Multiconfigurational time-dependent Hartree method to describe particle loss due to absorbing boundary conditions

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Absorbing boundary conditions in the form of a complex absorbing potential are routinely introduced in the Schrödinger equation to limit the computational domain or to study reactive scattering events using the multiconfigurational time-dependent Hartree (MCTDH) method. However, it is known that a pure wave-function description does not allow the modeling and propagation of the remnants of a system of which some parts are removed by the absorbing boundary. It was recently shown [S. Selstø and S. Kvaal, J. Phys. B: At. Mol. Opt. Phys. **43**, 065004 (2010)] that a master equation of Lindblad form was necessary for such a description. We formulate a MCTDH method for this master equation, usable for any quantum system composed of any mixture of species. The formulation is a strict generalization of pure-state propagation using standard MCTDH for identical particles and mixtures. We demonstrate the formulation with a numerical experiment.

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I. INTRODUCTION

Today, the *de facto* standard approach in *ab initio* quantum-mechanical many-particle propagation is the multiconfigurational time-dependent Hartree (MCTDH) method and its variations [1–7]. Already for $N = 2$ electrons in three dimensions, the full six-dimensional time-dependent Schrödinger equation is very hard to solve and can only be handled on supercomputers. With the MCTDH method for identical particles the exponential scaling of the Hilbert space dimension with respect to N is "postponed" to a higher number of particles, and the $N = 2$ propagation can be done on a single desktop computer. Current implementations can handle $N \leqslant 8$ electrons in cylindrical geometries reliably [8,9]. For bosons, the Pauli exclusion principle is absent, and the MCTDH method can treat hundreds [10] and even thousands of particles [11] in one-dimensional geometries, and recent multilayer MCTDH techniques allow *distinguishable* dimensions in the *thousands* with relative ease [7], showing great promise for extending the domain of application of MCTDH methods.

The MCTDH class of methods is derived using the time-dependent variational principle [12,13]. As such, it is energy conserving, unitary, and quasioptimal in the sense that the growth of the error in the 2-norm is locally minimized.

Ab initio dynamical problems in quantum mechanics are formulated on an infinite domain which must be truncated for numerical calculations. The numerical reflections implied by the truncations are usually dealt with using absorbing boundary conditions of some sort. The most common approach is to introduce a complex absorbing potential (CAP) in a region around the truncated domain [14]. That is, the Hamiltonian H is mapped to $H - i\Gamma$, where $\Gamma \geqslant 0$ is a local one-body potential vanishing on the domain of interest, and only taking nonzero values outside the domain. This approach is also used in order to calculate properties like reaction and ionization probabilities, and CAPs are routinely implemented in MCTDH codes [4,8,15–17].

Other absorbing operators are also common, such as the so-called transformative CAP (TCAP) [18], which is more or less equivalent with the nonlocal CAP obtained using smooth exterior scaling [19] or perfectly matched layers [20]. While *exact* and space-local absorbing boundary conditions may be formulated [21], they are in general nonlocal in time, and therefore impractical. In this work, we focus solely on a local CAP for simplicity, but any absorbing operator can be used.

Given a system of N particles, the wave function Ψ_N is normalized to the probability of finding *all* particles within the computational domain. With a CAP, Ψ_N evolves according to the non-Hermitian Schrödinger equation

$$i\frac{d}{dt}\Psi_N = (H - i\Gamma)\Psi_N. \tag{1}$$

An elementary calculation gives $\frac{d}{dt}\|\Psi_N\|^2 = -2\langle\Psi_N|\Gamma|\Psi_N\rangle$ for the probability derivative. Consequently, if the wave function overlaps the CAP, the whole wave function decays and eventually vanishes; it does *not* approach a wave function with a different number of particles. In other words, even with an absorbing boundary, one is stuck with an N-particle description. Information like ionization probabilities and reaction rates may be obtained from evolving Eq. (1) alone, but if the *remainder* of the system is desired, i.e., a description of the $N - 1$, $N - 2$ particle systems, etc., one is at a loss.

In a recent article it was argued that the solution is a density operator approach [22] because the loss of particles is an irreversible process; $H - i\Gamma$ is a non-Hermitian operator implying a preferred direction of time. The necessity of the quantum dynamical semigroup describing the evolution to be trace preserving, Markovian, and completely positive implies the applicability of the famous theorems due to Lindblad and Gorini and coworkers [23–25], giving a master equation in the so-called Lindblad form. The resulting equation is

$$\frac{d}{dt}\rho_n = -i[H,\rho_n] - \{\Gamma,\rho_n\} + 2\int \Gamma(x)\boldsymbol{\psi}(x)\rho_{n+1}\boldsymbol{\psi}(x)^\dagger\, dx, \tag{2}$$

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where ρ_n is the density operator for the n-particle subsystem, $0 \leqslant n \leqslant N$. The integral is over all discrete and continuous degrees of freedom. It should be noted that the non-Hermitian Schrödinger equation (1) is equivalent to the von Neumann equation

$$\frac{d}{dt}\rho_n = -i[H,\rho_n] - \{\Gamma,\rho_n\}$$

for each n-particle system. The original formulation of the N-particle problem is not changed, but extended to yield $n \leqslant N$ particle systems as a by-product. Importantly, nowhere is an *ad hoc* hypothesis introduced.

Let us point out, that Eq. (2) does not address other general and important problems concerning the CAP approach to absorbing boundary conditions, such as missing correlation effects. Such arise if, say, the computational domain is too small, so that particles can be removed "prematurely" by the CAP. This correlation information is lost forever and cannot be "built into" the fewer-particle systems.

Equation (2) describes the evolution of a *mixed state* due to irreversibility. The mixedness has two main sources: First, as the probability $\mathrm{tr}(\rho_N)$ of having N particles present is gradually reduced, the probability of $N' < N$ particles increases. In this intermediate stage ρ is a mixed state [22]. Second, the block $\rho_{N'}$ alone may be nonpure in the limit $t \to \infty$, as information about the absorbed particles is thrown away and since the exact N-body wave function depends on *all* particle coordinates. This limits the information that can be extracted from the decayed $N' < N$-body systems compared to a *full* evolution of the total wave function—a feature inherent in the the CAP approach to absorbing boundaries.

In this article, we formulate a MCTDH method for Eq. (2) for identical particles and mixtures. It is based on a so-called type II density operator manifold [3,26] and is fully variational. Such methods are usually called ρ-MCTDH methods (as opposed to Ψ-MCTDH methods for pure states), and ours can be viewed as a special case since the dissipative operators are in a very special form. On the other hand our point of view is more general as the problem is formulated in Fock space which is not considered for standard ρ-MCTDH methods; indeed the dissipative operators change the number of particles. The method, which we call ρ-CAP-MCTDH, turns out to be exactly trace preserving and a strict generalization of the Ψ-MCTDH method for pure states evolving according to the non-Hermitian Schrödinger equation with a CAP (1). The method is first formulated for identical fermions and bosons and then extended to arbitrary mixtures of species. We use the acronym ρ-CAP-MCTDH for all variations for clarity, instead of the distinction between MCTDHF (for fermions) and MCTDHB (for bosons), and so on. The derivation for identical particles is done in Sec. III, while the generalization is done in Sec. V, after a numerical experiment on a system of identical fermions is presented in Sec. IV. Not surprisingly, the resulting formulation is a direct generalization of the pure-state MCTDH treatment of mixtures [27].

To prepare for the ρ-CAP-MCTDH method, we give a brief derivation of Eq. (2) in Sec. II that underlines the inevitability and uniqueness of the master equation in the Lindblad form. We also show how the probability interpretation of $\|\Psi_N\|^2$, which is not purely quantum mechanical, can be interpreted in terms of measurements performed continuously in time.

II. LINDBLAD EQUATION FOR SYSTEMS WITH A CAP

A. Classical probabilities from a CAP

The evolution of Ψ_N under the non-Hermitian Schrödinger equation (1) is irreversible. It introduces a preferred direction in time, which is easily seen from the fact that the evolution cannot be reversed: eventually $\|\Psi_N\| > 1$, and the backward propagation may be nonexistent, even mathematically.

We now give an interpretation of the square norm $\|\Psi_N\|^2$ in terms of measurements performed continuously in time, thereby exposing the irreversibility. We stress that this is meant as an *illustration* and a helpful device for understanding the dynamics due to a CAP, and has no bearing on the mathematical discussion leading up to the Lindblad master equation (2). To this end, consider first a closed single-particle system, described by the Hamiltonian H—without a CAP—in the Hilbert space $\mathscr{H}_1$. Quantum mechanically, the squared norm $\|\Psi_1\|^2$ of the wave function is the probability of finding the particle *somewhere* in configuration space. Equivalently, it is the probability of obtaining the value 1 upon measurement of trivial observable I (the identity operator).

Adding a CAP $-i\Gamma$ to the Hamiltonian and keeping the probability interpretation of $\|\Psi_1\|^2$ has nontrivial implications. The description is obviously no longer in accordance with the basic postulates of quantum mechanics, since

$$\frac{d}{dt}\|\Psi_1\|^2 = -2\langle\Psi_1|\Gamma|\Psi_1\rangle \leqslant 0,$$

that is to say, total probability is *not conserved*.

Suppose we perform a single measurement on the observable P given by

$$P = \int_\Omega |x\rangle\langle x| dx,$$

i.e., of the projection operator P onto Ω, the truncated computational domain. It has two eigenvalues, 0 and 1, corresponding to finding the particle outside or inside Ω, respectively. We obtain the answer 0 with probability $1 - \|\Psi_1\|^2_\Omega = 1 - \langle\Psi_1|P|\Psi_1\rangle$ and the answer 1 with probability $\|\Psi_1\|^2_\Omega$. After measurement, the wave function collapses onto $(I - P)\Psi_1$ in the former case and $P\Psi_1$ in the latter (up to normalization constants). Note that the wave-function collapse is irreversible, as the original wave function cannot be reconstructed after the event.

Suppose we perform many experiments at short time intervals $t = n\tau$, $n = 0,1,2,\ldots$. Each experiment yields certain information about the system after the measurement: we know with certainty if the particle is in Ω or not. After n experiments, all giving 1 as the answer, the wave function is readily computed to be

$$\Psi_1(n\tau) = \frac{[Pe^{-i\tau H}]^n\Psi_1(0)}{\|[Pe^{-i\tau H}]^n\Psi_1(0)\|},$$

and the probability that n positive answers have been given is

$$p_n = \|[Pe^{-i\tau H}]^n\Psi_1(0)\|^2.$$

This probability is classical in the sense that it is a probability description of the history of our macroscopic measurement device, or of its printout on a sheet of paper if one prefers.

Let us define $\tilde{\Psi}_1(n\tau) = \sqrt{p_n}\Psi_1(n\tau) = [Pe^{-i\tau H}]^n\Psi_1(0)$, so that $\|\tilde{\Psi}_1(n\tau)\|^2 = p_n$. If we allow the approximation

$$P \approx \exp(-\tau\Gamma),$$

which dampens Ψ_1 strongly outside Ω, we get

$$Pe^{-i\tau H} \approx e^{-\tau\Gamma}e^{-i\tau H} = e^{-i\tau(H-i\Gamma)} + O(\tau^2).$$

In the limit of small τ, we see that $\tilde{\Psi}_1(t)$ is the solution to the Schrödinger equation with a CAP. $\|\tilde{\Psi}_1(t)\|^2$ is then the probability of finding the measurement apparatus in the state "the particle has not yet been detected outside Ω" at time t.

Our discussion is immediately suggestive of interpreting the CAP as an actual model for some external detecting device, which was already pointed out in an early publication on CAPs in quantum mechanics [14]. Although it is likely that Eq. (2) can be derived in such a way, it is not relevant here, as the Schrödinger equation with a CAP is our starting point. The above discussion is only intended as a means for understanding the irreversibility of the non-Hermitian dynamics. Whatever interpretation we use, we see that the single-particle system undergoes a transition to a zero-particle state (i.e., zero particles in Ω) in an irreversible way and that the probability of having $n = 1$ or $n = 0$ particles is not quantum mechanical.

A complete specification of the quantum state of the $n \leqslant 1$-particle system is a density operator in the Hilbert space $\mathscr{H}_1 \oplus \mathscr{H}_0$, where $\mathscr{H}_n$ is the Hilbert space of n particles. In this case, the density operator is, in block form,

$$\rho = \begin{pmatrix} |\tilde{\Psi}_1\rangle\langle\tilde{\Psi}_1| & 0 \\ 0 & (1 - \langle\tilde{\Psi}_1|\tilde{\Psi}_1\rangle) \end{pmatrix}.$$

Note that $\mathscr{H}_0$ is one dimensional, and the lower right block is just a non-negative real number, the probability of zero particles in Ω.

For a rigorous treatment of the above limiting process, see Chap. 7.4 in Ref. [28].

Generalizing the discussion to N particles is analogous to our discussion approximating $P \approx \exp(-i\Gamma)$ in the same way. $\|\tilde{\Psi}_N\|^2$ is then the probability of the measurement apparatus showing that all particles are inside Ω.

B. N-fermion systems with a CAP

Suppose a complete set of fermionic or bosonic creation operators $\{c_j^\dagger\}$, $j = 1,2,\ldots$, is given. An important formal property of $c_j^\dagger$ is that it defines a map from $\mathscr{H}_n$ to $\mathscr{H}_{n+1}$, the Hilbert spaces of n and $n+1$ fermions, respectively, and that they fulfill the (anti-)commutator relation

$$\{c_j^\dagger, c_k\}_\pm \equiv c_j^\dagger c_k \pm c_k c_j^\dagger = \delta_{jk}, \tag{3}$$

with the plus sign for fermions and the minus sign for bosons.

For us, it is natural to work within Fock space $\mathscr{H}$, defined by

$$\mathscr{H} \equiv \bigoplus_{n=0}^{\infty} \mathscr{H}_n,$$

containing all possible states with any number of particles. As operators in $\mathscr{H}$, the c_j are orthogonal in the Hilbert-Schmidt inner product,

$$\langle\langle c_j, c_k\rangle\rangle = \mathrm{tr}(c_j^\dagger c_k) = 0, \quad j \neq k,$$

and traceless,

$$\mathrm{tr}(c_j) = 0.$$

Given an n-particle Hamiltonian in first-quantized form, viz.,

$$H_n = \sum_{i=1}^{n} h(i) + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} u(i,j),$$

(where the indices i and j in the operators indicate which particles' degrees of freedom they act on) we may write it compactly in n-independent form using the expression

$$H = \sum_{jk} h_{jk} c_j^\dagger c_k + \frac{1}{2}\sum_{jklm} u_{jklm} c_j^\dagger c_k^\dagger c_m c_l, \tag{4}$$

where h_{jk} and u_{jklm} are the usual one- and two-particle integrals, respectively.

Adding a cap $\Gamma = \sum_{i=1}^n \Gamma(i)$ amounts to modifying the single-particle coefficients since

$$\Gamma = \sum_{jk} \Gamma_{jk} c_j^\dagger c_k. \tag{5}$$

It is important to note, that given the set $\{c_j^\dagger\}$, the second-quantized expressions of H and Γ are unique, and vice versa.

C. The Lindblad equation

We now discuss the master equation (2), introduced in Ref. [22], for a system of identical particles. We underline that the master equation *follows uniquely* from the probability interpretation of $\|\Psi_n\|^2$ for an n-particle wave function and the requirement of a Markovian, trace-preserving, and completely positive evolution. We also address some mathematical points omitted in Ref. [22].

Describing a system with a variable number of particles, we work with states in Fock space. Our starting point, the non-Hermitian Schrödinger equation with a given CAP, then reads

$$i\frac{d}{dt}\Psi = (H - i\Gamma)\Psi. \tag{6}$$

With an initial condition with exactly N particles, i.e., $\Psi(0) = \Psi_N \in \mathscr{H}_N$, this equation is equivalent to Eq. (1), which we repeat here for convenience:

$$i\frac{d}{dt}\Psi_N = (H - i\Gamma)\Psi_N. \tag{7}$$

This description is valid for all particle numbers N.

As Eq. (6) is irreversible, it is not possible to find some new Hamiltonian H' in Fock space that generates a unitary evolution which describes a decreasing number of particles and also reproduces Eq. (7). Instead, one must turn to a density operator description. For a density operator $\rho \in \mathrm{TC}(\mathscr{H})$,

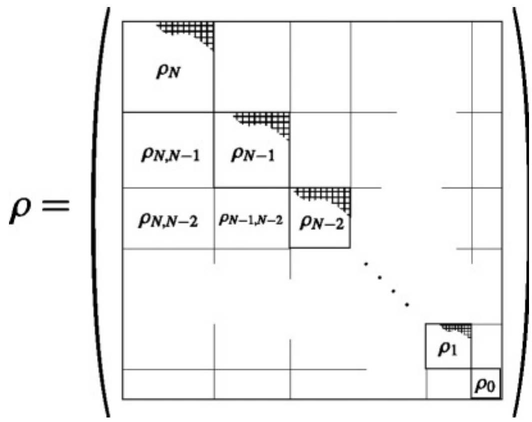

FIG. 1. Illustration of the block structure of the density operator in Fock space with at most N identical particles. In general, each block is infinite dimensional (except for ρ_0 which is 1×1). The diagonal blocks are emphasized, as for pure-state initial conditions $\rho = |\Psi_N\rangle\langle\Psi_N|$ the density operator turns out to be block diagonal.

the trace-class operators in Fock space [25,28], Eq. (6) is equivalent to the nontrace conserving von Neumann equation

$$\frac{d}{dt}\rho = -i[H,\rho] - \{\Gamma,\rho\}, \tag{8}$$

which is verified by a simple computation. The density operator ρ has a natural block structure. Letting P_n be the orthogonal projector onto $\mathscr{H}_n$, we have the resolution of the identity

$$I = \sum_{n=0}^{\infty} P_n.$$

Applying this to either side of ρ gives the decomposition

$$\rho = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \rho_{n,m}, \quad \rho_{n,m} \equiv P_n \rho P_m.$$

This block structure is depicted in Fig. 1. Projecting Eq. (8) from the left and right with P_n, we obtain

$$\frac{d}{dt}\rho_{n,n} = -i[H,\rho_{n,n}] - \{\Gamma,\rho_{n,n}\}, \tag{9}$$

which is equivalent to Eq. (7).

We wish to obtain a master equation for ρ that *does* preserve total probability. At all times, there is a probability $\mathrm{tr}(\rho_n)$ of having n particles (we define $\rho_n \equiv \rho_{n,n}$), and these should add up to $\mathrm{tr}(\rho) = \sum_n \mathrm{tr}(\rho_n) = 1$. Since the von Neumann equation is local in time, we require the master equation to be Markovian. Our master equation must reproduce Eq. (9) for $n = N$, where N is the number of particles initially present. Of course, for $n < N$ the master equation will end up with some source terms. This must hold for all N, i.e., our master equation should not depend on N; only the initial condition depends on N.

We also require the master equation to describe a physical system which in turn may interact with other quantum systems. A minimal requirement for such master equations is that its quantum semigroup be *completely positive*. Complete positivity roughly states that if our system is described together with a different system with Hilbert space $\mathscr{V}$, so that the combined state is $\sigma \in \mathrm{TC}(\mathscr{H} \otimes \mathscr{V})$, then the semigroup of σ preserves the self-adjoint positive semidefiniteness of σ. Surprisingly, requiring this property for the flow of ρ alone is not enough [24,25].

Let us for the moment assume that Fock space has a *finite dimension*, i.e., it is defined by a finite number L of creation operators. The theorem of Gorini and coworkers is now applicable [24]: Any trace-preserving, Markovian, and completely positive quantum dynamical semigroup has a master equation of the form

$$\frac{d}{dt}\rho = -i[H,\rho] + \mathscr{D}(\rho), \tag{10}$$

where the dissipative terms have the generic form

$$\mathscr{D}(\rho) = \sum_{\alpha\beta} d_{\alpha\beta}(2L_\beta \rho L_\alpha^\dagger - \{L_\alpha^\dagger L_\beta,\rho\}). \tag{11}$$

The operators L_α form a traceless, orthogonal set with the Hilbert-Schmidt inner product $\langle\langle\rho,\sigma\rangle\rangle = \mathrm{tr}(\rho^\dagger\sigma)$ [the operators are then linearly independent in $\mathrm{TC}(\mathscr{H})$], and $[d_{\alpha\beta}]$ is a Hermitian positive semidefinite matrix. Importantly, the quantum dynamical semigroup generated by Eq. (10) is uniquely given by H and $\mathscr{D}$ and vice versa.

The L_α play the role of a basis in $\mathrm{TC}(\mathscr{H})$, which is of dimension $\dim(\mathscr{H})^2$. It is of course not unique, but given a choice of basis, the coefficients $[d_{\alpha\beta}]$ are unique. Notice that the trace of the anticommutator term in Eq. (11) is equal to but of opposite magnitude compared to the term where ρ is sandwiched between L_β and $L_\alpha^\dagger$.

The von Neumann equation is *almost* of the form of Eq. (10); it lacks the "sandwiched terms" responsible for a compensation of the trace decrease due to the anticommutator, i.e.,

$$\frac{d}{dt}\rho = -i[H,\rho] - \sum_{jk}\Gamma_{jk}\{c_j^\dagger c_k,\rho\}.$$

As the operators $\{c_j\}$ are indeed traceless and orthogonal, it is immediately clear that the correct master equation is obtained by simply adding the sandwiched terms, i.e.,

$$\frac{d}{dt}\rho = -i[H,\rho] - \sum_{jk}\Gamma_{jk}\{c_j^\dagger c_k,\rho\} + 2\sum_{jk}\Gamma_{jk}c_k\rho c_j^\dagger. \tag{12}$$

If the dissipative terms are not chosen in *exactly* this form, Eq. (9) will not be reproduced for all N.

Indeed, consider an initial condition of the form

$$\rho(0) = |\Psi_N\rangle\langle\Psi_N|. \tag{13}$$

Projecting Eq. (12) from the left and right with P_n and P_m, respectively, we obtain the differential equation obeyed by the block $\rho_{n,m}$,

$$\frac{d}{dt}\rho_{n,m} = -i[H,\rho_{n,m}] - \{\Gamma,\rho_{n,m}\} + 2\sum_{jk}\Gamma_{jk}c_k\rho_{n+1,m+1}c_j^\dagger. \tag{14}$$

We see that the off-diagonal blocks $\rho_{n,m}$ with $n \neq m$ are identically zero with the initial condition (13). The compensating sandwich terms are seen to be responsible for transporting probability from the N-particle system into the $N-1$-particle system, and so on, downward along the diagonal blocks in Fig. 1. Moreover, the evolution of $\rho_{N,N}$ is equivalent to Eq. (7). Modifying the coefficients Γ_{jk} or adding more linearly independent operators to the set $\{c_j\}$ will void this for some N.

The theorem by Gorini and coworkers is only valid in a finite-dimensional Hilbert space. For infinite-dimensional spaces, Lindblad discovered a generalization for norm-continuous semigroups [23], for which H and Γ are necessarily bounded operators. This is rarely the case, but a Lindblad-type theorem for the general unbounded cases is simply not known [25]. On the other hand, all known examples of completely positive semigroups in infinite-dimensional spaces have generators in the generic form (11), with possibly unbounded H or $[d_{\alpha\beta}]$.

It now seems reasonable to remove the restriction of a finite-dimensional Fock space, which does not change the formal appearance of the Lindblad equation (12). Using the relation

$$\boldsymbol{\psi}(x)^\dagger \equiv \sum_j \overline{\varphi_j(x)} c_j^\dagger$$

for the field creation operators (creating a particle at x), where $\varphi_j(x)$ is the orthonormal single-particle basis function associated with $c_j^\dagger$, we arrive at the master equation

$$\frac{d}{dt}\rho = -i[H,\rho] - \{\Gamma,\rho\} + 2\int \Gamma(x)\boldsymbol{\psi}(x)\rho\boldsymbol{\psi}(x)^\dagger dx, \tag{15}$$

which in block form becomes

$$\frac{d}{dt}\rho_n = -i[H,\rho_n] - \{\Gamma,\rho_n\} + 2\int \Gamma(x)\boldsymbol{\psi}(x)\rho_{n+1}\boldsymbol{\psi}(x)^\dagger dx, \tag{16}$$

where we have assumed an N-particle initial condition $\rho(0) = \rho_N$.

We stress that the Lindblad equation (16) followed *only* from the probability interpretation of $\|\Psi_N\|^2$ and from the requirement that the master equation generates a Markovian, trace-preserving, and completely positive semigroup.

III. MCTDH FORMULATION FOR IDENTICAL PARTICLES

A. The ρ-CAP-MCTDH manifold

We now derive the ρ-CAP-MCTDH approximation to the Lindblad equation (15). This method is in a sense a combination of the Ψ-MCTDH method for identical particles [4–6,27], using second quantization, and the ρ-MCTDH method [3,26] for general density operators. Our method is necessarily formulated in Fock space and describes a variable number of particles. To the best of our knowledge, the general ρ-MCTDH method has not been formulated using second quantization in the literature. Moreover, the global variational principle employed in the Ψ-MCTDH method (the action integral point of view) is *not* applicable for dissipative systems, since $\mathscr{D}(\rho)$ is not self-adjoint. The second-quantization techniques used here are therefore somewhat different from the one usually taken in the pure-state approach. As the particular properties of the equations of motion for the present problem are more easily exposed in a thorough investigation, we choose to do a detailed derivation.

We repeat the Lindblad equation (15) for convenience:

$$\frac{d}{dt}\rho = \mathscr{L}(\rho) = -i[H,\rho] + \mathscr{D}(\rho) = -i[H,\rho] - \{\Gamma,\rho\} + 2\int \Gamma(x)\boldsymbol{\psi}(x)\rho\boldsymbol{\psi}(x)^\dagger dx. \tag{17}$$

Here, $\rho \in \mathrm{TC}(\mathscr{H})$ is a Fock-space density operator, which (in the exact equation) is block diagonal. $\boldsymbol{\psi}(x)$ destroys a particle at the configuration-space point $x \in X$. Typically $X = \mathbb{R}^3 \times \{\uparrow, \downarrow\}$ for a spin-1/2 fermion, i.e., $x = (\vec{r},m)$, although our derivations are completely independent of X.

For all $t \geqslant 0$, $\rho(t)$ is approximated by an element in the manifold $\mathscr{M} \subset \mathrm{TC}(\mathscr{H})$, with the inner product $\langle\langle\cdot,\cdot\rangle\rangle$ inherited from $\mathrm{TC}(\mathscr{M})$. (Strictly speaking, the inner product is inherited from the Hilbert space of Hilbert-Schmidt operators, in which $\mathrm{TC}(\mathscr{H})$ is dense. Not all Hilbert-Schmidt operators are trace class.) An approximate variational differential equation on $\mathscr{M}$ is sought. The time-dependent variational principle [2,12,13] chooses the time derivative $\dot{\rho} = d\rho/dt$ to minimize the local error in the norm induced by $\langle\langle\cdot,\cdot\rangle\rangle$ as follows:

$$\langle\langle\delta\rho, \dot{\rho} - \mathscr{L}(\rho)\rangle\rangle = 0, \quad \forall\delta\rho \in T_\rho\mathscr{M}, \tag{18}$$

where $T_\rho\mathscr{M}$ is the tangent space at ρ, i.e., the space of all possible time derivatives of ρ. Consequently, the right-hand-side $\mathscr{L}(\rho)$ of Eq. (17) is projected orthogonally onto $T_\rho\mathscr{M}$, and we have

$$\dot{\rho} = \operatorname*{argmin}_{\sigma\in T_\rho\mathscr{M}} \|\sigma - \mathscr{L}\rho\|.$$

We choose $\mathscr{M}$ as the so-called "type II" density operator manifold [3,17,26], albeit with a slight generalization as we consider Fock space instead of a fixed number of particles. There is an alternate way of defining a variational manifold, the "type I" manifold, but it does not reduce to the usual MCTDH method in the case of a pure state.

The manifold $\mathscr{M}$ is defined as follows. Given a finite set φ of L single-particle functions (SPFs) $\varphi_j \in \mathscr{H}_1$, $1 \leqslant j \leqslant L$, and their corresponding creation operators $c_j^\dagger$,

$$c_j^\dagger = \int_X \varphi_j(x)\boldsymbol{\psi}(x)^\dagger dx,$$

we consider the subspace $\mathscr{V}_n$ of $\mathscr{H}_n$ spanned by all possible linearly independent n-body functions built using products of $c_j^\dagger$,

$$\Phi_{J[n]} = c_{j_1}^\dagger c_{j_2}^\dagger \cdots c_{j_n}^\dagger \Phi_{\mathrm{vac}}.$$

The notation $J[n]$ means an ordered tuple $(j_1, j_2, \ldots, j_n)$ of n single-particle indices, i.e., $j_1 \leqslant j_2 \leqslant \cdots \leqslant j_n$. For fermions, $\Phi_{J[n]}$ is a Slater determinant and $j_1 < j_2 < \cdots < j_n$, while for bosons it is a permanent. We then consider the subspace $\mathscr{V}$ of Fock space,

$$\mathscr{V} = \bigoplus_{n=0}^{N} \mathscr{V}_n,$$

spanned by all the Φ_J, where J means an ordered tuple with n indeterminate. As we describe at most N particles, we truncate at $n \leqslant N$ in order to ensure a finite-dimensional space. (For bosons any number of particles may occupy each φ_j, creating an infinite-dimensional space if we do not truncate the sum, even with L finite.)

Each $\rho \in \mathscr{M}$ is now defined as an arbitrary linear operator in $\mathscr{V}$, viz.,

$$\rho = \sum_{JK} |\Phi_J\rangle B_{JK} \langle \Phi_K|, \quad B_{JK} \in \mathbb{C}.$$

We see that ρ is a matrix with respect to a time-dependent orthonormal basis. We denote by $\mathbf{B}$ the matrix formed by the B_{JK}, i.e., the Galerkin matrix. To sum up, ρ is parametrized in terms of an arbitrary matrix $\mathbf{B}$ with respect to the basis generated by an arbitrary set of L SPFs φ.

The set φ may *formally* be extended to a *complete* orthonormal basis $\tilde{\varphi}$ for $\mathscr{H}_1$, a (usually infinite) set of functions $\varphi_s, s > L$, such that the second-quantized Hamiltonian is given by Eq. (4) and the CAP by Eq. (5), but where the expansion coefficients in general depend on the particular value for φ and $\tilde{\varphi}$. This will be of use later on.

B. Parametric redundancy and tangent space

For a given $\rho \in \mathscr{M}$, the parameters φ and B are not unique. Since $\mathscr{V}$ is determined only by the subspace spanned by φ, not the individual φ_j, any unitary change

$$\varphi_j \longrightarrow \sum_k \varphi_k G_{kj}, \quad G = \mathsf{U}(L),$$

where $\mathsf{U}(L)$ is the unitary group of $L \times L$ matrices, yields the same space $\mathscr{V}$, and therefore the same operators ρ can be parametrized. Under the group element G, the basis functions transform as

$$\Phi_{J[n]} \longrightarrow \sum_{k_1} \cdots \sum_{k_n} G_{k_1 j_1} \cdots G_{j_n k_n} \Phi_{K[n]}$$
$$\equiv \sum_{K[N]}{}' \mathscr{G}_{K[n],J[n]} \Phi_{K[n]},$$

where the sum $\sum'_{K[n]}$ is over *all* multi-indices of length n, and not only ordered ones. Defining the transformation of $\mathbf{B}$ by

$$B_{JK} \longrightarrow \sum_{J'K'}{}' \mathscr{G}^*_{J'J} B_{J'K'} \mathscr{G}_{K'K},$$

we see that

$$\rho \longrightarrow \rho.$$

Moreover, B_{JK} are all independent parameters, showing that $\mathsf{U}(L)$ is in fact the *largest* group of transformations leaving ρ invariant.

The nonuniqueness of φ and B implies that given a derivative (tangent vector) $\dot{\rho} \in T_\rho\mathscr{M}$, the derivatives $\dot{\varphi}$ and $\dot{\mathbf{B}}$ are not unique. This phenomenon arises in all MCTDH-type methods, and we give a somewhat more mathematical description than the usual one.

Suppose $\rho(t) \in \mathscr{M}$ is a given smooth path. There exists $\varphi_0(t)$ and $\mathbf{B}_0(t)$ such that $\rho(t) = \rho(\varphi_0(t),\mathbf{B}_0(t))$. By the considerations above, *any* other possible parameter path is of the form $(\varphi(t),\mathbf{B}(t)) = (\varphi_0(t)G(t),\mathscr{G}(t)^\dagger \mathbf{B}_0 \mathscr{G}(t))$, where $\varphi_0(t)G(t)$ stands for the transformation

$$\varphi_{0,j}(t) \longrightarrow \varphi_j(t) = \sum_k \varphi_{0,k}(t) G_{kj}(t).$$

(We consider φ a "matrix" whose columns are φ_j.) All derivatives of φ_0 are of the form

$$\dot{\varphi}_0 = \varphi_0 \eta + \chi, \quad \langle \varphi_{0,j} | \chi_k \rangle = 0.$$

The functions χ_j are all independent. Since $GG^\dagger = I_L$, we find that $\dot{G} = gG$, with $-g^\dagger = g \in \mathsf{u}(L)$, the Lie algebra of the Lie group $\mathsf{U}(L)$. The transformed $\varphi = \varphi_0 G$ then has the derivative

$$\dot{\varphi} = \frac{d}{dt}\varphi_0 G = [\varphi_0(\eta + g) + \chi]G,$$

and it is seen that if we choose $g = -\eta$, then φ is in fact unique, since $\dot{G} = \eta G$ uniquely specifies $G(t)$. This is equivalent to the condition

$$\langle \varphi_j | \dot{\varphi}_k \rangle = 0, \quad \forall j, k.$$

This condition is the standard one in all MCTDH-type methods and is described already in one of the founding MCTDH theory publications [1].

In this way, there is a there is a one-to-one map between triples $(\dot{\varphi},\dot{\mathbf{B}},g)$ and $\dot{\rho}$, with $g \in \mathsf{u}(L)$. The element g is then called a *gauge choice*, and the gauge choice induces a unique parametrization $(\varphi(t),\mathbf{B}(t))$ of $\rho(t)$. This kind of differential geometrical structure is called a principal bundle [29] and is familiar in quantum field theory—but it arises in a completely different way!

It is easily verified that

$$\frac{d}{dt}\Phi_J = \frac{d}{dt} c^\dagger_{j_1} \cdots c^\dagger_{j_n} \Phi_{\text{vac}} = D\Phi_J,$$

where D is the operator

$$D \equiv \sum_{j=1}^{L} \dot{c}^\dagger_j c_j$$

and where $\dot{c}^\dagger_j$ is as the operator that creates the single-particle function $\dot{\varphi}_j$. We observe that for *any two* single-particle functions u and v, not necessarily normalized, the relation

$$\{c(u),c^\dagger(v)\}_\pm \equiv c(u)c^\dagger(v) \pm c^\dagger(v)c(u) = \langle u|v\rangle$$

is obtained by expanding each operator in the field creation operators.

We are now ready to consider an arbitrary time derivative of an element $\rho(t) \in \mathscr{M}$:

$$\dot{\rho} = \sum_{J,K} |\dot{\Phi}_J\rangle B_{J,K} \langle \Phi_K| + |\Phi_J\rangle \dot{B}_{J,K} \langle \Phi_K| + |\Phi_J\rangle B_{J,K} \langle \dot{\Phi}_K|$$
$$= D\rho + \rho D^\dagger + \sum_{J,K} |\Phi_J\rangle \dot{B}_{J,K} \langle \Phi_K|. \tag{19}$$

In order to perform the projections in Eq. (18), we must identify all linearly independent tangent vectors, i.e., all independent admissible infinitesimal variations of ρ. This amounts to varying the $B_{J,K}$ independently, and the φ_j independently, but according to a specific choice of gauge. For simplicity, we consider the choice $\langle \varphi_j | \dot{\varphi}_k \rangle = 0$, which generates the simplest equations and is also the most common in MCTDH theory.

From this it follows that the admissible time derivatives of φ_j are arbitrary functions $\vartheta = Q\vartheta$, where

$$Q \equiv I - \sum_k |\varphi_k\rangle\langle\varphi_k|.$$

Moreover,

$$\langle\Phi_J|\dot{\Phi}_K\rangle = \langle\Phi_J|D|\Phi_K\rangle = 0, \quad \forall J,\ K.$$

Now, the independent variations of ρ can be divided into two groups: For each pair J, K, the matrix element $B_{J,K}$ can be changed, giving the tangent vector

$$\delta\rho = |\Phi_J\rangle\langle\Phi_K|. \tag{20}$$

An arbitrary change $\vartheta = Q\vartheta$ in φ_j consistent with the gauge choice gives

$$\delta\rho = c^\dagger(\vartheta)c_j\rho + \rho c_j^\dagger c(\vartheta). \tag{21}$$

Inserting these two expressions into the variational principle yields a complete set of differential equations for $\mathbf{B}$ in the first case and φ in the latter.

C. Equations of motion

We use the notation $\widetilde{\sum}_j$ to indicate a sum over the *complete* set of SPFs. We let $\mathbf{H}$ be the Galerkin matrix of H, i.e.,

$$H_{JK} \equiv \langle\Phi_J|H|\Phi_K\rangle,$$

and analogously define $\mathbf{G}$ to be the Galerkin matrix of Γ. We let $\mathbf{c}_j$ be the Galerkin matrix of c_j, which in fact is independent of φ:

$$(c_j)_{JK} = \langle\Phi_J|c_j|\Phi_K\rangle = \langle\Phi'_J|c'_j|\Phi'_K\rangle. \tag{22}$$

The primed quantities correspond to *any* other choice of SPFs. The independence follows from the (anti-)commutator (3) which only depends on orthonormality.

The Galerkin matrices of H and Γ can be expressed as

$$\mathbf{H} = \sum_{jk} h(\varphi)_{jk}\mathbf{c}_j^\dagger\mathbf{c}_k + \frac{1}{2}\sum_{jklm} u(\varphi)_{jklm}\mathbf{c}_j^\dagger\mathbf{c}_k^\dagger\mathbf{c}_m\mathbf{c}_l, \tag{23}$$

$$\mathbf{G} = \sum_{jk}\Gamma(\varphi)_{jk}\mathbf{c}_j^\dagger\mathbf{c}_k. \tag{24}$$

The expansion coefficients are dependent on φ at time t, but the creation and annihilation matrices are not. The Galerkin matrices are naturally expressed using some fixed, abstract basis due to Eq. (22). Existing methodology for computing matrix-vector and matrix-matrix products can be re-used by referring to this basis.

To derive the equations of motion, we begin by inserting $\delta\rho$ from Eq. (20) into the variational principle (18). For the term $\langle\langle\delta\rho,\dot{\rho}\rangle\rangle$ and the term containing $[H,\rho]$, and for the sandwich term, we obtain, respectively,

$$\left\langle\langle|\Phi_J\rangle\langle\Phi_K|,\sum_{J'K'}\dot{B}_{J'K'}|\Phi_{J'}\rangle\langle\Phi_{K'}| + D\rho + \rho D^\dagger\rangle\right\rangle = \mathrm{tr}\left[|\Phi_K\rangle\langle\Phi_J|\left(\sum_{J'K'}|\Phi_{J'}\rangle\dot{B}_{J'K'}\langle\Phi_{K'}| + D\rho + \rho D^\dagger\right)\right] = \dot{B}_{JK}, \tag{25}$$

$$\langle\langle|\Phi_J\rangle\langle\Phi_K|,-i[H,\rho]\rangle\rangle = -i\,\mathrm{tr}\left[|\Phi_K\rangle\langle\Phi_J|\left(H\sum_{J'K'}|\Phi_{J'}\rangle B_{J'K'}\langle\Phi_{K'}| - \sum_{J'K'}|\Phi_{J'}\rangle B_{J'K'}\langle\Phi_{K'}|H\right)\right] = (-i[\mathbf{H},\mathbf{B}])_{JK}, \tag{26}$$

$$\left\langle\langle|\Phi_J\rangle\langle\Phi_K|,\widetilde{\sum_{jk}}\Gamma_{jk}c_k\rho c_j^\dagger\rangle\right\rangle = \mathrm{tr}\left[|\Phi_K\rangle\langle\Phi_J|\left(\widetilde{\sum_{jk}}\Gamma_{jk}c_k\sum_{J'K'}|\Phi_{J'}\rangle B_{J'K'}\langle\Phi_{K'}|c_j^\dagger\right)\right] = \sum_{jk}\Gamma_{jk}(\mathbf{c}_k\mathbf{B}\mathbf{c}_j^\dagger)_{JK}. \tag{27}$$

In Eq. (25) the terms containing D vanish since $\langle\varphi_j|\dot{\varphi}_k\rangle = \{c_j,\dot{c}_k^\dagger\}_\pm = 0$. A calculation similar to Eq. (26) yields

$$\langle\langle|\Phi_J\rangle\langle\Phi_K|,\{\Gamma,\rho\}\rangle\rangle = (\{\mathbf{G},\mathbf{B}\})_{JK}. \tag{28}$$

Assembling Eqs. (25) through (28), we get the equation of motion for $\mathbf{B}$:

$$\dot{\mathbf{B}} = -i[\mathbf{H},\mathbf{B}] - \{\mathbf{G},\mathbf{B}\} + 2\sum_{jk}\Gamma_{jk}\mathbf{c}_k\mathbf{B}\mathbf{c}_j^\dagger.$$

We now make the observation that $\dot{\mathbf{B}}^\dagger = \dot{\mathbf{B}}$, showing that $\rho^\dagger = \rho$ is preserved during evolution, which we may use when we turn to the projection onto the tangent vector in Eq. (21). Let F be an arbitrary operator, and calculate

$$\begin{aligned}\langle\langle\delta\rho,F\rho + \rho F^\dagger\rangle\rangle &= \mathrm{tr}\{[c(\vartheta)^\dagger c_j\rho + \rho c_j^\dagger c(\vartheta)](F\rho + \rho F^\dagger)\}\\ &= \mathrm{tr}[c(\vartheta)^\dagger c_j\rho F\rho + c(\vartheta)^\dagger c_j\rho^2F^\dagger\\ &\quad + \rho c_j^\dagger c(\vartheta)F\rho + \rho c_j^\dagger c(\vartheta)\rho F^\dagger]\\ &= 2\mathrm{Re}\,\mathrm{tr}[c_j^\dagger c(\vartheta)F\rho^2],\end{aligned}$$

since $c(\vartheta)\rho \equiv 0$, as $c(\vartheta)$ annihilates a function orthogonal to all the φ_j.

Setting $F = D = \sum_k \dot{c}_k^\dagger c_k$ we obtain

$$\begin{aligned}\langle\langle\delta\rho,D\rho + \rho D^\dagger\rangle\rangle &= \sum_k 2\mathrm{Re}\,\mathrm{tr}[c_j^\dagger c(\vartheta)\dot{c}_k^\dagger c_k\rho^2]\\ &= \sum_k 2\mathrm{Re}\langle\vartheta|\dot{\varphi}_k\rangle\mathrm{tr}(c_j^\dagger c_k\rho^2),\end{aligned}$$

and we note in passing that $\langle\langle\delta\rho,|\Phi_J\rangle\dot{B}_{JK}\langle\Phi_K|\rangle\rangle = 0$, again since $c(\vartheta)|\Phi_J\rangle = 0$.

The "sandwich" term in the master equation also gives zero contribution, since

$$\mathrm{tr}[c(\vartheta)^\dagger c_j \rho c_l \rho c_m^\dagger] = \mathrm{tr}[\rho c_m^\dagger c(\vartheta)^\dagger c_j \rho] = 0,$$

since $c(\vartheta) c_m |\Phi_J\rangle = 0$.

In these calculations $\vartheta = Q\vartheta$ is arbitrary. Choosing $-i\vartheta$ instead turns "Re" into "Im," so we may drop taking the real part. Assembling this, we get the equation

$$i \sum_k \langle \vartheta | \dot{\varphi}_k \rangle \mathrm{tr}(c_j^\dagger c_k \rho^2) = \mathrm{tr}[c_j^\dagger c(\vartheta) F \rho^2], \tag{29}$$

with $F = H - i\Gamma$, and the equation must hold for all ϑ and all j.

We now compute the right-hand side of Eq. (29) for arbitrary single-particle and two-particle operators F. Suppose at first

$$F = \widetilde{\sum_{jk}} f_{jk} c_j^\dagger c_k, \quad f_{jk} = \langle \varphi_j | f | \varphi_k \rangle.$$

Upon insertion in Eq. (29), we find

$$\begin{aligned}\mathrm{tr}[c_j^\dagger c(\vartheta) F \rho^2] &= \widetilde{\sum_{kl}} f_{kl} \mathrm{tr}[c_j^\dagger c(\vartheta) c_k^\dagger c_l \rho^2] \\ &= \widetilde{\sum_k} \sum_l \langle \vartheta | \varphi_k \rangle \langle \varphi_k | f | \varphi_l \rangle \mathrm{tr}(c_j^\dagger c_l \rho^2) \\ &= \sum_l \langle \vartheta | f | \varphi_l \rangle \mathrm{tr}(c_j^\dagger c_l \rho^2).\end{aligned}$$

In the last calculation, we used $\widetilde{\sum}_j |\varphi_j\rangle\langle\varphi_j| = I$.

Second, suppose F is a two-particle operator, viz.,

$$F = \frac{1}{2} \widetilde{\sum_{jklm}} f_{jklm} c_j^\dagger c_k^\dagger c_m c_l, \quad f_{jklm} = \langle \varphi_j \varphi_k | f | \varphi_l \varphi_m \rangle,$$

where we assume $f_{jklm} = f_{kjml}$. The inner product is on $\mathscr{H}_1 \otimes \mathscr{H}_1$, i.e., the brackets are not antisymmetrized. Now the right-hand side of Eq. (29) becomes

$$\begin{aligned}&\mathrm{tr}[c_j^\dagger c(\vartheta) F \rho^2] \\ &= \frac{1}{2} \widetilde{\sum_{klmn}} f_{klmn} \mathrm{tr}[c_j^\dagger c(\vartheta) c_k^\dagger c_l^\dagger c_n c_m \rho^2] \\ &= \frac{2}{2} \widetilde{\sum_k} \sum_{lmn} \langle \vartheta | \varphi_k \rangle \langle \varphi_k \varphi_l | f | \varphi_m \varphi_n \rangle \mathrm{tr}(c_j^\dagger c_l^\dagger c_n c_m \rho^2) \\ &= \sum_{lmn} \langle \vartheta \varphi_l | f | \varphi_m \varphi_n \rangle \mathrm{tr}(c_j^\dagger c_l^\dagger c_n c_m \rho^2).\end{aligned}$$

In the first step, we used the symmetry of f_{klmn} and the (anti-)commutator relation for the creation operators, the result being the same regardless of particle statistics.

Three-particle operators, or even higher, are computed in a similar fashion. For a three-body operator,

$$F = \frac{1}{3!} \widetilde{\sum_{jkl}} \widetilde{\sum_{pqr}} f_{jklpqr} c_j^\dagger c_k^\dagger c_l^\dagger c_r c_q c_p,$$

we obtain the right-hand side

$$\mathrm{tr}[c_j^\dagger c(u) F \rho^2] = \frac{1}{2!} \sum_{klpqr} \langle \vartheta \varphi_k \varphi_l | f | \varphi_p \varphi_q \varphi_r \rangle \mathrm{tr}(c_j^\dagger c_k^\dagger c_l^\dagger c_r c_q c_p \rho^2).$$

Generally, the combinatorial factor $n!^{-1}$ in front of the n-body operator becomes $(n-1)!^{-1}$ due to symmetry properties.

The matrix

$$S_{jk} \equiv \mathrm{tr}(c_j^\dagger c_k \rho^2) = \mathrm{tr}(\mathbf{c}_j^\dagger \mathbf{c}_k \mathbf{B}^2) \tag{30}$$

defines the ρ-CAP-MCTDH analog of the *reduced one-body density matrix* entering at the same location in standard Ψ-MCTDH theory. Similarly, the analog of the reduced two-body density matrix is defined by

$$S^{(2)}_{jklm} \equiv \mathrm{tr}(c_j^\dagger c_k^\dagger c_m c_l \rho^2) = \mathrm{tr}(\mathbf{c}_j^\dagger \mathbf{c}_k^\dagger \mathbf{c}_m \mathbf{c}_l \mathbf{B}^2), \tag{31}$$

and so on.

We may now assemble the various one- and two-body contributions to the SPF equation of motion:

$$\begin{aligned} i \sum_k \langle \vartheta | \dot{\varphi}_k \rangle S_{jk} &= \sum_k \langle \vartheta | (h - i\Gamma) | \varphi_k \rangle S_{jk} \\ &\quad + \sum_{klm} \langle \vartheta \varphi_k | u | \varphi_l \varphi_m \rangle \varphi_l S^{(2)}_{jklm},\end{aligned}$$

which holds for *all* $\vartheta = Q\vartheta$. Since $\dot{\varphi}_j = Q\dot{\varphi}_j$, we arrive at the final single-particle equations of motion:

$$\begin{aligned} i \sum_k \dot{\varphi}_k S_{jk} &= Q \sum_k (h - i\Gamma) \varphi_k S_{jk} \\ &\quad + \sum_{klm} Q \langle \cdot\, \varphi_k | u | \varphi_l \varphi_m \rangle \varphi_l S^{(2)}_{jklm} \\ &= Q \sum_k (h - i\Gamma) \varphi_k S_{jk} + \sum_{klm} Q U_{km} \varphi_l S^{(2)}_{jklm},\end{aligned}$$

where

$$\langle \cdot\, \varphi_k | u | \varphi_l \varphi_m \rangle \equiv \int \overline{\varphi_k(y)} u(x,y) \varphi_l(x) \varphi_m(y) dy,$$

and where the mean-field potentials U_{km} are defined by

$$U_{km}(x) \equiv \int \overline{\varphi_k(y)} u(x,y) \varphi_m(y) dy. \tag{32}$$

Assuming $u(x,y)$ to be a local potential, $U_{km}(x)$ is also a local one-body potential.

D. Discussion

Let us sum up the equations of motion for the density operator ρ. The Galerkin matrix elements $B_{J,K}$ evolves according to

$$\dot{\mathbf{B}} = -i[\mathbf{H},\mathbf{B}] - \{\mathbf{G},\mathbf{B}\} + 2 \sum_{jk} \Gamma_{jk} \mathbf{c}_k \mathbf{B} \mathbf{c}_j^\dagger, \tag{33}$$

while the SPFs evolve according to

$$i \sum_k \dot{\varphi}_k S_{jk} = Q \sum_k (h - i\Gamma) \varphi_k S_{jk} + \sum_{klm} Q U_{km} \varphi_l S^{(2)}_{jklm}, \tag{34}$$

where S_{jk}, $S^{(2)}_{jklm}$, and $U_{km}(x)$ are defined in Eqs. (30), (31), and (32), respectively.

Equation (34) is virtually identical to the standard Ψ-MCTDH equation of motion for the SPFs. The only difference lies in the definitions of S and $S^{(2)}$. As for Eq. (33), we see that the main difference lies in the evolution of a *matrix* $\mathbf{B}$ instead of a coefficient vector.

Equation (34) is typically discretized using discrete-variable representation techniques, FFT methods, and finite differences or similar [17], and the single-particle operator $h - i\Gamma$ is then represented correspondingly. Equivalently, the single-particle space $\mathscr{H}_1$ is approximated by the finite-dimensional space dictated by the discretization, inducing a finite-dimensional Fock space to begin with. Note that even though $h - i\Gamma$ is non-Hermitian, orthonormality of φ is conserved during evolution.

Like in standard Ψ-MCTDH methods, the matrix S needs to be inverted to evaluate the SPF differential equation; a well-known issue with MCTDH-type methods. It may happen that S becomes singular for some reason, in which case a regularization approach is needed [17]. In most applications, this happens very rarely; typically at $t = 0$ due to the choice of initial conditions, but experience suggests it does not affect the final results. This is, however, not trivial from a mathematical point of view, and for the sake of definiteness in the present work, we check that S is nonsingular for our numerical experiment in Sec. IV.

Equation (33) should be compared with the original Lindblad equation (12). Also, if $\dot{\varphi} \equiv 0$, we obtain the variational equation of motion in a fixed linear basis, i.e., what is obtained using a full configuration-interaction-type approach. However, the Galerkin matrices defined in Eqs. (23) and (24) have the time-dependent coefficients h_{jk}, u_{jklm}, and Γ_{jk} which must be computed along the flow. This is a nontrivial task in general, and techniques common for Ψ-MCTDH methods can be employed to deal with this in approximate ways [8,17].

Note that $\mathbf{B}$ retains the natural block structure with respect to the number of particles [cf. Eq. (14)]. Equation (33) can be written as

$$\dot{\mathbf{B}}_n = -i[\mathbf{H},\mathbf{B}_n] - \{\mathbf{G},\mathbf{B}_n\} + 2\sum_{jk} \Gamma_{jk}\mathbf{c}_k\mathbf{B}_{n+1}\mathbf{c}_j^\dagger$$

and this is the most memory-economical representation, since the off-diagonal blocks vanish if $\rho(0)$ is a pure state with N particles. In that case, $\mathbf{B}_N$ can furthermore be represented by a vector $\Psi_N \in \mathscr{V}_N$ at all times, and there is no need to propagate the full block. Due to the presence of *all* the blocks in the definition of S and $S^{(2)}$, however, this pure state cannot be evolved with the Ψ-MCTDH method independently of the other blocks.

If the dissipative terms vanish (i.e., if $\Gamma = 0$), and if $\rho(0)$ is a pure state, the evolution is easily seen to be equivalent to a Ψ-MCTDH calculation. In the ρ-MCTDH method, $\mathrm{tr}(\rho)$ is not in general conserved [17], but it is so for closed systems, i.e., when $\mathscr{D}(\rho) \equiv 0$. However, it is easily checked in the present case that, indeed,

$$\frac{d}{dt}\mathrm{tr}(\rho) = \frac{d}{dt}\mathrm{tr}(\mathbf{B}) = 0.$$

Also, energy $\mathrm{tr}(H\rho)$ is exactly conserved if $\mathrm{tr}(\Gamma\rho) = 0$, that is to say, whenever the system does not touch the CAP.

For the actual implementation of the evolution equations, it is useful to employ a generic enumeration scheme for the many-body basis states. In many-body codes, the Galerkin matrices (other than $\mathbf{B}$) are rarely constructed in memory; instead the single- and double-particle integrals are kept in memory and the explicit action of H is computed using Eq. (23), for which the actions of $\mathbf{c}_j$ and $\mathbf{c}_j^\dagger$ are implemented, for example, via mapping techniques as suggested in Ref. [30] or simply using binary integers to represent a fermion state and bitwise manipulations to define the action of $\mathbf{c}_j$, etc., a common technique in many-body nuclear physics calculations [31].

As for choosing initial conditions, we observe that as a generalization of the Ψ-MCTDH method capable of treating particle loss, a pure state $\rho(0) = |\Psi_N\rangle\langle\Psi_N|$ will be the usual choice. In that case, experience from the Ψ-MCTDH method can be applied [17]. Typical choices are single determinants and permanents or stationary states computed by imaginary-time propagation, or combinations thereof as in the numerical experiment below.

IV. NUMERICAL EXPERIMENT

We present a numerical experiment for a model problem consisting of spin-polarized fermions in one spatial dimension. We study a situation where the initial state is a pure state with $N = 3$ particles whose norm gradually decreases due to a CAP. The situation is similar to the study in Ref. [9].

We truncate the domain $\mathbb{R}$ to $[-R, +R]$, where $R = 20$. The single-particle Hamiltonian of our model is

$$h = T + V(x) = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + V(x),$$

where the one-body potential is of Gaussian shape

$$V(x) = -8\exp[-1.25x^2]. \tag{35}$$

Numerically we find that $V(x)$ supports four bound one-body states. We choose a very simple CAP of standard power form:

$$\Gamma(x) = \theta(|x| - R')(|x| - R')^2, \tag{36}$$

where $\theta(x)$ is the Heaviside function. The particles are unaffected by the CAP in the region $[-R', R']$, where we set $R' = 16$. We have verified that in the energy ranges of the calculations, very little reflection or transmission is generated by Γ. Figure 2 shows the Gaussian well and the absorber.

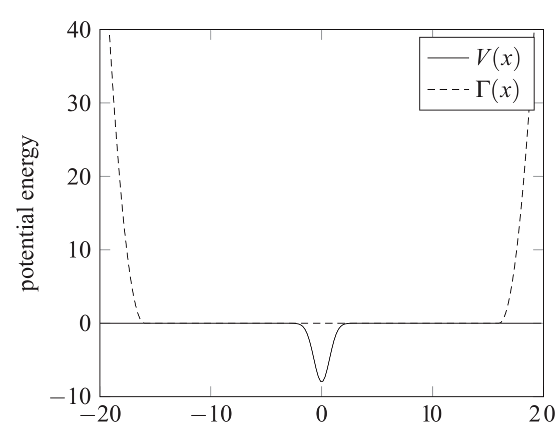

FIG. 2. Single-particle trap potential $V(x)$ and complex absorbing potential $\Gamma(x)$ used in the numerical experiment. The trap potential is Gaussian [see Eq. (35)], and the absorber is quadratic outside $[-16,16]$ [see Eq. (36)].

The particles interact via a smoothed Coulomb potential,

$$u(x_1,x_2) = 2[(x_1 - x_2)^2 + 0.1^2]^{-1/2},$$

which is long ranged.

For discretizing the one-body space, we choose the standard fast-Fourier-transform-based method with $N_{\text{grid}} = 128$ equidistant points with spacing $\Delta x = 2R/N_{\text{grid}}$ [32].

For propagating the master equation, we choose a variational splitting scheme [29,33], propagating the equations of motion with $H' = T$, i.e., kinetic energy only for a time step $\tau/2$, then $H' = H - T$ for a time step τ, and finally $H' = T$ for a time step $\tau/2$ again. This constitutes the propagation of a complete time step τ. While being simple, the scheme has the advantage of having local error $O(\tau^3)$, that the T propagation is numerically exact, and that the time step is not restricted to be $\tau = O(\Delta x^2)$. The potential step is integrated using a standard explicit fourth-order Runge-Kutta method for simplicity, which is sufficient for our purposes.

The initial condition is chosen as follows. Let $\Psi_2(x_1,x_2)$ be the two-body ground state of the CAP-less Hamiltonian. This is computed numerically by propagating the *standard* Ψ-MCTDH equations in imaginary time $t = -is$ using $L = 4$ single-particle states. It follows that this state is also a stationary for the present ρ-CAP-MCTDH method with a CAP as long as the overlap with the CAP is negligible. We have checked that this is indeed the case: Propagating the master equation with the two-body state as the initial condition leads to an absorption probability of 2.7×10^{-10} at $t = t_{\text{final}} = 30$ which can safely be ignored.

We act upon Ψ_2 with a creation operator $c(g)^\dagger$, where $g(x)$ is a Gaussian of the form

$$g(x) = QC \exp[-(x+2)^2/0.75 + i3x],$$

where Q projects away the four SPFs in the initial condition. $g(x)$ describes an incoming particle of momentum $k = 3$ starting out at $x_0 = -2$. The final three-body initial state is then

$$\rho(0) = c^\dagger(g)|\Psi_2\rangle\langle\Psi_2|c(g).$$

The initial φ then consists of the $L = 5$ functions consisting of the four SPFs from the ground-state computation and the single state $g(x)$.

Using this initial condition, we propagate $\rho(t)$ for $t \leqslant t_{\text{final}} = 30$. Figure 3 shows a space-time graph of the particle density $n(x,t)$ given by

$$n(x,t) \equiv \text{tr}[\boldsymbol{\psi}^\dagger(x)\boldsymbol{\psi}(x)\rho(t)].$$

As expected, the plot shows the initial advance of the Gaussian wave packet and its scattering off the well and the two-particle ground state. It is seen that scattering occurs both in the forward and in the backward direction. The scattered probability is absorbed upon entering the region $|x| \geqslant R'$, and a system composed of less than three particles is seen to remain. Superficially, it is an oscillating two-particle system. The system's energy is $E \approx -7.355$.

However, the process is more complex, and by computing the probabilities $p_n(t) = \text{tr}[\rho_n(t)]$ of having n particles in the system we may see what happens in more detail. In Fig. 4, p_n is plotted for each $1 \leqslant n \leqslant 3$. As the scattered probability density is absorbed, the probability of having $n = 3$ particles decreases and the probability of $n = 2$ increases correspondingly. However, especially the absorption of the backscattered wave reveals something interesting: the probability of having $n = 1$ particle in the system clearly becomes significant in this process: the bound two-particle system has a significant probability of being ionized by the collision, leaving a single particle. By inspecting the probability density $n_1(x,t) = \text{tr}[\boldsymbol{\psi}^\dagger(x)\boldsymbol{\psi}(x)\rho_1(t)]$ we verify that it corresponds to a bound one-body state superimposed on the two-body state. The probability $p_0 \approx 3.43 \times 10^{-4}$ at $t = t_{\text{final}}$, showing a very small probability of all particles vanishing. It is therefore not plotted.

Although the initial bound two-particle state had negligible overlap with the CAP, there may still be errors introduced

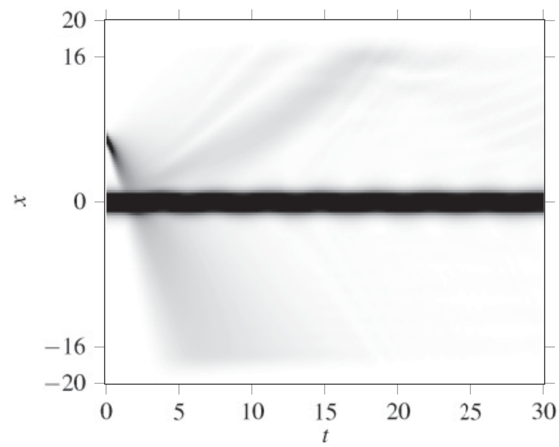

FIG. 3. Space-time graph of square root $\sqrt{n(x,t)}$ of particle density in the numerical experiment. Darker areas have higher density. The square root enhances contrast, but exaggerates low densities. From the plot, we can see that a single-particle function of Gaussian form is scattered off a bound two-particle state in a Gaussian well. The reflected and transmitted parts are absorbed by the CAP, revealing an oscillating trapped function of fewer particles.

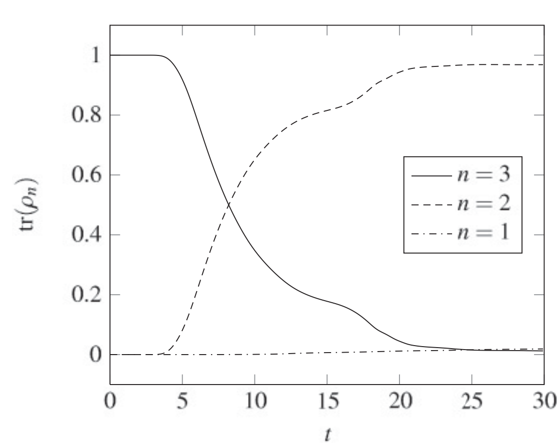

FIG. 4. Plot of the probabilities $p_n = \text{tr}(\rho_n)$ of having n particles in the system as a function of t. The absorption events seen in Fig. 3 are seen to correspond to marked changes in the probabilities. p_0 is too small to merit an interesting plot.

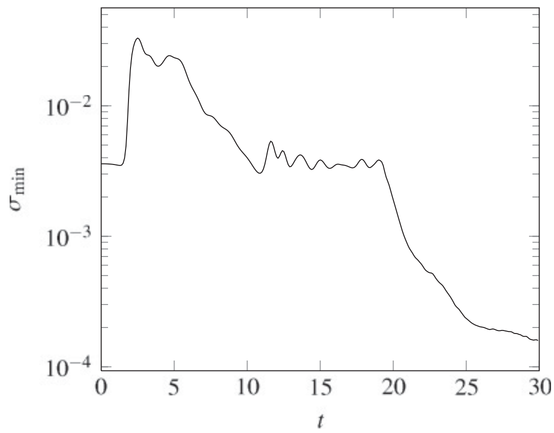

FIG. 5. Smallest eigenvalue of the matrix S which needs to be inverted at each t. As one particle is almost entirely absorbed, the smallest eigenvalue falls off rapidly. It peters out at $\approx 1.57 \times 10^{-4}$, safely away from zero.

by placing the CAP too close to the interacting system. For example, if a particle is absorbed prematurely, the remaining system may miss some correlations. Moreover, there seems to be a finite remaining probability of having three particles in the system. This is most likely due to reflections off or transmissions through the nonideal absorber Γ (which only was chosen for illustrative purposes), and not a bound three-body state. We have not investigated this in detail for the present experiment.

Finally, we address the nonsingularity of the matrix S in Eq. (34). In Fig. 5 the smallest eigenvalue of S is plotted as a function of t. At the very last leg of the evolution, this eigenvalue $\sigma_{\min}$ drops off quickly.

A sharp falloff of $\sigma_{\min}$ is to be expected when a particle is almost entirely absorbed. This may be understood in terms of a noninteracting system. If interactions are not present, the whole system may be described by the SPFs alone, each evolving according to the non-Hermitian Schrödinger equation under the single-particle Hamiltonian $h - i\Gamma$. Thus, the eigenvalues σ_j only change because of the CAP. As a particle is absorbed, one eigenvalue goes to zero.

Usually, small eigenvalues σ_j give very rapidly changing SPFs. However, we have observed that the natural orbital corresponding to $\sigma_{\min}$, which we observe resides in the CAP region and thus represents the absorbed particle, does not change significantly in the last leg of the evolution. This indicates that the SPF no longer becomes relevant for the description in the sense that the right-hand side of Eq. (34) decouples from this SPF. In this way, the near-singularity of S stemming from particle absorption may in fact have no impact at all on the evolution. This may be related to the simple fact that for a pure two-fermion system, the single-particle reduced density matrix is singular whenever L is an odd number. (It is easy to show that the eigenvalues are zero or of multiplicity 2 in the two-fermion case.) We cannot draw any firm conclusions concerning this from our simple experiment, except for pointing out that S becoming singular may have different causes and consequences compared to pure-state MCTDH.

V. MIXTURES OF SPECIES

The ρ-CAP-MCTDH formulation for identical particles is readily generalized to mixtures of arbitrary number of species of particles, such as mixtures of ^{3}He and ^{4}He (fermions and bosons). Using second quantization, the derivation becomes analogous to the treatment in Sec. III and Ref. [27], so we only state the main results here.

Like Ref. [27] we consider two different species of particles A and B for simplicity, as the generalization to the K species follows immediately. Each species has a Fock space $\mathscr{H}^{(i)}$, $i = A, B$. The total Hilbert space is the product space

$$\mathscr{H} = \mathscr{H}^{(A)} \otimes \mathscr{H}^{(B)}.$$

Each species is assigned a set $\varphi^{(i)}$ of single-particle states $\varphi^{(A)}(x)$ and $\varphi^{(B)}(y)$, but they have no *a priori* connection, as the single-particle spaces may be very different. Consequently, the operators $a_j^{(\dagger)}$ (for species A) and $b_k^{(\dagger)}$ (for species B) all commute since the species are distinguishable from each other. As previously, the creation operators are used to construct finite-dimensional Fock spaces $\mathscr{V}^{(i)}$ with determinant or permanent basis functions $\Phi_J^{(i)}$. For the product space, the basis functions are

$$\Phi_{J[n]}^{(A)} \otimes \Phi_{K[m]}^{(B)} = a_{j_1}^\dagger \cdots a_{j_n}^\dagger b_{k_1}^\dagger \cdots b_{k_m}^\dagger \Phi_{\text{vac}}.$$

Note that as the particles are distinguishable, we speak of (n,m)-particle states. Fock space is divided into subspaces with n particles of species A and m particles of species B. The density operator ρ will then be block diagonal with respect to the particle numbers:

$$\rho = \sum_{n=0}^{N_A} \sum_{m=0}^{N_B} \rho_{n,m},$$

where N_i are the maximum number of particles in the system, determined by the initial condition.

Each species has its internal Hamiltonian, but for the equations not to separate into the previously studied case, we need an interaction. A generic two-body interspecies interaction may be written as

$$W = \sum_{i=1}^{n} \sum_{j=1}^{m} w(x_i, y_j) = \sum_{j,l=1}^{L^{(A)}} \sum_{k,m=1}^{L^{(B)}} w_{jklm} a_j^\dagger a_l b_k^\dagger b_m$$

in first and second quantization form, respectively. Here,

$$w_{jklm} = \langle \varphi_j^{(A)} \varphi_k^{(B)} | w(x,y) | \varphi_l^{(A)} \varphi_m^{(B)} \rangle.$$

The usual factor $1/2$ is not present, since the particles are not identical.

Each species also has its own absorber $\Gamma^{(i)}$, which need not have any *a priori* relation.

Working through the equations of motion, noting that each species' SPFs are independent from each other, we obtain the following equation for the Galerkin matrix blocks $\mathbf{B}_{n,m}$:

$$\begin{aligned}\dot{\mathbf{B}}_{n,m} &= -i[\mathbf{H}, \mathbf{B}_{n,m}] - \{\mathbf{G}^{(A)} + \mathbf{G}^{(B)}, \mathbf{B}_{n,m}\} \\ &\quad + 2 \sum_{jk} \Gamma_{jk}^{(A)} \mathbf{a}_k \mathbf{B}_{n+1,m} \mathbf{a}_j^\dagger + 2 \sum_{jk} \Gamma_{jk}^{(B)} \mathbf{b}_k \mathbf{B}_{n,m+1} \mathbf{b}_j^\dagger,\end{aligned}$$

with $\mathbf{H} = \mathbf{H}^{(A)} + \mathbf{H}^{(B)} + \mathbf{W}$ and an otherwise obvious notation.

We obtain an SPF equation of motion for each species. They contain species-specific analogs $S^{(i)}$ of S, and of the mean fields $U^{(i)}$ of U, and also *interspecies* analogs of the reduced two-body density matrix elements $S^{(AB,2)}$ and mean fields due to W, exactly as in the Ψ-MCTDH method [27]. These are defined by

$$S^{(AB,2)}_{jklm} \equiv S^{(BA,2)}_{kjml} \equiv \mathrm{tr}(\rho^2 a_j^\dagger a_l b_k^\dagger b_m),$$
$$W^{(A)}_{km} \equiv \int \overline{\varphi^{(B)}(y)} w(x,y) \varphi^{(B)}(y) dy, \text{and} W^{(B)}_{km}$$

and

$$W^{(B)}_{km} \equiv \int \overline{\varphi^{(A)}(x)} w(x,y) \varphi^{(A)}(x) dx,$$

respectively. We get the SPF equations of motion

$$i \sum_j \dot{\varphi}_j^{(A)} S_{kj}^{(A)} = Q^{(A)} \Bigg[\sum_j (h^{(A)} - i\Gamma^{(A)}) \varphi_j^{(A)} S_{kj}^{(A)} + \sum_{klm} U_{km}^{(A)} \varphi_l^{(A)} S_{jklm}^{(A,2)} + \sum_{klm} W_{km}^{(A)} \varphi_l^{(A)} S_{jklm}^{(AB,2)} \Bigg],$$
$$i \sum_j \dot{\varphi}_j^{(B)} S_{kj}^{(B)} = Q^{(B)} \Bigg[\sum_j (h^{(B)} - i\Gamma^{(B)}) \varphi_j^{(B)} S_{kj}^{(B)} + \sum_{klm} U_{km}^{(B)} \varphi_l^{(B)} S_{jklm}^{(B,2)} + \sum_{klm} W_{km}^{(B)} \varphi_l^{(B)} S_{lmjk}^{(AB,2)} \Bigg].$$

These equations have an obvious symmetry with respect to particle species interchange. These equations are identical to those given in Ref. [27], except for the reduced density matrices being defined in terms of a density operator and not a pure state.

The generalization to K species is straightforward, and we refrain from going into further detail. Note, however, that one interesting special case is obtained when the number of species equals the number of initial particles, so that the initial state is a density operator in the space

$$\mathscr{H} = \mathscr{H}_1^{(1)} \otimes \mathscr{H}_1^{(2)} \otimes \cdots \otimes \mathscr{H}_1^{(K)}.$$

In this case it seen that, as all particles in the system are in fact distinguishable, we have obtained the usual ρ-MCTDH method for distinguishable degrees of freedom, but with a CAP. Of course, the same can be said of the pure-state MCTDH method for mixtures of particles—as we approach $K = N$ species, where N is the number of particles, we are back at the plain MCTDH method for distinguishable particles, and the circle is closed: the MCTDH method for identical particles can be viewed as a MCTDH method with (anti-)symmetry constraints on the coefficients, and the plain MCTDH method can be viewed as an N-species MCTDH method for mixtures.

VI. CONCLUSION

A system of N particles described by a Hamiltonian with a CAP evolves irreversibly in time. In order to describe the remaining particles as some are lost to the absorber, a master equation in Lindblad form in Fock space is needed, as first demonstrated in Ref. [22]. This equation was discussed at length, and a Fock space ρ-MCTDH method, ρ-CAP-MCTDH, was presented that is a strict generalization of a standard pure-state MCTDH evolution for identical particles or mixtures. A numerical experiment on a simple system of $N = 3$ spin-polarized fermions was reported.

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[1] H.-D. Meyer, U. Manthe, and L. Cederbaum, Chem. Phys. Lett. **165**, 73 (1990).
[2] M. H. Beck, A. Jäckle, G. A. Worth, and H. D. Meyer, Phys. Rep. **324**, 1 (2000).
[3] A. Raab and H.-D. Meyer, Theor. Chem. Acc. **104**, 358 (2000).
[4] J. Zanghellini, M. Kitzler, C. Fabian, T. Brabec, and A. Scrinzi, Laser Phys. **13**, 1064 (2003).
[5] O. E. Alon, A. I. Streltsov, and S. Cederbaum, J. Chem. Phys. **127**, 154103 (2007).
[6] O. E. Alon, A. I. Streltsov, and L. S. Cederbaum, Phys. Rev. A **77**, 033613 (2008).
[7] O. Vendrell and H.-D. Meyer, J. Chem. Phys. **134**, 044135 (2011).
[8] J. Caillat, J. Zanghellini, M. Kitzler, O. Koch, W. Kreuzer, and A. Scrinzi, Phys. Rev. A **71**, 012712 (2005).
[9] M. Nest and T. Klamroth, Phys. Rev. A **72**, 012710 (2005).
[10] K. Sakmann, A. I. Streltsov, O. E. Alon, and L. S. Cederbaum, Phys. Rev. Lett. **103**, 220601 (2009).
[11] A. Streltsov, K. Sakmann, O. Alon, and L. Cederbaum, Phys. Rev. A **83**, 043604 (2011).
[12] C. Lubich, Math. Comp. **74**, 765 (2005).
[13] J. Broeckhove, L. Lathouwers, E. Kesteloot, and P. Van Leuven, Chem. Phys. Lett. **149**, 547 (1988).
[14] R. Kosloff and D. Kosloff, J. Comput. Phys. **63**, 363 (1986).
[15] A. Jäckle and H.-D. Meyer, J. Chem. Phys. **105**, 6778 (1996).
[16] J. Muga, J. Palao, B. Navarro, and I. Egusquiza, Phys. Rep. **395**, 357 (2004).
[17] H.-D. Meyer, F. Gatti, and G. A. Worth (Editors), *Multidimensional Quantum Dynamics: MCTDH Theory and Applications* (Wiley, Weinheim, Germany, 2009).
[18] U. Riss and H.-D. Meyer, J. Phys. B **31**, 2279 (1998).

[19] N. Moiseyev, J. Phys. B **31**, 1431 (1998).
[20] A. Nissen, H. Karlsson, and G. Kreiss, J. Chem. Phys. **133**, 054306 (2010).
[21] A. Arnold, VLSI Design **6**, 313 (1998).
[22] S. Selstø and S. Kvaal, J. Phys. B **43**, 065004 (2010).
[23] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).
[24] V. Gorini, A. Kossakowski, and E. Sudarshan, J. Math. Phys. **17**, 821 (1976).
[25] R. Alicki and K. Lendi, *Quantum Dynamical Semigroups and Applications*, Lecture Notes in Physics Vol. 17 (Springer, Heidelberg, Germany, 2007).
[26] A. Raab, I. Burghardt, and H.-D. Meyer, J. Chem. Phys. **111**, 8759 (1999).
[27] O. E. Alon, A. I. Streltsov, and L. S. Cederbaum, Phys. Rev. A **76**, 062501 (2007).
[28] E. Davies, *Quantum Theory of Open Systems* (Academic Press, London, UK, 1976).
[29] C. Lubich, *From Quantum to Classical Molecular Dynamics: Reduced Models and Numerical Analysis* (European Mathematical Society, Zürich, Switzerland, 2008).
[30] A. I. Streltsov, O. E. Alon, and L. S. Cederbaum, Phys. Rev. A **81**, 022124 (2010).
[31] R. Whitehead, A. Watt, B. Cole, and I. Morrison, Adv. Nucl. Phys. **9**, 123 (1977).
[32] H. Tal-Ezer and R. Kosloff, J. Chem. Phys. **81**, 3967 (1984).
[33] C. Lubich, Appl. Numer. Math. **48**, 355 (2004).