right| \phi_a \right\rangle + \frac{\lambda_a}{2} \langle \hat{N}_a (\hat{N}_a - 1) \rangle \langle \phi_a^2 | \phi_a^2 \rangle \\ &\quad + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle \langle \phi_a \psi_m | \phi_a \psi_m \rangle + \sqrt{2} \lambda_{con} \langle \hat{b}_a^\dagger \hat{b}_a^\dagger \hat{c}_m \rangle \langle \phi_a^2 | \psi_m \rangle, \\ \mu_m(t) &= \langle \hat{N}_m \rangle \left\langle \phi_m \left| \hat{h}^{(m)} - i \frac{\partial}{\partial t} \right| \phi_m \right\rangle + \frac{\lambda_m}{2} \langle \hat{N}_m (\hat{N}_m - 1) \rangle \\ &\quad \times \langle \phi_m^2 | \phi_m^2 \rangle + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle \langle \phi_a \psi_m | \phi_a \psi_m \rangle \\ &\quad + \frac{\lambda_{con}}{\sqrt{2}} \langle \hat{c}_m^\dagger \hat{b}_a \hat{b}_a \rangle \langle \psi_m | \phi_a^2 \rangle. \end{aligned} \quad (\text{A5})$$

Substituting Eq. (A5) into Eq. (A1), employing the identities

$$\begin{aligned} &\left[\langle \hat{N}_a \rangle \left(\hat{h}^{(a)} - i \frac{\partial}{\partial t} \right) + \lambda_a \langle \hat{N}_a (\hat{N}_a - 1) \rangle | \phi_a |^2 \right. \\ &\quad \left. + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle | \psi_m |^2 \right] | \phi_a \rangle \\ &\quad + \sqrt{2} \lambda_{con} \langle \hat{b}_a^\dagger \hat{b}_a^\dagger \hat{c}_m \rangle \phi_a^* | \psi_m \rangle - \mu_a(t) | \phi_a \rangle \\ &= (1 - | \phi_a \rangle \langle \phi_a |) \left\{ \left[\langle \hat{N}_a \rangle \left(\hat{h}^{(a)} - i \frac{\partial}{\partial t} \right) \right. \right. \\ &\quad \left. \left. + \lambda_a \langle \hat{N}_a (\hat{N}_a - 1) \rangle | \phi_a |^2 + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle | \psi_m |^2 \right] | \phi_a \rangle \right. \\ &\quad \left. + \sqrt{2} \lambda_{con} \langle \hat{b}_a^\dagger \hat{b}_a^\dagger \hat{c}_m \rangle \phi_a^* | \psi_m \rangle \right\}, \\ &\left[\langle \hat{N}_m \rangle \left(\hat{h}^{(m)} - i \frac{\partial}{\partial t} \right) + \lambda_m \langle \hat{N}_m (\hat{N}_m - 1) \rangle | \psi_m |^2 \right. \\ &\quad \left. + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle | \phi_a |^2 \right] | \psi_m \rangle \\ &\quad + \frac{\lambda_{con}}{\sqrt{2}} \langle \hat{c}_m^\dagger \hat{b}_a \hat{b}_a \rangle \phi_a | \phi_a \rangle - \mu_m(t) | \psi_m \rangle \\ &= (1 - | \psi_m \rangle \langle \psi_m |) \left\{ \left[\langle \hat{N}_m \rangle \left(\hat{h}^{(m)} - i \frac{\partial}{\partial t} \right) \right. \right. \\ &\quad \left. \left. + \lambda_m \langle \hat{N}_m (\hat{N}_m - 1) \rangle | \psi_m |^2 + \lambda_{am} \langle \hat{N}_a \hat{N}_m \rangle | \phi_a |^2 \right] | \psi_m \rangle \right. \\ &\quad \left. + \frac{\lambda_{con}}{\sqrt{2}} \langle \hat{c}_m^\dagger \hat{b}_a \hat{b}_a \rangle \phi_a | \phi_a \rangle \right\}, \end{aligned} \quad (\text{A6})$$

and dividing the result, respectively, by $\langle \hat{N}_a \rangle$ and $\langle \hat{N}_m \rangle$, the equations of motion (16) and (17) are obtained.

To eliminate the projection operators in front of the time derivatives in Eq. (A6), i.e., $\hat{\mathbf{P}}^{(a)} = 1 - | \phi_a \rangle \langle \phi_a |$ and $\hat{\mathbf{P}}^{(m)} = 1 - | \psi_m \rangle \langle \psi_m |$ on the left-hand sides of Eq. (16), we exploit the invariance property of the wave function $\Psi(t)$. Consider the following phase transformations of the orbitals and coefficients:

$$\begin{aligned} \bar{\phi}_a(\mathbf{r}, t) &= e^{+i\beta_a(t)} \phi_a(\mathbf{r}, t), \quad \bar{\psi}_m(\mathbf{r}, t) = e^{+i\gamma_m(t)} \psi_m(\mathbf{r}, t), \\ \bar{C}_p(t) &= e^{-i[(N-2p)\beta_a(t) + p\gamma_m(t)]} C_p(t), \quad p = 0, \dots, [N/2]. \end{aligned} \quad (\text{A7})$$

Combining these phase transformations, the wave function does not change: $|\Psi(t)\rangle = \sum_{p=0}^{[N/2]} C_p(t) |N-2p, p; t\rangle = \sum_{p=0}^{[N/2]} \bar{C}_p(t) |N-2p, p; \bar{t}\rangle$. We should also recall that transforming the orbitals goes along with transforming the corresponding annihilation, creation operators [another way to look at this is that the field operators $\hat{\Psi}_a(\mathbf{r})$ and $\hat{\Psi}_m(\mathbf{r})$ are time-independent, basis-set-independent quantities and, consequently, transforming the orbitals requires the reverse transformation of the annihilation operators]. Thus, Eq. (A7) implies also the phase transformations

$$\hat{b}_a(t) = e^{-i\beta_a(t)} \hat{b}_a(t), \quad \hat{c}_m(t) = e^{-i\gamma_m(t)} \hat{c}_m(t) \quad (\text{A8})$$

for the atomic and molecular annihilation operators.

Now, plugging Eqs. (A7) and (A8) into the equations of motion (16) for the orbitals and Eq. (22) for the expansion coefficients [see also Eqs. (A4) and (A6)], and choosing the phases

$$\begin{aligned} \beta_a(t) &= \int^t i \langle \phi_a(t') | \dot{\phi}_a(t') \rangle dt', \\ \gamma_m(t) &= \int^t i \langle \psi_m(t') | \dot{\psi}_m(t') \rangle dt', \end{aligned} \quad (\text{A9})$$

equations of motion (20) and (23) are found. We note that the phases $\beta_a(t)$ and $\gamma_m(t)$ are real quantities since $\langle \phi_a(t) | \dot{\phi}_a(t) \rangle = 1$ and $\langle \psi_m(t) | \dot{\psi}_m(t) \rangle = 1$, respectively, for all times.

2. The general multiconfigurational theory

When the expressions for the field operators $\hat{\Psi}_a(\mathbf{r})$ and $\hat{\Psi}_m(\mathbf{r})$ in terms of the time-dependent orbitals, Eq. (5), are substituted into the generic many-body Hamiltonian (1)–(3), one obtains

$$\begin{aligned} \hat{H}^{(2a \Rightarrow m)} &= \sum_{k,q} h_{kq}^{(a)} \hat{b}_k^\dagger \hat{b}_q + \sum_{k,s,l,q} W_{ksql}^{(a)} \hat{b}_k^\dagger \hat{b}_s^\dagger \hat{b}_l \hat{b}_q + \sum_{k',q'} h_{k'q'}^{(m)} \hat{c}_{k'}^\dagger \hat{c}_{q'} \\ &\quad + \sum_{k',s',l',q'} W_{k's'l',q'}^{(m)} \hat{c}_{k'}^\dagger \hat{c}_{s'}^\dagger \hat{c}_{l'} \hat{c}_{q'} \\ &\quad + \sum_{k,k',q,q'} W_{kk'qq'}^{(am)} \hat{b}_k^\dagger \hat{b}_{k'} \hat{b}_q \hat{c}_{q'}^\dagger \hat{c}_{q'} \end{aligned}$$

$$+ \frac{1}{\sqrt{2}} \sum_{k',k,q} [W_{k'kq}^{(2a \rightarrow m)} \hat{c}_k^\dagger \hat{b}_k \hat{b}_q + W_{qkk'}^{(m \rightarrow 2a)} \hat{b}_q^\dagger \hat{b}_k^\dagger \hat{c}_{k'}]. \tag{A10}$$

The one-body, two-body, and conversion matrix elements appearing in Eq. (A10) are given by

$$h_{kq}^{(a)} = \int \phi_k^*(\mathbf{r},t) \hat{h}^{(a)}(\mathbf{r}) \phi_q(\mathbf{r},t) d\mathbf{r},$$

$$W_{ksql}^{(a)} = \int \int \phi_k^*(\mathbf{r},t) \phi_s^*(\mathbf{r}',t) \hat{W}^{(a)}(\mathbf{r},\mathbf{r}') \phi_q(\mathbf{r},t) \phi_l(\mathbf{r}',t) d\mathbf{r} d\mathbf{r}',$$

$$h_{k'q'}^{(m)} = \int \psi_{k'}^*(\mathbf{r},t) \hat{h}^{(m)}(\mathbf{r}) \psi_{q'}(\mathbf{r},t) d\mathbf{r},$$

$$W_{k's'q'l'}^{(m)} = \int \int \psi_{k'}^*(\mathbf{r},t) \psi_{s'}^*(\mathbf{r}',t) \times \hat{W}^{(m)}(\mathbf{r},\mathbf{r}') \psi_{q'}(\mathbf{r},t) \psi_{l'}(\mathbf{r}',t) d\mathbf{r} d\mathbf{r}',$$

$$W_{kk'qq'}^{(am)} = \int \int \phi_k^*(\mathbf{r},t) \psi_{k'}^*(\mathbf{r}',t) \times \hat{W}^{(am)}(\mathbf{r},\mathbf{r}') \phi_q(\mathbf{r},t) \psi_{q'}(\mathbf{r}',t) d\mathbf{r} d\mathbf{r}',$$

$$W_{k'kq}^{(2a \rightarrow m)} = \int \int \psi_{k'}^* \left(\frac{\mathbf{r} + \mathbf{r}'}{2}, t \right) \hat{W}^{(2a \rightarrow m)}(\mathbf{r},\mathbf{r}') \times \phi_k(\mathbf{r},t) \phi_q(\mathbf{r}',t) d\mathbf{r} d\mathbf{r}' \\ = \int \int \psi_{k'}^*(\mathbf{r},t) \hat{W}^{(2a \rightarrow m)} \left(\mathbf{r} + \frac{\mathbf{r}'}{2}, \mathbf{r} - \frac{\mathbf{r}'}{2} \right) \times \phi_k \left(\mathbf{r} + \frac{\mathbf{r}'}{2}, t \right) \phi_q \left(\mathbf{r} - \frac{\mathbf{r}'}{2}, t \right) d\mathbf{r} d\mathbf{r}',$$

$$W_{qkk'}^{(m \rightarrow 2a)} = \int \int \phi_q^*(\mathbf{r},t) \phi_k^*(\mathbf{r}',t) \hat{W}^{(m \rightarrow 2a)}(\mathbf{r},\mathbf{r}') \times \psi_{k'} \left(\frac{\mathbf{r} + \mathbf{r}'}{2}, t \right) d\mathbf{r} d\mathbf{r}' = \{W_{k'kq}^{(2a \rightarrow m)}\}^*. \tag{A11}$$

The change of variables used for $W_{k'kq}^{(2a \rightarrow m)}$ is needed in order to perform the variation of this term with respect to the molecular orbitals, see below.

Now, the expectation value appearing in the functional action (30) when expressed explicit with respect to the orbitals reads

$$\left\langle \Psi(t) \left| \hat{H}^{(2a \rightarrow m)} - i \frac{\partial}{\partial t} \right| \Psi(t) \right\rangle = \sum_{k,q=1}^M \rho_{kq}^{(a)} \left[h_{kq}^{(a)} - \left(i \frac{\partial}{\partial t} \right)_{kq}^{(a)} \right] + \frac{1}{2} \sum_{k,s,l,q=1}^M \rho_{kslq}^{(a)} W_{ksql}^{(a)} + \sum_{k',q'=1}^{M'} \rho_{k'q'}^{(m)} \left[h_{k'q'}^{(m)} - \left(i \frac{\partial}{\partial t} \right)_{k'q'}^{(m)} \right] \\ + \frac{1}{2} \sum_{k',s',l',q'=1}^{M'} \rho_{k's'l'q'}^{(m)} W_{k's'q'l'}^{(m)} + \sum_{k,q=1}^M \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)} W_{kk'qq'}^{(am)} + \frac{1}{\sqrt{2}} \sum_{k,q=1}^M \sum_{k'=1}^{M'} [\rho_{k'kq}^{(2a \rightarrow m)} W_{k'kq}^{(2a \rightarrow m)} \\ + \rho_{qkk'}^{(m \rightarrow 2a)} W_{qkk'}^{(m \rightarrow 2a)}] - i \sum_{\substack{p=0 \\ \vec{n}^p, \vec{m}^p}}^{[N/2]} C_{\vec{n}^p, \vec{m}^p}^* \frac{\partial C_{\vec{n}^p, \vec{m}^p}}{\partial t}, \tag{A12}$$

where

$$\left(i \frac{\partial}{\partial t} \right)_{kq}^{(a)} = i \int \phi_k^*(\mathbf{r},t) \frac{\partial \phi_q(\mathbf{r},t)}{\partial t} d\mathbf{r}, \quad \left(i \frac{\partial}{\partial t} \right)_{k'q'}^{(m)} = i \int \psi_{k'}^*(\mathbf{r},t) \frac{\partial \psi_{q'}(\mathbf{r},t)}{\partial t} d\mathbf{r}. \tag{A13}$$

Equating the variation of the functional action (30) with respect to the orbitals to zero, making use of Eq. (A12), the following equations are obtained:

$$\sum_{q=1}^M \left\{ \left[\rho_{kq}^{(a)} \left(\hat{h}^{(a)} - i \frac{\partial}{\partial t} \right) + \sum_{s,l=1}^M \rho_{kslq}^{(a)} \hat{W}_{sl}^{(a)} + \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)} \hat{W}_{k'q'}^{(am)} \right] |\phi_q\rangle + \sqrt{2} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m \rightarrow 2a)} \hat{W}_{qk'}^{(m \rightarrow 2a)} \right\} = \sum_{j=1}^M \mu_{kj}^{(a)} |\phi_j\rangle, \quad k = 1, \dots, M, \\ \sum_{q'=1}^{M'} \left[\rho_{k'q'}^{(m)} \left(\hat{h}^{(m)} - i \frac{\partial}{\partial t} \right) + \sum_{s',l'=1}^{M'} \rho_{k's'l'q'}^{(m)} \hat{W}_{s'l'}^{(m)} + \sum_{k,q=1}^M \rho_{kk'qq'}^{(am)} \hat{W}_{kq}^{(am)} \right] |\psi_{q'}\rangle + \frac{1}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a \rightarrow m)} \hat{W}_{kq}^{(2a \rightarrow m)} = \sum_{j=1}^{M'} \mu_{k'j}^{(m)} |\psi_{j'}\rangle, \\ k' = 1, \dots, M'. \tag{A14}$$

One delicate point in performing the variation of $W_{k'kq}^{(2a-m)}$ [the last term in the second line of the expectation value Eq. (A12)] with respect to the molecular orbitals $\psi_{k'}^*(\mathbf{r}, t)$ is worth mentioning. To perform this variation, a change of the integration variables \mathbf{r}, \mathbf{r}' to the center of mass $\mathbf{R} = \frac{\mathbf{r} + \mathbf{r}'}{2}$ and relative $\bar{\mathbf{r}} = \mathbf{r} - \mathbf{r}'$ coordinates is required. Assigning thereafter back $\mathbf{R} \rightarrow \mathbf{r}, \bar{\mathbf{r}} \rightarrow \mathbf{r}'$, the matrix element $W_{k'kq}^{(2a-m)}$ is rewritten in a form, see Eq. (A11), which is amenable to explicit variation with respect to $\psi_{k'}^*(\mathbf{r}, t)$.

The next step is to eliminate the Lagrange multipliers $\{\mu_{kj}^{(a)}(t)\}$ and $\{\mu_{k'j'}^{(m)}(t)\}$. Making use of the orthonormality properties of the atomic and molecular orbitals, $\langle \phi_k(t) | \phi_q(t) \rangle = \delta_{kq}$ and $\langle \psi_{k'}(t) | \psi_{q'}(t) \rangle = \delta_{k'q'}$, and taking the corresponding scalar products of Eq. (A14) with respect to the orbitals, we obtain explicit expressions for the Lagrange multipliers,

$$\begin{aligned} \mu_{kj}^{(a)}(t) &= \sum_{q=1}^M \left\{ \rho_{kq}^{(a)} \left[h_{jq}^{(a)} - \left(i \frac{\partial}{\partial t} \right)_{jq}^{(a)} \right] + \sum_{s,l=1}^M \rho_{kslq}^{(a)} W_{jsl}^{(a)} \right. \\ &\quad \left. + \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)} W_{jk'qq'}^{(am)} + \sqrt{2} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m-2a)} W_{qjk'}^{(m-2a)} \right\}, \\ \mu_{k'j'}^{(m)}(t) &= \sum_{q'=1}^{M'} \left\{ \rho_{k'q'}^{(m)} \left[h_{j'q'}^{(m)} - \left(i \frac{\partial}{\partial t} \right)_{j'q'}^{(m)} \right] \right. \\ &\quad \left. + \sum_{s',l'=1}^{M'} \rho_{k's'l'q'}^{(m)} W_{j's'l'q'}^{(m)} + \sum_{k,q=1}^M \rho_{kk'qq'}^{(am)} W_{kj'q'}^{(am)} \right\} \\ &\quad + \frac{1}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a-m)} W_{j'kq}^{(2a-m)}. \end{aligned} \quad (\text{A15})$$

Substituting Eq. (A15) into Eq. (A14), making use of the identities

$$\begin{aligned} &\sum_{q=1}^M \left\{ \left[\rho_{kq}^{(a)} \left(\hat{h}^{(a)} - i \frac{\partial}{\partial t} \right) + \sum_{s,l=1}^M \rho_{kslq}^{(a)} \hat{W}_{sl}^{(a)} \right. \right. \\ &\quad \left. \left. + \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)} \hat{W}_{k'q'}^{(am)} \right] |\phi_q\rangle \right. \\ &\quad \left. + \sqrt{2} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m-2a)} \hat{W}_{qk'}^{(m-2a)} \right\} - \sum_{u=1}^M \mu_{ku}^{(a)} |\phi_u\rangle \\ &= \left(1 - \sum_{u=1}^M |\phi_u\rangle \langle \phi_u| \right) \\ &\quad \times \sum_{q=1}^M \left\{ \left[\rho_{kq}^{(a)} \left(\hat{h}^{(a)} - i \frac{\partial}{\partial t} \right) \right. \right. \\ &\quad \left. \left. + \sum_{s,l=1}^M \rho_{kslq}^{(a)} \hat{W}_{sl}^{(a)} + \sum_{k',q'=1}^{M'} \rho_{kk'qq'}^{(am)} \hat{W}_{k'q'}^{(am)} \right] |\phi_q\rangle \right\} \end{aligned}$$

$$\begin{aligned} &+ \sqrt{2} \sum_{k'=1}^{M'} \rho_{qkk'}^{(m-2a)} \hat{W}_{qk'}^{(m-2a)} \left. \right\}, \quad k = 1, \dots, M, \\ &\sum_{q'=1}^{M'} \left[\rho_{k'q'}^{(m)} \left(\hat{h}^{(m)} - i \frac{\partial}{\partial t} \right) + \sum_{s',l'=1}^{M'} \rho_{k's'l'q'}^{(m)} \hat{W}_{s'l'}^{(m)} \right. \\ &\quad \left. + \sum_{k,q=1}^M \rho_{kk'qq'}^{(am)} \hat{W}_{kq}^{(ma)} \right] |\psi_{q'}\rangle \\ &+ \frac{1}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a-m)} \hat{W}_{kq}^{(2a-m)} - \sum_{u'=1}^{M'} \mu_{k'u'}^{(m)} |\psi_{u'}\rangle \\ &= \left(1 - \sum_{u'=1}^{M'} |\psi_{u'}\rangle \langle \psi_{u'}| \right) \\ &\quad \times \left\{ \sum_{q'=1}^{M'} \left[\rho_{k'q'}^{(m)} \left(\hat{h}^{(m)} - i \frac{\partial}{\partial t} \right) \right. \right. \\ &\quad \left. \left. + \sum_{s',l'=1}^{M'} \rho_{k's'l'q'}^{(m)} \hat{W}_{s'l'}^{(m)} + \sum_{k,q=1}^M \rho_{kk'qq'}^{(am)} \hat{W}_{kq}^{(ma)} \right] |\psi_{q'}\rangle \right. \\ &\quad \left. + \frac{1}{\sqrt{2}} \sum_{k,q=1}^M \rho_{k'kq}^{(2a-m)} \hat{W}_{kq}^{(2a-m)} \right\}, \quad k' = 1, \dots, M', \end{aligned} \quad (\text{A16})$$

and multiplying the result, respectively, by the inverse of the reduced one-body density matrices and summing over $\sum_{k=1}^M \{\rho^{(a)}(t)\}_{jk}^{-1}$ and $\sum_{k'=1}^{M'} \{\rho^{(m)}(t)\}_{j'k'}^{-1}$, we obtain equations of motion such as Eq. (33) with general interactions.

Finally, to eliminate the projection operators $\hat{\mathbf{P}}^{(a)} = 1 - \sum_{u=1}^M |\phi_u\rangle \langle \phi_u|$ and $\hat{\mathbf{P}}^{(m)} = 1 - \sum_{u'=1}^{M'} |\psi_{u'}\rangle \langle \psi_{u'}|$ in front of the time derivatives [see Eqs. (A16) and (33)], we employ the invariance properties of the wave function $\Psi(t) = \bar{\Psi}(t)$, where $\{\phi_k(\mathbf{r}, t)\} \rightarrow \{\bar{\phi}_k(\mathbf{r}, t)\}$, $\{\psi_{k'}(\mathbf{r}, t)\} \rightarrow \{\bar{\psi}_{k'}(\mathbf{r}, t)\}$, and $\{C_{\bar{n}\bar{p}\bar{m}\bar{p}}(t)\} \rightarrow \{\bar{C}_{\bar{n}\bar{p}\bar{m}\bar{p}}(t)\}$. For this, consider the following time-dependent matrices:

$$\mathbf{D}^{(a)}(t), D_{kq}^{(a)} = i \langle \phi_k(t) | \dot{\phi}_q(t) \rangle, \quad \mathbf{D}^{(m)}(t), D_{k'q'}^{(m)} = i \langle \psi_{k'}(t) | \dot{\psi}_{q'}(t) \rangle. \quad (\text{A17})$$

The matrices $\mathbf{D}^{(a)}(t)$ and $\mathbf{D}^{(m)}(t)$ are Hermitian matrices [because the respective orbitals are normalized and orthogonal to one another, $\langle \phi_k(t) | \phi_q(t) \rangle = \delta_{kq}$ and $\langle \psi_{k'}(t) | \psi_{q'}(t) \rangle = \delta_{k'q'}$] and hence can be diagonalized

$$\begin{aligned} \{\mathbf{T}^{(a)}(t)\}^\dagger \mathbf{D}^{(a)}(t) \mathbf{T}^{(a)}(t) &= \mathbf{d}^{(a)}(t), \\ \{\mathbf{T}^{(m)}(t)\}^\dagger \mathbf{D}^{(m)}(t) \mathbf{T}^{(m)}(t) &= \mathbf{d}^{(m)}(t), \end{aligned} \quad (\text{A18})$$

where $\mathbf{d}^{(a)}(t)$ and $\mathbf{d}^{(m)}(t)$ are the diagonal matrices of the respective eigenvalues. Now, we define the unitary transformations (which are *symbolically* integrated),

$$i\dot{U}_{sq}^{(a)}(t) = - \sum_{k=1}^M D_{sk}^{(a)}(t) U_{kq}^{(a)}(t) \Rightarrow \mathbf{U}^{(a)}(t) = e^{+i\int^t \mathbf{D}^{(a)}(t') dt'} \mathbf{U}^{(a)}(0),$$

$$i\dot{U}_{s'q'}^{(m)}(t) = - \sum_{k'=1}^M D_{s'k'}^{(m)}(t) U_{k'q'}^{(m)}(t) \Rightarrow \mathbf{U}^{(m)}(t) = e^{+i\int^t \mathbf{D}^{(m)}(t') dt'} \mathbf{U}^{(m)}(0), \quad (\text{A19})$$

with the initial conditions defined in the limit $\tau \rightarrow 0$ as (see in this respect Ref. [33])

$$\mathbf{U}^{(a)}(\tau) = \mathbf{T}^{(a)}(0) e^{+i\tau \mathbf{d}^{(a)}(0)}, \quad \mathbf{U}^{(m)}(\tau) = \mathbf{T}^{(m)}(0) e^{+i\tau \mathbf{d}^{(m)}(0)}. \quad (\text{A20})$$

Then, the unitary transformations of the orbitals

$$\bar{\phi}_q(\mathbf{r}, t) = \sum_{k=1}^M U_{kq}^{(a)}(t) \phi_k(\mathbf{r}, t), \quad q = 1, \dots, M,$$

$$\bar{\psi}_{q'}(\mathbf{r}, t) = \sum_{k'=1}^{M'} U_{k'q'}^{(m)}(t) \psi_{k'}(\mathbf{r}, t), \quad q' = 1, \dots, M' \quad (\text{A21})$$

lead to the desired result—equations of motion (37) and (44)—where the projection operators $\hat{\mathbf{P}}^{(a)}$ and $\hat{\mathbf{P}}^{(m)}$ have been eliminated from the left-hand sides.

The transformation $\{C_{\bar{n}p\bar{m}p}(t)\} \rightarrow \{\bar{C}_{\bar{n}p\bar{m}p}(t)\}$ accompanying Eq. (A21) carries equations of motion (39) for the expansion coefficients to the respective final result, Eqs. (40) and (47). It is instructive to obtain this result by proving that the equations of motion for the expansion coefficients are *form invariant*. Namely, if $\mathcal{H}^{(2a=m)}(t) \mathbf{C}(t) = i \frac{\partial \mathbf{C}(t)}{\partial t}$ are satisfied for the untransformed quantities $[\{C_{\bar{n}p\bar{m}p}(t)\}, \{\phi_k(\mathbf{r}, t)\}, \{\psi_{k'}(\mathbf{r}, t)\}]$ then $\bar{\mathcal{H}}^{(2a=m)}(t) \bar{\mathbf{C}}(t) = i \frac{\partial \bar{\mathbf{C}}(t)}{\partial t}$ are satisfied for the transformed ones $[\{\bar{C}_{\bar{n}p\bar{m}p}(t)\}, \{\bar{\phi}_k(\mathbf{r}, t)\}, \{\bar{\psi}_{k'}(\mathbf{r}, t)\}]$. The proof is straightforward. Equating the variation of the functional action [Eqs. (30) and (32)] with respect to the expansion coefficients to zero, the result can be written as follows: $\langle \bar{n}^p, \bar{m}^p; t | \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} | \bar{\Psi}(t) \rangle, \forall p, \bar{n}^p, \bar{m}^p$. Since the transformed configurations $\{|\bar{n}^p, \bar{m}^p; t\rangle\}$ are given as linear combinations of the untransformed configurations $\{|\bar{n}^p, \bar{m}^p; t\rangle\}$, the operator $\hat{H}^{(2a=m)} - i \frac{\partial}{\partial t}$ does not depend on the orbitals, and $|\bar{\Psi}(t)\rangle = |\Psi(t)\rangle$, we immediately obtain $\langle \bar{n}^p, \bar{m}^p; t | \hat{H}^{(2a=m)} - i \frac{\partial}{\partial t} | \bar{\Psi}(t) \rangle, \forall p, \bar{n}^p, \bar{m}^p$, which concludes our proof. To our needs, since the transformed orbitals (A21) obey the differential conditions $\langle \bar{\phi}_k | \dot{\bar{\phi}}_q \rangle = 0; k, q = 1, \dots, M$ and $\langle \bar{\psi}_{k'} | \dot{\bar{\psi}}_{q'} \rangle = 0; k', q' = 1, \dots, M'$ [see Eq. (38)], the respective equations of motion for the transformed coefficients boil down to $\bar{\mathbf{H}}^{(2a=m)}(t) \bar{\mathbf{C}}(t) = i \frac{\partial \bar{\mathbf{C}}(t)}{\partial t}$ [see Eqs. (40) and (47)].

APPENDIX B: MATRIX ELEMENTS WITH MULTICONFIGURATIONAL WAVE FUNCTIONS IN SYSTEMS WITH PARTICLE CONVERSION

There are two types of matrix elements in the theory. The first type are matrix elements of the many-body Hamiltonian with respect to the configurations. These matrix elements are expressed using the matrix elements of the one-body terms, two-body interaction terms, and the conversion term with respect to the atomic and molecular orbitals. The second type of matrix elements are the matrix elements of the reduced density matrices appearing in the theory, which are expressed in terms of the expansion coefficients.

In this appendix we prescribe these matrix elements. It is easy to connect the matrix elements of particle-conserving operators to the corresponding matrix elements appearing in the available multiconfigurational theories for identical particles and mixtures. This assignment will shorten substantially the discussion below. The matrix elements of particle nonconserving operators will be presented in full detail.

1. Matrix elements of the Hamiltonian

The many-body Hamiltonian [Eqs. (1)–(3)] is written as a sum of particle-conserving and particle nonconserving parts: $\hat{H}^{(2a=m)} = \hat{H}^{(am)} + \hat{W}^{(2a=m)}$. The matrix elements of the particle-conserving part $\hat{H}^{(am)}$, see Eqs. (1) and (2), between two general configurations derive from the following relation:

$$\left\langle \bar{n}^p, \bar{m}^p; t \left| \hat{H}^{(am)} - i \frac{\partial}{\partial t} \right| \bar{n}'^p, \bar{m}'^p; t \right\rangle = \delta_{p,p'} \left\langle \bar{n}^p, \bar{m}^p; t \left| \hat{H}^{(am)} - i \frac{\partial}{\partial t} \right| \bar{n}'^p, \bar{m}'^p; t \right\rangle. \quad (\text{B1})$$

Thus, it corresponds to a matrix element of a mixture with $N-2p$ atoms and p molecules *without conversion*. The matrix elements of the Hamiltonian of a mixture of two kinds of bosons with respect to two general configurations have been prescribed within the respective particle-conserving multiconfigurational theory for Bose-Bose mixtures, the MCTDH-BB theory, see Ref. [54].

To evaluate the matrix elements of the particle-nonconserving part of the Hamiltonian, $\hat{W}^{(2a=m)} = \hat{W}^{(2a \rightarrow m)} + \hat{W}^{(m \rightarrow 2a)}$, see Eqs. (1) and (3), between two general configurations we have to introduce a shorthand notation for different configurations. The reference configuration is denoted by $|\bar{n}^p, \bar{m}^p; t\rangle = |n_1^p, \dots, n_k^p, \dots, n_q^p, \dots, n_M^p; m_1^p, \dots, m_{k'}^p, \dots, m_{M'}^p; t\rangle$. We remind that the occupation numbers satisfy the relations: $|\bar{n}^p| = n_1^p + \dots + n_M^p = N-2p$ and $|\bar{m}^p| = m_1^p + \dots + m_{M'}^p = p$, where p is the number of molecules. Now, the configuration $|\bar{n}_{kk}^{p-1}, \bar{m}_{k'}^p; t\rangle \equiv |n_1^p, \dots, n_k^p + 1, \dots, n_q^p + 1, \dots, n_M^p; m_1^p, \dots, m_{k'}^p - 1, \dots, m_{M'}^p; t\rangle$ differs from $|\bar{n}^p, \bar{m}^p; t\rangle$ by having $p-1$ molecules and $N-2p+2$ atoms, where a molecule in the k' th orbital has dissociated to two atoms, one in the k th orbital and the second in the q th orbital; and the configuration $|\bar{n}_{kk}^{p-1}, \bar{m}_{k'}^{p-1}; t\rangle \equiv |n_1^p, \dots, n_k^p$

$+2, \dots, n_M^p; m_1^p, \dots, m_{k'}^p-1, \dots, m_{M'}^p; t$ differs from $|\vec{n}^p, \vec{m}^p; t\rangle$ by having $p-1$ molecules and $N-2p+2$ atoms, where a molecule in the k' th orbital has dissociated to two atoms, both in the k th orbital. We employ a nomenclature where the same ordering of the orbitals ϕ_1, \dots, ϕ_M and $\psi_1, \dots, \psi_{M'}$ as in Eq. (26) is kept for all configurations. In this nomenclature the following states are equivalent: $|\vec{n}_{kq}^{p-1}, \vec{m}_{k'}^{p-1}; t\rangle \equiv |\vec{n}_{qk}^{p-1}, \vec{m}_{k'}^{p-1}; t\rangle$.

With this notation, the nonvanishing matrix elements of the particle-nonconserving part of the Hamiltonian follow from

$$\begin{aligned} & \langle \vec{n}^p, \vec{m}^p; t | \hat{W}^{(2a \rightarrow m)} | \vec{n}_{kq}^{p-1}, \vec{m}_{k'}^{p-1}; t \rangle \\ &= \frac{1}{\sqrt{2}} W_{k'kq}^{(2a \rightarrow m)} \sqrt{m_{k'}^p (n_k^p + 1) (n_q^p + 1)}, \quad k < q, \\ & \langle \vec{n}^p, \vec{m}^p; t | \hat{W}^{(2a \rightarrow m)} | \vec{n}_{kk}^{p-1}, \vec{m}_{k'}^{p-1}; t \rangle \\ &= \frac{1}{\sqrt{2}} W_{k'kk}^{(2a \rightarrow m)} \sqrt{m_{k'}^p (n_k^p + 1) (n_k^p + 2)}, \end{aligned} \quad (\text{B2})$$

and the relation $\langle \vec{n}^p, \vec{m}^p; t | \hat{W}^{(m \rightarrow 2a)} | \vec{n}^{p'}, \vec{m}^{p'}; t \rangle = \{ \langle \vec{n}^{p'}, \vec{m}^{p'}; t | \hat{W}^{(2a \rightarrow m)} | \vec{n}^p, \vec{m}^p; t \rangle \}^*$. We note that $W_{k'kq}^{(2a \rightarrow m)} = W_{k'qk}^{(2a \rightarrow m)}$ because $\hat{W}^{(2a \rightarrow m)}(\mathbf{r}, \mathbf{r}') = \hat{W}^{(2a \rightarrow m)}(\mathbf{r}', \mathbf{r})$. To summarize, direct coupling in the matrix representation of the Hamiltonian with respect to the configurations exists due to the particle-nonconserving part of the Hamiltonian $\hat{W}^{(2a \rightarrow m)}$ between configurations with p and $p-1$ molecules only, for $p=1, \dots, [N/2]$.

2. Matrix elements of reduced density matrices

The multiconfigurational ansatz (26) can be written in the following form:

$$|\Psi(t)\rangle = \sum_{p=0}^{[N/2]} |\Psi_p(t)\rangle, \quad (\text{B3})$$

where each $|\Psi_p(t)\rangle = \sum_{\vec{n}^p, \vec{m}^p} C_{\vec{n}^p, \vec{m}^p}^p(t) |\vec{n}^p, \vec{m}^p; t\rangle$ is a (non-normalized) many-particle wave function with a definite number of p molecules and $N-2p$ atoms, and thus “describes” a bosonic mixture *without conversion*. Consequently, the matrix elements of the particle-conserving reduced density matrices can be expressed as follows:

$$\rho_{kq}^{(a)}(t) = \langle \hat{b}_k^\dagger \hat{b}_q \rangle = \sum_{p=0}^{[N/2]} \langle \Psi_p(t) | \hat{b}_k^\dagger \hat{b}_q | \Psi_p(t) \rangle,$$

$$\rho_{k'q'}^{(m)}(t) = \langle \hat{c}_{k'}^\dagger \hat{c}_{q'} \rangle = \sum_{p=0}^{[N/2]} \langle \Psi_p(t) | \hat{c}_{k'}^\dagger \hat{c}_{q'} | \Psi_p(t) \rangle,$$

$$\rho_{kslq}^{(a)}(t) = \langle \hat{b}_k^\dagger \hat{b}_s^\dagger \hat{b}_l \hat{b}_q \rangle = \sum_{p=0}^{[N/2]} \langle \Psi_p(t) | \hat{b}_k^\dagger \hat{b}_s^\dagger \hat{b}_l \hat{b}_q | \Psi_p(t) \rangle,$$

$$\rho_{k's'l'q'}^{(m)}(t) = \langle \hat{c}_{k'}^\dagger \hat{c}_s^\dagger \hat{c}_{l'} \hat{c}_{q'} \rangle = \sum_{p=0}^{[N/2]} \langle \Psi_p(t) | \hat{c}_{k'}^\dagger \hat{c}_s^\dagger \hat{c}_{l'} \hat{c}_{q'} | \Psi_p(t) \rangle,$$

$$\rho_{kk'qq'}^{(am)}(t) = \langle \hat{b}_k^\dagger \hat{b}_q \hat{c}_{k'}^\dagger \hat{c}_{q'} \rangle = \sum_{p=0}^{[N/2]} \langle \Psi_p(t) | \hat{b}_k^\dagger \hat{b}_q \hat{c}_{k'}^\dagger \hat{c}_{q'} | \Psi_p(t) \rangle. \quad (\text{B4})$$

In other words, the matrix elements of the particle-conserving reduced density matrices can be readily read from the reduced density matrices of the respective particle-conserving multiconfigurational theory for Bose-Bose mixtures, the MCTDH-BB theory, see Ref. [54].

The matrix elements of the particle-nonconserving reduced density matrices are given explicitly by

$$\begin{aligned} \rho_{k'kq}^{(2a \rightarrow m)} &= \langle \hat{c}_{k'}^\dagger \hat{b}_k \hat{b}_q \rangle \\ &= \sum_{p=0}^{[N/2]} \sum_{\vec{n}^p, \vec{m}^p} C_{\vec{n}^p, \vec{m}^p}^* C_{\vec{n}_{kq}^{p-1}, \vec{m}_{k'}^{p-1}} \sqrt{m_{k'}^p (n_k^p + 1) (n_q^p + 1)}, \\ & \quad k < q, \end{aligned}$$

$$\rho_{k'kk}^{(2a \rightarrow m)} = \sum_{p=0}^{[N/2]} \sum_{\vec{n}^p, \vec{m}^p} C_{\vec{n}^p, \vec{m}^p}^* C_{\vec{n}_{kk}^{p-1}, \vec{m}_{k'}^{p-1}} \sqrt{m_{k'}^p (n_k^p + 1) (n_k^p + 2)}. \quad (\text{B5})$$

All other matrix elements are derived from the symmetry of the conversion operator, $\rho_{k'qk}^{(2a \rightarrow m)} = \rho_{k'qk}^{(2a \rightarrow m)}$, and the Hermiticity relation $\rho_{qkk'}^{(m \rightarrow 2a)}(t) = \{ \rho_{k'kq}^{(2a \rightarrow m)}(t) \}^*$.

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