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Multiconfigurational expansions of density operators: equations of motion and their properties

A. Raab, H.-D. Meyer

Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, INF 229, 69120 Heidelberg, Germany

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Abstract. Multiconfigurational expansions of density operators which may be used in numerical treatments of the dynamics of closed and open quantum systems are introduced. The expansions of the density operators may be viewed as analogues of those used in the multiconfiguration time-dependent Hartree (MCTDH) method, which is a well-established and highly efficient method for propagating wavepackets in several dimensions. There is no unique multiconfigurational representation of a density operator and two sensible types of MCTDH-like expansions are studied. Equations of motion for these multiconfigurational expansions are presented by adopting the Dirac–Frenkel/McLachlan variational principle (or variants of thereof). Various properties of these sets of equations of motion are derived for closed and open system dynamics. The numerical and technical aspects of this approach have been recently discussed by us [(1999) *J Chem Phys* 111: 8759]. Here we discuss the formal aspects of the approach in a more general context.

Key words: Propagation of density operators – Multiconfiguration time-dependent Hartree method – Quantum dynamics of closed and open systems

1 Introduction

During the last two decades the numerical treatment of the dynamics of molecular quantum systems in the time-dependent picture has become a popular and successful approach. For pure states in closed quantum systems one has to solve the time-dependent Schrödinger equation. The standard method is to use a product basis set or grid representation for the wavefunction and the Hamiltonian and to solve the resulting equation of motion for the expansion coefficients by an appropriate integration scheme [1–3]. This method works well for systems of low dimensionality, but is not feasible for larger systems because the numerical effort grows exponentially with increasing number of degrees of freedom. Further approximations are thus necessary if one wants to investigate the dynamics of larger systems.

A convenient way is to restrict the shape of the wavefunction by a suitable parameterisation or sophisticated expansion rather than by straightforward basis set expansion. A well-known approach motivated by semiclassical ideas is to choose the Gaussian trial form for the wavepacket [4]. If the potential is smooth and large masses and high energies are involved this form is well justified. Using Gaussian wavepackets allows systems with a large number of degrees of freedom to be treated since only a few parameters are involved, but the accuracy of the method is often insufficient. Further approaches which restrict the shape of the wavefunction are the time-dependent Hartree (TDH) [5, 6] and the multiconfiguration TDH (MCTDH) methods [7–10]. In the TDH method an *n*-dimensional wavefunction is represented as the product of *n* one-dimensional time-dependent wavefunctions. The method can be applied to rather large systems but its drawback is the loss of correlation among the various degrees of freedom. The MCTDH method generalises the TDH method by expressing the wavefunction as a sum of Hartree products. The accuracy of the MCTDH method depends on the number of Hartree products included and the (numerically exact) standard method as well as the TDH method are included as limiting cases. The MCTDH method enables the treatment of systems with a comparatively large number of degrees of freedom, typically 8–12. The most impressive examples to date are recent calculations in our group for the pyrazine molecule, for which the motion of all 24 vibrational modes could be treated accurately [11, 12]. Hence, the wavepacket evolves on the S_1 and the S_2 potential-energy surfaces, which are vibronically coupled through a conical intersection, making the dynamics nonseparable and complicated.

Given a parameterised form of the wavefunction, a set of differential equations, known as equations of motion, is derived in the previously mentioned methods by employing the variational principle of Dirac [5] and Frenkel [13]. This variational principle has been reformulated by McLachlan using a stricter argumentation

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Correspondence to: A. Raab

[6]. It ensures that the resulting approximate wavefunction is optimal in a sense we will specify in Sect. 2.

Besides wavefunction propagation, the numerical propagation of density operators has gained increasing interest in recent years [14–25]. In contrast to wavefunctions, density operators are used to describe, for example, closed systems at finite temperature for which the corresponding state is a statistical mixture. The most important advantage of the density operator formalism, however, is the possibility to include the effects of an environment on the system dynamics. In this way one can describe open quantum systems and their non-equilibrium dynamics [26–31].

The numerical treatment of density operators is more difficult than the treatment of wavefunctions since the number of dynamical variables is doubled and hence the effort for time propagation is squared [16]. Standard methods, formulated by analogy with the wavefunction case, can normally be applied to systems with no more than two or three degrees of freedom. The use of parameterised density operators is therefore a promising approach for treating larger systems. As already proposed by McLachlan [6] and discussed in more detail by Heller [4] the Dirac–Frenkel/McLachlan variational principle (DFMVP) can also be formulated for density operators. However, both authors showed for a Hartree type of density operator and closed-system dynamics that the mean value of the energy might not be conserved. While McLachlan therefore rejected the application of the variational principle to Hartree-type density operators, Heller suggested the use of a Lagrangian constraint to remove this unphysical feature.

The aim of this article is to analytically investigate multiconfigurational expansions of density operators and their equations of motion which are based on the DFMVP. Our interest in these equations stems from practical applications of the MCTDH method to the propagation of density operators [25]; however, the results are rather general. In Sect. 2 we briefly review the DFMVP. In Sect. 3 multiconfigurational expansions of the density operator are introduced to which the DFMVP is applied. These expansions are similar to those used in the MCTDH method for wavepackets [7–12]. In the following section we focus on two special types of parameterised density operators. The first type is an expansion in terms of products of one-dimensional Hermitian density operators and the second type is an expansion in terms of ket-bra products of wavefunctions. Both types of MCTDH-like expansions were recently proposed by us and the second one was tested numerically [25]. Here our interest is to investigate more formally the expansions and to provide proofs for their properties. This also sheds light on the problems reported by McLachlan [6] and Heller [4]. In Sects. 5 and 6 we discuss the features of these expansions for closed and open systems. Finally we summarise and discuss our results in Sect. 7.

2 The DFMVP

The variational method due to Dirac [5] and Frenkel [13] has been known for a long time. It was proposed in 1930 for the approximate solution of the time-dependent Schrödinger equation

$$\dot{\Psi} = -iH\Psi \ , \tag{1}$$

where the wavefunction, Ψ, is restricted to take some specific form determined by a set of parameters. Equations of motion for these parameters are derived from the variational principle

$$\langle \delta\Psi | i\dot{\Psi} - H\Psi \rangle = 0 \ , \tag{2}$$

where $\delta\Psi$ denotes possible variations of Ψ with respect to the parameters. Frenkel's original derivation of Eq. (2) was criticised by McLachlan in 1964 [6] because of difficulties in the argumentation. He suggested in his work to alternatively minimise $\| i\dot{\Psi} - H\Psi \|$ and derived from this requirement an equation rather similar to Eq. (2):

$$\mathrm{Re}\, \langle \delta\Psi | i\dot{\Psi} - H\Psi \rangle = 0 \ . \tag{3}$$

Equations (2) and (3) were investigated by several authors [4, 6, 32–34]. It was shown that these equations are equivalent if for each variation, $\delta\Psi$, its complex conjugate is also a possible variation. The most detailed discussion of this point is given in Ref. [34].

In the following we assume that the wavefunction Ψ is parameterised by n complex parameters a_k, $1 \leq k \leq n$. For the sake of convenience we adopt the vector notation $\mathbf{a} = (a_1, a_2, \ldots, a_n)^{\mathrm{T}}$. We assume further that the wavefunctions $\Psi(\mathbf{a})$ form a smooth manifold, M, such that continuous derivatives, $\partial\Psi(\mathbf{a})/\partial a_k$, exist. The derivative of $\Psi(\mathbf{a})$ with respect to time is then given by

$$\dot{\Psi}(\mathbf{a}) = \sum_{k=1}^{n} \frac{\partial\Psi(\mathbf{a})}{\partial a_k} \dot{a}_k \ . \tag{4}$$

To describe possible solutions, $\dot{\Psi}(\mathbf{a})$, it is convenient to introduce tangent spaces [34].

Definition: The tangent space of $\Psi(\mathbf{a})$ on M is given by

$$\mathrm{TM}(\mathbf{a}) = \left\{ \delta\Psi \middle| \delta\Psi = \sum_{k=1}^{n} \frac{\partial\Psi(\mathbf{a})}{\partial a_k} \delta a_k, \quad \delta a_k \in \mathscr{C} \right\} \ . \tag{5}$$

The optimal solution to the Schrödinger equation Eq. (1) is given by the condition

$$\| \dot{\Psi}(\mathbf{a}) + iH\Psi(\mathbf{a}) \| = \min \ , \tag{6}$$

which is equivalent to finding a $\dot{\Psi} \in \mathrm{TM}(\mathbf{a})$ closest to $-iH\Psi(\mathbf{a})$. This, in turn, is equivalent to $\dot{\Psi}(\mathbf{a})$ being the projection of $-iH\Psi(\mathbf{a})$ onto $\mathrm{TM}(\mathbf{a})$.

Theorem 1: (DFMVP) The condition represented by Eq. (6) is equivalent to

$$\langle \delta\Psi | \dot{\Psi}(\mathbf{a}) + iH\Psi(\mathbf{a}) \rangle = 0, \quad \delta\Psi \in \mathrm{TM}(\mathbf{a}) \ . \tag{7}$$

Remarks:

1. The parameters a_k may be generalised from numbers to functions. In this case the partial derivatives above are to be replaced by the Fréchet derivative [35].

2. If the parameters a_k, $1 \le k \le n$, are real one obtains instead of Eq. (7)

   $$\mathrm{Re}\,\langle \delta\Psi|\dot{\Psi}(\mathbf{a}) + iH\Psi(\mathbf{a})\rangle = 0, \quad \delta\Psi \in \mathrm{TM}(\mathbf{a}) \ , \tag{8}$$

   which is the variational principle of McLachlan derived in a different way. This illustrates that the parameterisation determines whether Eq. (7) or Eq. (8) is to be applied, while both variational principles are based on the same optimisation Eq. (6). We will therefore not distinguish between them and refer to the literature for further discussion [33, 34].
3. If the parameterisation is not injective, i.e. if $\mathbf{a} \neq \mathbf{b}$ with $\mathbf{\Psi}(\mathbf{a}) = \mathbf{\Psi}(\mathbf{b})$, then one must introduce suitable constraints in order to remove this ambiguity and to arrive at unique equations of motion.

The DFMVP Eq. (7) leads to a set of differential equations of first order for the coefficients, which are usually called equations of motion. We assume that the equations of motion can be solved uniquely for a given time interval (t_1, t_2) and initial condition $\mathbf{a}(t_1)$. We remark that in practical applications one sometimes has to employ a regularisation procedure to achieve this goal.

3 Application of the variational principle to density operators

In the following we apply the DFMVP to density operators. The evolution in time of a quantum system within the density operator formalism is given by a first-order differential equation

$$\dot{\rho} = \mathscr{L}(\rho) \ , \tag{9}$$

where $\mathscr{L}$ is a linear (super) operator [26, 28]. For closed systems the latter reads (Liouville–von Neumann equation) [26]

$$\mathscr{L}(\rho) = -i[H, \rho] \ , \tag{10}$$

where H is the Hamiltonian of the system. This is the counterpart of the Schrödinger equation Eq. (1) for wavefunctions and leads to a unitary evolution of ρ. For open systems various approaches for $\mathscr{L}$ exist. A prominent one is that of Lindblad and Gorini et al. [29–31]

$$\mathscr{L}(\rho) = -i[H, \rho] + \sum_j \left(V_j \rho V_j^\dagger - \frac{1}{2} V_j^\dagger V_j \rho - \frac{1}{2} \rho V_j^\dagger V_j \right) , \tag{11}$$

which leads to a completely positive semigroup evolution of ρ. We will discuss the dynamics of open systems in more detail in Sect. 6.

From a formal viewpoint we start with a (separable) Hilbert space, $\mathscr{H}$, of wavefunctions. Using the nomenclature of Ref. [36] the density operator ρ is a positive trace-class operator with $\mathrm{Tr}\{\rho\} = 1$ acting on $\mathscr{H}$. We assume that ρ is parameterised and that an optimal solution, $\dot{\rho}$, to Eq. (9) is sought. For the sake of simplicity we omit in the following the individual parameter configuration which determines ρ and $\dot{\rho}$. Unfortunately the set of trace-class operators, $\mathscr{S}_1$, is a Banach space but not a Hilbert space and the DFMVP cannot be applied. However, $\mathscr{S}_1$ is dense in the Hilbert space $\mathscr{S}_2$ of Hilbert–Schmidt operators, which is equipped with the scalar product

$$\langle A|B\rangle = \mathrm{Tr}\{A^\dagger B\}, \quad A, B \in \mathscr{S}_2 \ . \tag{12}$$

This scalar product can be used to formulate the DFMVP for density operators:

$$\langle \delta\rho|\dot{\rho} - \mathscr{L}(\rho)\rangle = \mathrm{Tr}\{\delta\rho^\dagger(\dot{\rho} - \mathscr{L}(\rho))\} = 0 \ . \tag{13}$$

As mentioned in Sect. 1 the variational principle Eq. (13) was introduced by McLachlan for closed systems [6]. Furthermore, Eq. (13) is equivalent to minimising $\|\dot{\rho} - \mathscr{L}(\rho)\|$ in the tangent space which is a closed subspace of $\mathscr{S}_2$ ($\|A\| = \sqrt{\mathrm{Tr}\{A^\dagger A\}}$ for $A \in \mathscr{S}_2$).

As mentioned previously the density operator ρ has some further properties: It is positive and self-adjoint. The question then arises under which conditions the latter property is conserved by the DFMVP. We have seen that the DFMVP Eq. (13) is equivalent to minimising $\|\dot{\rho} - \mathscr{L}(\rho)\|$. Since $\rho = \rho^\dagger$ and $\mathscr{L}(\rho) = \mathscr{L}(\rho)^\dagger$ one may write Eq. (13) as

$$\mathrm{Tr}\{\delta\rho^\dagger[\dot{\rho} - \mathscr{L}(\rho)]\}^* = \mathrm{Tr}\{\delta\rho[\dot{\rho}^\dagger - \mathscr{L}(\rho)]\} = 0 \ . \tag{14}$$

This is equivalent to

$$\|\dot{\rho}^\dagger - \mathscr{L}(\rho)\| = \min, \quad \dot{\rho}^\dagger \in \mathrm{TM}^\dagger = \{x^\dagger | x \in \mathrm{TM}\} \ , \tag{15}$$

where $\mathrm{TM}^\dagger$ is the adjoint tangent space. We now can formulate the condition under which ρ remains Hermitian.

Theorem 2: Let $\dot{\rho}$ denote the solution of the DFMVP. Then $\dot{\rho} = \dot{\rho}^\dagger$ if $\dot{\rho} \in \mathrm{TM}^\dagger$.

Proof: Let $\dot{\rho} \in \mathrm{TM}^\dagger$, which is equivalent to $\dot{\rho}^\dagger \in \mathrm{TM}$. Then

$$\mathrm{Tr}\{\dot{\rho}[\dot{\rho} - \mathscr{L}(\rho)]\} = 0 \ . \tag{16}$$

We now obtain

$$\begin{aligned}
\|\dot{\rho} - \dot{\rho}^\dagger\|^2 &= \mathrm{Tr}\{(\dot{\rho}^\dagger - \dot{\rho})(\dot{\rho} - \dot{\rho}^\dagger)\} \\
&= \mathrm{Tr}\{\dot{\rho}(\dot{\rho}^\dagger - \dot{\rho})\} + \mathrm{Tr}\{\dot{\rho}(\dot{\rho}^\dagger - \dot{\rho})\}^* \\
&= 2\mathrm{Re}[\mathrm{Tr}\{\dot{\rho}(\dot{\rho}^\dagger - \dot{\rho})\}] \\
&= 2\mathrm{Re}[\mathrm{Tr}\{\dot{\rho}(\dot{\rho}^\dagger - \mathscr{L}(\rho))\} \\
&\qquad + \mathrm{Tr}\{\dot{\rho}(\mathscr{L}(\rho) - \dot{\rho})\}] \\
&= 0 \ ,
\end{aligned} \tag{17}$$

since $\dot{\rho} \in \mathrm{TM}$ (always!) and $\dot{\rho} \in \mathrm{TM}^\dagger$ by assumption. The opposite direction is trivial since $\dot{\rho}^\dagger \in \mathrm{TM}^\dagger$.

Theorem 2 shows, on the one hand, that $\dot{\rho} = \dot{\rho}^\dagger$ can always be achieved by an appropriate parameterisation of ρ yielding a large enough tangent space. On the other hand, for a given parameterisation one may prove the conservation of hermiticity of ρ by showing that $\dot{\rho}$ is an element of $\mathrm{TM}^\dagger$.

4 MCTDH-like expansions of density operators and their equations of motion

In this section we apply the DFMVP to particular types of parameterised density operators which play an important role in practical applications [21, 25]. We start with an MCTDH-like expansion

$$\rho = \sum_{\mathscr{T}=1}^{N} B_{\mathscr{T}}(t)\Omega_{\mathscr{T}}(t) \ , \tag{18}$$

where the $B_{\mathscr{T}}(t)$ are expansion coefficients and the $\Omega_{\mathscr{T}}(t)$ are trace-class operators. For the latter we distinguish two types. The first type is a product of f trace-class operators acting on Hilbert spaces, $\mathscr{H}_\kappa$, $1 \le \kappa \le f$,

$$\Omega_{\mathscr{T}}(t) = \sigma^{(1)}_{\tau_1}(t) \cdot \ldots \cdot \sigma^{(f)}_{\tau_f}(t), \quad \mathscr{T} = (\tau_1, \ldots, \tau_f) \ , \tag{19}$$

and the Hilbert space, $\mathscr{H}$, on which the $\Omega_{\mathscr{T}}(t)$ act is given by $\mathscr{H} = \mathscr{H}_1 \otimes \cdots \otimes \mathscr{H}_f$. Here f denotes the number of degrees of freedom. Taking n_κ so-called single-particle density operators (SPDOs) $\sigma^{(\kappa)}_{\tau_\kappa}$ for each degree of freedom, κ, the total number of expansion terms in Eq. (18) becomes $N = n_1 \cdot \ldots \cdot n_f$. The second type of $\Omega_{\mathscr{T}}(t)$ we consider is a ket-bra product of wavefunctions

$$\Omega_{\mathscr{T}}(t) = |\Phi_J(t)\rangle\langle\Phi_L(t)|, \quad \mathscr{T} = (J,\ L) \ . \tag{20}$$

The wavefunctions Φ_J are later taken as Hartree products

$$\Phi_J = \varphi^{(1)}_{j_1} \cdot \varphi^{(2)}_{j_2} \cdot \ldots \cdot \varphi^{(f)}_{j_f} \tag{21}$$

with so-called single-particle functions (SPFs) $\varphi^{(\kappa)}_{j_\kappa}$, $1 \le \kappa \le f$. Taking n_κ SPFs for the κth degree of freedom yields $N = n_1^2 \cdot \ldots \cdot n_f^2$ configurations. However, for the time being we do not need to specify the wavefunctions Φ_J and may consider them as general parameterised multidimensional wavefunctions. We should remark that both types of expansions of ρ (i.e. in SPDOs or SPFs) were recently discussed by us [25] when generalising the MCTDH algorithm from wavepacket propagation to the time evolution of density operators.

To obtain a self-adjoint representation of ρ we assume for the first type of expansion

$$B_{\tau_1,\ldots,\tau_f} = B^*_{\tau_1,\ldots,\tau_f}, \quad \sigma^{(\kappa)}_{\tau_\kappa} = \sigma^{(\kappa)\dagger}_{\tau_\kappa} \ , \tag{22}$$

and for the second type

$$B_{J,L} = B^*_{L,J} \ . \tag{23}$$

We shall denote the first approach to represent ρ [i.e. Eqs. (18), (19), (22)] as density operator of type 1 and the second approach [i.e. Eqs. (18), (20), (23)] as density operator of type 2.

The tangent space for type 1 density operators is given by

$$\delta\rho = \sum_{\mathscr{T}} \delta B_{\mathscr{T}}\Omega_{\mathscr{T}} + \sum_{\kappa=1}^{f}\sum_{\nu=1}^{n_\kappa} \Pi^{(\kappa)}_\nu \delta\sigma^{(\kappa)}_\nu \ , \tag{24}$$

where we have introduced so-called single-hole density operators

$$\Pi^{(\kappa)}_\nu = \sum_{\mathscr{T}_\kappa} B_{\mathscr{T}_\kappa,\nu}\Omega_{\mathscr{T}_\kappa} \ , \tag{25}$$

with

$$\begin{aligned} &\Omega_{\mathscr{T}_\kappa} = \sigma^{(1)}_{\tau_1} \cdot \ldots \cdot \sigma^{(\kappa-1)}_{\tau_{\kappa-1}} \cdot \sigma^{(\kappa+1)}_{\tau_{\kappa+1}} \cdot \ldots \cdot \sigma^{(f)}_{\tau_f}, \\ &(\mathscr{T}_\kappa, \nu) = (\tau_1 \ldots \tau_{\kappa-1}\nu\tau_{\kappa+1} \ldots \tau_f) \ . \end{aligned} \tag{26}$$

We assume that the variations $\delta B_{\mathscr{T}}$ and $\delta\sigma^{(\kappa)}_\nu$ are arbitrary. The parameterisation [Eqs. (18), (19)] is not injective as different coefficients and SPDOs $\sigma^{(\kappa)}_\mu$ may result in the same density operator, ρ. To ensure a unique representation we further introduce the constraints

$$\left\langle \sigma^{(\kappa)}_\mu \middle| \sigma^{(\kappa)}_\nu \right\rangle = \delta_{\mu\nu} \tag{27}$$

$$\left\langle \sigma^{(\kappa)}_\mu \middle| \dot{\sigma}^{(\kappa)}_\nu \right\rangle = 0 \ . \tag{28}$$

More general constraints are discussed in the Appendix and in Ref. [25]. Note that the constraints lift the ambiguity in the representation of $\dot{\rho}$ but do not restrict the variational space. There thus appear no Lagrange parameters. The equations of motion for the coefficients $B_{\mathscr{T}}$ and the SPDOs resulting from the DFMVP are derived in Ref. [25]. They are given by

$$\dot{B}_{\mathscr{T}} = \langle \Omega_{\mathscr{T}} | \mathscr{L}\rho \rangle \tag{29}$$

$$\dot{\boldsymbol{\sigma}}^{(\kappa)} = \left(1 - \mathscr{P}^{(\kappa)}\right)\left(\mathscr{D}^{(\kappa)}\right)^{-1} \langle \mathscr{L} \rangle^{(\kappa)} \boldsymbol{\sigma}^{(\kappa)} \ . \tag{30}$$

We have used here the vector notation

$$\boldsymbol{\sigma}^{(\kappa)} = \left(\sigma^{(\kappa)}_1, \ldots, \sigma^{(\kappa)}_{n_\kappa}\right)^{\mathrm{T}} \ . \tag{31}$$

$\mathscr{P}^{(\kappa)}$ is a projector on the (Hilbert–Schmidt) space spanned by the SPDOs for the κth degree of freedom

$$\mathscr{P}^{(\kappa)} = \sum_{\nu=1}^{n_\kappa} \left| \sigma^{(\kappa)}_\nu \right\rangle \left\langle \sigma^{(\kappa)}_\nu \right| \ , \tag{32}$$

and $\langle \mathscr{L} \rangle^{(\kappa)}$ are mean fields defined as

$$\langle \mathscr{L} \rangle^{(\kappa)}_{\mu\nu} = \left\langle \Pi^{(\kappa)}_\mu \middle| \mathscr{L}\Pi^{(\kappa)}_\nu \right\rangle \ . \tag{33}$$

An important role is played by the coefficients of the squared reduced densities, $\mathrm{Tr}\{\rho^\dagger\rho\}_\kappa$,

$$\mathscr{D}^{(\kappa)}_{\mu\nu} = \left\langle \Pi^{(\kappa)}_\mu \middle| \Pi^{(\kappa)}_\nu \right\rangle \ , \tag{34}$$

where $\mathrm{Tr}\{\cdot\}_\kappa$ denotes the partial trace over all but the κth degree of freedom. If the corresponding matrices, $\mathscr{D}^{(\kappa)}$, are regular the equations of motion of the SPDOs can be solved uniquely, otherwise $\mathscr{D}^{(\kappa)}$ must be regularised [7, 8, 10]. The regularisation does not change (or only marginally changes) $\dot{\rho}$ as it changes the time evolution of only those SPDOs which are unoccupied (or only weakly occupied). The equations of motion [Eqs. (29), (30)] form a system of coupled nonlinear ordinary differential equations of first order. Moreover, the MCTDH density operator converges towards the (numerically) exact density operator with increasing numbers of SPDOs.

Proposition 1: The DFMVP conserves the hermiticity of ρ expanded according to type 1, i.e.

$$\dot{\rho} = \dot{\rho}^\dagger, \quad \dot{B}_{\mathscr{T}} = \dot{B}^*_{\mathscr{T}} \quad \forall\, \mathscr{T} \ , \tag{35}$$

and if $\mathscr{D}^{(\kappa)}$ are regular

$$\dot{\sigma}^{(\kappa)}_\mu = \dot{\sigma}^{(\kappa)\dagger}_\mu \quad \forall\, \mu, \kappa \ . \tag{36}$$

Proof: Since for each variation $\delta B_{\mathscr{T}}$ and $\delta\sigma_\nu^{(\kappa)}$ the complex conjugate $(\delta B_{\mathscr{T}})^*$ and the adjoint $\left(\delta\sigma_\nu^{(\kappa)}\right)^\dagger$ are also possible variations, and since $\Omega_{\mathscr{T}}$ and $\Pi_\nu^{(\kappa)}$ are self-adjoint we obtain $\mathrm{TM} = \mathrm{TM}^\dagger$. From theorem 2 we conclude therefore that $\dot{\rho} = \dot{\rho}^\dagger$. $\dot{\rho}$ is given by

$$\dot{\rho} = \sum_{\mathscr{T}} \dot{B}_{\mathscr{T}} \Omega_{\mathscr{T}} + \sum_{\kappa=1}^{f} \sum_{\nu=1}^{n_\kappa} \Pi_\nu^{(\kappa)} \dot{\sigma}_\nu^{(\kappa)} \ , \tag{37}$$

and using the constraints [Eqs. (27), (28)], $\Omega_{\mathscr{T}} = \Omega_{\mathscr{T}}^\dagger$ and $\dot{\rho} = \dot{\rho}^\dagger$, we obtain

$$\dot{B}_{\mathscr{T}} = \langle \Omega_{\mathscr{T}} | \dot{\rho} \rangle = \mathrm{Tr}\{\Omega_{\mathscr{T}} \dot{\rho}\} = \mathrm{Tr}\{\Omega_{\mathscr{T}} \dot{\rho}\}^* = \dot{B}_{\mathscr{T}}^* \ . \tag{38}$$

To prove the last assertion we define the self-adjoint operator

$$\tilde{\rho} := \dot{\rho} - \sum_{\mathscr{T}} \dot{B}_{\mathscr{T}} \Omega_{\mathscr{T}} = \sum_{\kappa=1}^{f} \sum_{\nu=1}^{n_\kappa} \Pi_\nu^{(\kappa)} \dot{\sigma}_\nu^{(\kappa)} \ . \tag{39}$$

Using again the constraints [Eqs. (27), (28)] we define further

$$a_\mu^{(\kappa)} = \mathrm{Tr}\left\{\Pi_\mu^{(\kappa)} \tilde{\rho}\right\}_\kappa = \sum_\nu \left\langle \Pi_\mu^{(\kappa)} \middle| \Pi_\nu^{(\kappa)} \right\rangle \dot{\sigma}_\nu^{(\kappa)} = \sum_\nu \mathscr{D}_{\mu\nu}^{(\kappa)} \dot{\sigma}_\nu^{(\kappa)} \ . \tag{40}$$

Adopting a vector notation one obtains

$$\dot{\boldsymbol{\sigma}}^{(\kappa)} = \left(\mathscr{D}^{(\kappa)}\right)^{-1} \mathbf{a}^{(\kappa)} \ . \tag{41}$$

Since $a_\mu^{(\kappa)} = a_\mu^{(\kappa)\dagger}$ by construction and since $\mathscr{D}^{(\kappa)}$ are real this proves $\dot{\sigma}_\mu^{(\kappa)} = \dot{\sigma}_\mu^{(\kappa)\dagger}$ for all μ, κ.

We now investigate type 2 density operators, which have been introduced previously. The tangent space is given by

$$\delta\rho = \sum_{J,L} \delta B_{J,L} |\Phi_J\rangle\langle\Phi_L| + B_{J,L}\left(|\delta\Phi_J\rangle\langle\Phi_L| + |\Phi_J\rangle\langle\delta\Phi_L|\right) \ . \tag{42}$$

We assume that for each variation $\delta B_{J,L}$ and $\delta\Phi_J$ the complex conjugate is also a possible variation. As for type 1, we introduce constraints to ensure a unique representation of $\dot{\rho}$:

$$\langle \Phi_J | \Phi_L \rangle = \delta_{JL} \tag{43}$$

$$\langle \Phi_J | \dot{\Phi}_L \rangle = 0 \ . \tag{44}$$

More general constraints are discussed in the Appendix and in Ref. [25].

Proposition 2: For type 2 density operators the DFMVP yields

$$\dot{\rho} = \dot{\rho}^\dagger, \quad \dot{B}_{J,L} = \dot{B}_{L,J}^* \quad \forall J, L \ . \tag{45}$$

Proof: We first investigate the possible variations $\delta\rho$ [c.f. Eq. (42)]. Since each term

$$B_{J,L}(|\delta\Phi_J\rangle\langle\Phi_L| + |\Phi_J\rangle\langle\delta\Phi_L|) + B_{L,J}(|\delta\Phi_L\rangle\langle\Phi_J| + |\Phi_L\rangle\langle\delta\Phi_J|) \tag{46}$$

is self-adjoint and the variations $\delta B_{J,L}$ are arbitrary, we see that $\delta\rho^\dagger \in \mathrm{TM}$ for each $\delta\rho \in \mathrm{TM}$ and therefore $\mathrm{TM} = \mathrm{TM}^\dagger$. Using theorem 2 one obtains $\dot{\rho} = \dot{\rho}^\dagger$. $\dot{\rho}$ is given by

$$\dot{\rho} = \sum_{J,L} \dot{B}_{J,L} |\Phi_J\rangle\langle\Phi_L| + \sum_{J,L} B_{J,L}\left(|\dot{\Phi}_J\rangle\langle\Phi_L| + |\Phi_J\rangle\langle\dot{\Phi}_L|\right) \ . \tag{47}$$

To prove the second assertion we define

$$\tilde{\rho} := \dot{\rho} - \sum_{J,L} B_{J,L}\left(|\dot{\Phi}_J\rangle\langle\Phi_L| + |\Phi_J\rangle\langle\dot{\Phi}_L|\right) = \sum_{J,L} \dot{B}_{J,L} |\Phi_J\rangle\langle\Phi_L| \ . \tag{48}$$

Since each term

$$B_{J,L}\left(|\dot{\Phi}_J\rangle\langle\Phi_L| + |\Phi_J\rangle\langle\dot{\Phi}_L|\right) + B_{L,J}\left(|\dot{\Phi}_L\rangle\langle\Phi_J| + |\Phi_L\rangle\langle\dot{\Phi}_J|\right) \tag{49}$$

is self-adjoint we obtain $\tilde{\rho}^\dagger = \tilde{\rho}$. Using the constraint Eq. (43) yields $\dot{B}_{J,L} = \langle \Phi_J | \tilde{\rho} | \Phi_L \rangle$ and thus

$$\dot{B}_{J,L}^* = \langle \Phi_J | \tilde{\rho} | \Phi_L \rangle^* = \langle \Phi_L | \tilde{\rho} | \Phi_J \rangle = \dot{B}_{L,J} \ . \tag{50}$$

Finally we turn to the MCTDH expansion of ρ in SPFs [c.f. Eq. (21)] introduced previously. The equations of motion of the coefficients $B_{J,L}$ and the SPFs are derived in Ref. [25]. They read

$$\dot{B}_{J,L} = \langle \Phi_J | \mathscr{L}(\rho) | \Phi_L \rangle \tag{51}$$

$$\dot{\boldsymbol{\varphi}}^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \mathrm{Tr}\{\mathscr{L}(\rho)\rho\}_\kappa \left(\mathscr{D}^{(2),(\kappa)}\right)^{-1} \boldsymbol{\varphi}^{(\kappa)} \ . \tag{52}$$

We have introduced here the vector notation

$$\boldsymbol{\varphi}^{(\kappa)} = \left(\varphi_1^{(\kappa)}, \ldots, \varphi_{n_\kappa}^{(\kappa)}\right)^{\mathrm{T}} \ , \tag{53}$$

and $\mathscr{D}^{(2),(\kappa)}$ are given by

$$\mathscr{D}_{jl}^{(2),(\kappa)} = \left\langle \varphi_l^{(\kappa)} \middle| \mathrm{Tr}\{\rho^2\}_\kappa \middle| \varphi_j^{(\kappa)} \right\rangle \tag{54}$$

where the superscript$^{(2)}$ indicates that the density operator, ρ, enters quadratically. $\mathrm{Tr}\{\cdot\}_\kappa$ denotes the partial trace over all but the κth degree of freedom; however, the trace is taken only over the finite dimensional space spanned by $\{\Phi_J\}$. Finally

$$P^{(\kappa)} := \sum_j \left|\varphi_j^{(\kappa)}\right\rangle \left\langle \varphi_j^{(\kappa)}\right| \tag{55}$$

is defined as the projector on the space spanned by the single-particle functions for the κth degree of freedom. We should remark that the above equations of motion again form a system of coupled nonlinear ordinary differential equations of first order.

5 Closed systems

In this section we investigate properties of the DFMVP applied to density operators which represent states of closed systems. The corresponding equation of motion within the density operator formalism is the Liouville–

von Neumann equation [Eqs. (9), (10)]. This equation has the same formal structure as the Schrödinger equation Eq. (1) since with respect to the Hilbert–Schmidt scalar product Eq. (12) $\mathscr{K} = [H, \cdot]$ is a self-adjoint linear operator acting on the Hilbert space of Hilbert–Schmidt operators $\mathscr{S}_2$ [37]. We can therefore transfer the following theorem known for the DFMVP applied to wavefunctions [10] to the present case.

Theorem 3: The equations of motion derived from the DFMVP conserve

$$\|\rho\| = \sqrt{\mathrm{Tr}\{\rho^2\}} \tag{56}$$

if $\rho \in \mathrm{TM}$.

Theorem 3 is valid for all types of density operators as it follows directly from the DFMVP Eq. (13). However, from a physical point of view the question of whether $\mathrm{Tr}\{\rho\}$ and $\mathrm{Tr}\{\rho H\}$ are conserved is more interesting than the property stated by theorem 3. Unfortunately these quantities are usually difficult to investigate for applications of the DFMVP to density operators since they do not occur explicitly in the formalism. We therefore restrict the following discussion to type 2 density operators for which interesting results can be derived.

5.1 Results for type 2 density operators

The DFMVP for closed systems reads

$$\mathrm{Tr}\{\delta\rho^\dagger(i\dot{\rho} - [H, \rho])\} = 0 \ , \tag{57}$$

where $\delta\rho$ is given by Eq. (42). A straightforward calculation of the coefficients yields

$$i\dot{B}_{J,L} = \sum_M \langle\Phi_J|H|\Phi_M\rangle B_{M,L} - B_{J,M}\langle\Phi_M|H|\Phi_L\rangle \ . \tag{58}$$

This equation is also given by Eq. (51) in a more general form and does not depend on the specific parameterisation of the wavefunctions Φ_J. Defining $H_{J,L} := \langle\Phi_J|H|\Phi_L\rangle$ and adopting a matrix notation one can rewrite Eq. (58) as

$$\dot{\mathbf{B}} = -i[\mathbf{H}, \mathbf{B}] \ . \tag{59}$$

Note that $\mathbf{H}$ is time-dependent if the wavefunctions Φ_J are time-dependent.

Proposition 3: If the wavefunctions Φ_J are time-independent for all J then $\mathrm{Tr}\{\rho^n H\}$, $n = 1, 2, 3, \ldots$, is conserved.

Proof:

$$\mathrm{Tr}\{\rho^n H\} = \mathrm{Tr}\{\mathbf{B}^n\mathbf{H}\} \tag{60}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{Tr}\{\rho^n H\} &= -i\sum_{k=1}^{n}\mathrm{Tr}\{\mathbf{B}^{k-1}[\mathbf{H},\mathbf{B}]\mathbf{B}^{n-k}\mathbf{H}\}\\ &= -i\sum_{k=1}^{n}\mathrm{Tr}\{\mathbf{B}^{k-1}\mathbf{H}\mathbf{B}^{n-k+1}\mathbf{H}\}\\ &\quad + i\sum_{k=1}^{n}\mathrm{Tr}\{\mathbf{B}^{k}\mathbf{H}\mathbf{B}^{n-k}\mathbf{H}\}\\ &= -i\mathrm{Tr}\{\mathbf{H}\mathbf{B}^n\mathbf{H}\} + i\mathrm{Tr}\{\mathbf{B}^n\mathbf{H}^2\}\\ &= 0 \ .\end{aligned} \tag{61}$$

The case of time-independent wavefunctions Φ_J yields a usual basis-set expansion of ρ within the fixed basis $\{\Phi_J\}$. For this situation proposition 3 shows in particular that the mean energy, $\langle H\rangle = \mathrm{Tr}\{\rho H\}$, is conserved. In the following, however, we investigate the more interesting case of a time-dependent basis set $\{\Phi_J\}$.

Since the matrix $\mathbf{B}$ is self-adjoint there exists an eigensystem $\{p_M, \mathbf{A}_M\}$ where p_M are the eigenvalues corresponding to the eigenvectors $\mathbf{A}_M$ and

$$p_M = \sum_{J,L} A^*_{J,M} B_{J,L} A_{L,M} \tag{62}$$

$$B_{J,L} = \sum_M A_{J,M} p_M A^*_{L,M} \ . \tag{63}$$

We can rewrite ρ in terms of the eigensystem as

$$\begin{aligned}\rho &= \sum_{J,L} B_{J,L}|\Phi_J\rangle\langle\Phi_L|\\ &= \sum_{J,L,M} A_{J,M}p_M A^*_{L,M}|\Phi_J\rangle\langle\Phi_L|\\ &= \sum_M p_M|\Psi_M\rangle\langle\Psi_M| \ ,\end{aligned} \tag{64}$$

where

$$|\Psi_M\rangle = \sum_J A_{J,M}|\Phi_J\rangle \ . \tag{65}$$

This is an equivalent parameterisation of type 2 density operators.

Proposition 4: If the equations of motion can be solved uniquely for a given time interval $t_1 \le t \le t_2$ then for the eigensystem $\{p_M, \mathbf{A}_M\}$ the DFMVP yields

$$\dot{p}_M = 0, \quad \dot{\mathbf{A}}_M = -i\mathbf{H}\mathbf{A}_M \quad \forall M \ , \tag{66}$$

and for the eigenfunctions

$$\langle\Psi_L|\dot{\Psi}_M + iH\Psi_M\rangle = 0 \quad \forall L, M \ . \tag{67}$$

Proof: To derive an expression for $\mathbf{B}(t)$ we introduce $\mathscr{L}(t) = -i[\mathbf{H}(t), \cdot]$ and the propagator

$$\mathbf{P}(t, t_1) := 1 + \sum_{k=1}^{\infty}\int_{t_1}^{t}\int_{t_1}^{\tau_1}\ldots\int_{t_1}^{\tau_{k-1}}\mathscr{L}(\tau_1)\ldots\mathscr{L}(\tau_k)\mathrm{d}\tau_1\ldots\mathrm{d}\tau_k \ . \tag{68}$$

In this way we obtain $\mathbf{B}(t) = \mathbf{P}(t, t_1)\mathbf{B}(t_1)$ for $t_1 \le t \le t_2$. By introducing the time-ordering operator,

$$T(\mathscr{L}(\tau_1)\mathscr{L}(\tau_2)\ldots\mathscr{L}(\tau_k)) = \mathscr{L}(\tau_{i_1})\mathscr{L}(\tau_{i_2})\ldots\mathscr{L}(\tau_{i_k}), \quad \tau_{i_1} \ge \tau_{i_2} \ge \cdots \ge \tau_{i_k} \ , \tag{69}$$

the propagator can be rewritten in a more convenient form

$$\mathbf{P}(t,t_1) = T\exp\left(\int_{t_1}^{t} \mathscr{L}(\tau)\mathrm{d}\tau\right) \ . \tag{70}$$

This leads to

$$\begin{aligned}\mathbf{B}(t) &= \mathbf{P}(t,t_1)\mathbf{B}(t_1)\\ &= T\exp\left(-i\int_{t_1}^{t}\mathbf{H}(\tau)\mathrm{d}\tau\right)\\ &\qquad \times \mathbf{B}(t_1)T\exp\left(i\int_{t_1}^{t}\mathbf{H}(\tau)\mathrm{d}\tau\right) \ ,\end{aligned} \tag{71}$$

from which Eq. (66) immediately follows. Using Eq. (44) we obtain further

$$\begin{aligned}\langle \mathbf{A}_L|\dot{\mathbf{A}}_M + i\mathbf{H}\mathbf{A}_M\rangle &= \langle \Psi_L|\dot{\Psi}_M + iH\Psi_M\rangle\\ &= 0 \quad \forall L,M \ .\end{aligned} \tag{72}$$

Proposition 4 has some interesting consequences.

Corollary 1: A pure state remains pure.

Corollary 2: $\mathrm{Tr}\{\rho^n\}$, $n = 1,2,3,\ldots$, is conserved.

Proof:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{Tr}\{\rho^n\} = \frac{\mathrm{d}}{\mathrm{d}t}\mathrm{Tr}\{\mathbf{B}^n\} = \frac{\mathrm{d}}{\mathrm{d}t}\sum_M p_M^n = 0 \ . \tag{73}$$

because of the constraints [Eqs. (43), (44)].
For the parameterisation Eq. (64) of ρ we conclude from proposition 4 that

$$\dot{\rho} = \sum_M p_M\big(|\dot{\Psi}_M\rangle\langle\Psi_M| + |\Psi_M\rangle\langle\dot{\Psi}_M|\big) \ . \tag{74}$$

The variations $\delta\rho$ are now given by

$$\delta\rho = \sum_M p_M(|\delta\Psi_M\rangle\langle\Psi_M| + |\Psi_M\rangle\langle\delta\Psi_M|) \ , \tag{75}$$

which will be inserted in the DFMVP Eq. (57) in the following. Since

$$\begin{aligned}i\dot{\rho} - [H,\rho] = \sum_M p_M\big(&|i\dot{\Psi}_M - H\Psi_M\rangle\langle\Psi_M|\\ &+ |\Psi_M\rangle\langle i\dot{\Psi}_M - H\Psi_M|\big)\end{aligned} \tag{76}$$

we obtain

$$\sum_M p_M^2\big(\langle\delta\Psi_M|i\dot{\Psi}_M - H\Psi_M\rangle + \text{c.c.}\big) = 0 \ , \tag{77}$$

where we have used Eq. (67) and c.c. denotes the complex conjugate. This equation leads to

$$\sum_M p_M^2\langle\delta\Psi_M|i\dot{\Psi}_M - H\Psi_M\rangle = 0 \ , \tag{78}$$

since for each variation $\delta\Psi_M$ its complex conjugate is also a possible variation. We thus see that the DFMVP leads to a variational principle for the eigensystem for type 2 density operators. If, on the other hand, we start from this variational principle a straightforward calculation shows that proposition 4 is then also valid. Hence, the above argumentation can also be performed in the opposite direction for type 2 density operators, i.e. starting from Eq. (78) one is led to the DFMVP Eq. (57).

Theorem 4: For type 2 density operators the DFMVP Eq. (57) is equivalent to

$$\sum_M p_M^2\langle\delta\Psi_M|i\dot{\Psi}_M - H\Psi_M\rangle = 0 \quad \text{and} \tag{79}$$

$$\sum_M p_M^2\|i\dot{\Psi}_M - H\Psi_M\|^2 = \min \ . \tag{80}$$

Proof: Equation (79) is treated in the previous discussion. Adopting the vector notation $\mathbf{\Psi} = (p_1\Psi_1, p_2\Psi_2, p_3\Psi_3,\ldots)^{\mathrm{T}}$ Eq. (79) can be rewritten as

$$\langle\delta\mathbf{\Psi}|i\dot{\mathbf{\Psi}} - H\mathbf{\Psi}\rangle = 0 \ . \tag{81}$$

This is the DFMVP for $\mathbf{\Psi} \in \mathscr{H}^M$ where M is the number of wavefunctions Φ_J. Because of theorem 1, Eq. (81) is equivalent to

$$\|i\dot{\mathbf{\Psi}} - H\mathbf{\Psi}\|^2 = \min \tag{82}$$

and one arrives at Eq. (80).

Since Eqs. (79) and (80) can be interpreted as generalised versions of the DFMVP for wavefunctions Eq. (2), one finds

Corollary 3: The DFMVP Eq. (57) applied to type 2 density operators, ρ, is equivalent to the DFMVP for wavefunctions Eq. (2) if ρ is pure.

Corollary 4: For type 2 density operators the DFMVP Eq. (57) conserves $\mathrm{Tr}\{\rho^2H\}$.

Proof: Using Eq. (64) and the nomenclature introduced in the proof of theorem 4 yields

$$\mathrm{Tr}\{\rho^2H\} = \sum_M p_M^2\langle\Psi_M|H|\Psi_M\rangle = \langle\mathbf{\Psi}|H|\mathbf{\Psi}\rangle \ . \tag{83}$$

As proved in Ref. [10] the variational principle [Eqs. (81), (82)] conserves $\langle\mathbf{\Psi}|H|\mathbf{\Psi}\rangle$.

Corollary 4 shows that in general the mean energy $\langle H\rangle$ is conserved if ρ is pure, but that for mixtures the DFMVP may lead to unphysical results. The reason for this is that the DFMVP uses the Hilbert–Schmidt scalar product, which lets the statistical weights enter quadratically. This sheds light on the problems reported by McLachlan [6] and Heller [4]. We will discuss this point further in Sect. 5.2, where we present an alternative approach which conserves $\langle H\rangle$.

5.2 Alternative approach for type 2 density operators

In Sect. 5.1 we showed that the DFMVP Eq. (57) applied to type 2 density operators may lead to a violation of the conservation of the mean energy, $\langle H\rangle$. As mentioned there, the main reason for this behaviour is the formulation of the DFMVP employing the Hilbert–

Schmidt scalar product. Inspired by theorem 4 we now present an alternative approach to generalising the DFMVP for wavefunctions Eq. (2) where the statistical weights, p_M, enter linearly, leading to a conservation of $\langle H \rangle$.

In the following we assume the type 2 representation of ρ [c.f. Eq. (64)] with corresponding constraints. Especially, we assume that $p_M \geq 0$ for all M. Using the nomenclature of Sect. 5.1 we introduce the generalised wavefunction vector $\boldsymbol{\Psi} = (\sqrt{p_1}\Psi_1, \sqrt{p_2}\Psi_2, \ldots)^{\mathrm{T}}$. If we apply the usual DFMVP for wavefunctions Eq. (2) to $\boldsymbol{\Psi}$ we obtain

$$\langle \delta\boldsymbol{\Psi} | i\dot{\boldsymbol{\Psi}} - H\boldsymbol{\Psi} \rangle = 0 \ , \tag{84}$$

which is equivalent to

$$\| i\dot{\boldsymbol{\Psi}} - H\boldsymbol{\Psi} \|^2 = \min \ . \tag{85}$$

This leads to

Proposition 5: The variational principle

$$\sum_M p_M \langle \delta\Psi_M | i\dot{\Psi}_M - H\Psi_M \rangle = 0 \tag{86}$$

is equivalent to

$$\sum_M p_M \| i\dot{\Psi}_M - H\Psi_M \|^2 = \min \ . \tag{87}$$

If ρ is pure this is equivalent to the usual DFMVP for wavefunctions [Eq. (2)].

Proposition 6: The variational principle [Eqs. (86), (87)] conserves $\langle H \rangle = \mathrm{Tr}\{\rho H\}$.

Proof: The proof is similar to the one of corollary 4. Since

$$\mathrm{Tr}\{\rho H\} = \sum_M p_M \langle \Psi_M | H | \Psi_M \rangle = \langle \boldsymbol{\Psi} | H | \boldsymbol{\Psi} \rangle \tag{88}$$

one can conclude from the theorem in Ref. [10] that $\langle \boldsymbol{\Psi} | H | \boldsymbol{\Psi} \rangle$ is conserved.

The above considerations have made use of the eigensystem which has to be determined before the variational principle can be applied. This is prohibitive for practical applications but in the following we derive more convenient and useful equations, avoiding the explicit use of the eigensystem.

The variations of the wavefunctions Ψ_M are given by

$$\delta\Psi_M = \sum_J A_{J,M} |\delta\Phi_J\rangle + \sum_J \delta A_{J,M} |\Phi_M\rangle \tag{89}$$

and

$$\dot{\Psi}_M = \sum_J A_{J,M} |\dot{\Phi}_J\rangle + \sum_J \dot{A}_{J,M} |\Phi_M\rangle \ . \tag{90}$$

We consider now variations of the coefficients $A_{J,M}$ and assume $\delta\Phi_J = 0$ for all J. Inserting in Eq. (86) and taking into account the constraints [Eqs. (43), (44)] leads to

$$\begin{aligned} i \sum_{J,M} & p_M \delta A^*_{J,M} \dot{A}_{J,M} \\ &= \sum_{J,M,L} p_M \delta A^*_{J,M} A_{L,M} \langle \Phi_J | H | \Phi_L \rangle \ . \end{aligned} \tag{91}$$

Since the variations $\delta A_{J,M}$ are arbitrary and $p_M \neq 0$ we obtain $\dot{\mathbf{A}}_M = -i\mathbf{H}\mathbf{A}_M$ for all M.[1] Using

$$B_{J,L} = \sum_M A_{J,M} p_M A^*_{L,M} \tag{92}$$

yields $\dot{\mathbf{B}} = -i[\mathbf{H}, \mathbf{B}]$, i.e. the equations of motion for the coefficients are identical to those obtained from the DFMVP [Eq. (57)]. We should remark at this point that corollaries 1 and 2 of proposition 4 are also valid for this approach. We now consider variations of the wavefunctions Φ_J and assume $\delta A_{J,M} = 0$ for all J, M. Equation (86) then reads

$$\sum_{J,M,L} p_M A^*_{J,M} \langle \delta\Phi_J | iA_{L,M}\dot{\Phi}_L + i\dot{A}_{L,M}\Phi_L - A_{L,M}H\Phi_L \rangle = 0 \ . \tag{93}$$

For the following we will make use of

$$H\rho|\Phi_J\rangle = \sum_L B_{L,J} |H\Phi_L\rangle = \sum_{L,M} p_M A_{L,M} A^*_{J,M} |H\Phi_L\rangle \tag{94}$$

and

$$\begin{aligned} \rho H |\Phi_J\rangle &= \sum_{L,K} B_{L,K} |\Phi_L\rangle\langle\Phi_K|H|\Phi_J\rangle \\ &= \sum_{L,K,M} p_M A_{L,M} A^*_{K,M} |\Phi_L\rangle\langle\Phi_K|H|\Phi_J\rangle \\ &= \sum_{L,M} p_M A_{L,M} \left(\sum_K \langle\Phi_J|H|\Phi_K\rangle A_{K,M} \right)^* |\Phi_L\rangle \\ &= i \sum_{L,M} p_M A_{L,M} \dot{A}^*_{J,M} |\Phi_L\rangle \ . \end{aligned} \tag{95}$$

Furthermore,

$$\begin{aligned} \dot{\rho}|\Phi_J\rangle = \sum_{J,M,L} p_M \Big(& \dot{A}_{L,M} A^*_{J,M} |\Phi_L\rangle + A_{L,M} \dot{A}^*_{J,M} |\Phi_L\rangle \\ & + A_{L,M} A^*_{J,M} |\dot{\Phi}_L\rangle \Big) \end{aligned} \tag{96}$$

is used. These three relations together with Eq. (93) yield

Proposition 7: For type 2 density operators the variational principle [Eqs. (86), (87)] is equivalent to

$$\sum_J \langle \delta\Phi_J | i\dot{\rho} - [H, \rho] | \Phi_J \rangle = 0 \ , \tag{97}$$

$$\dot{\mathbf{B}} = -i[\mathbf{H}, \mathbf{B}] \ . \tag{98}$$

We now apply the variational principle [Eqs. (86), (87)] to the MCTDH expansion of ρ in SPFs [c.f. Eq.(21)] introduced in Sect. 4. The variations of the wavefunctions Φ_J are given by

$$\delta\Phi_J = \sum_{\kappa, J_\kappa, j_\kappa} \Phi_{J_\kappa} \delta\varphi^{(\kappa)}_{j_\kappa} \ , \tag{99}$$

---

[1] The configurations with $p_M = 0$ do not contribute and can therefore be omitted

where

$$\Phi_{J_\kappa} = \varphi_{j_1}^{(1)} \cdot \ldots \cdot \varphi_{j_{\kappa-1}}^{(\kappa-1)} \cdot \varphi_{j_{\kappa+1}}^{(\kappa+1)} \cdot \ldots \cdot \varphi_{j_f}^{(f)} ,$$
$$J_\kappa = (j_1, \ldots, j_{\kappa-1}, j_{\kappa+1}, \ldots, j_f) \ . \tag{100}$$

Inserting in Eq. (97) yields

$$\sum_{\kappa,j} \left\langle \delta\varphi_j^{(\kappa)} \middle| \mathrm{Tr}\{i\dot{\rho} - [H,\rho]\}_\kappa \middle| \varphi_j^{(\kappa)} \right\rangle = 0 \ , \tag{101}$$

where $\mathrm{Tr}\{\cdot\}_\kappa$ denotes the partial trace over all but the κth degree; however, again restricted to the space spanned by $\{\Phi_J\}$. We assume arbitrary variations $\delta\varphi_j^{(\kappa)}$ and since

$$\langle \Phi_J | i\dot{\rho} - [H,\rho] | \Phi_L \rangle = 0 \quad \forall J, L \ , \tag{102}$$

we obtain

$$\mathrm{Tr}\{i\dot{\rho} - [H,\rho]\}_\kappa \varphi_j^{(\kappa)} = 0 \quad \forall j, \kappa \ . \tag{103}$$

The partial traces in these equations lead to mean fields where ρ enters linearly. They are part of the linear mean-field approach proposed by us in Ref. [25]. The derivation of the equations of motion for the SPFs is given in Ref. [25] and the final result is

$$\dot{B}_{J,L} = \langle \Phi_J | \mathscr{L}(\rho) | \Phi_L \rangle \tag{104}$$

$$\dot{\boldsymbol{\varphi}}^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \mathrm{Tr}\{\mathscr{L}(\rho)\}_\kappa \left(\mathscr{D}^{(1),(\kappa)}\right)^{-1} \boldsymbol{\varphi}^{(\kappa)} \ . \tag{105}$$

This set of equations of motion is rather similar to the one derived from the DFMVP [c.f. Eqs. (51), (52)]. The equations of motion for the coefficients are identical and only those for the SPFs differ. The main differences are the mean fields, where ρ now enters linearly. The matrices $\mathscr{D}^{(1),(\kappa)}$ are given by

$$\mathscr{D}_{jl}^{(1),(\kappa)} = \left\langle \varphi_l^{(\kappa)} \middle| \mathrm{Tr}\{\rho\}_\kappa \middle| \varphi_j^{(\kappa)} \right\rangle \ . \tag{106}$$

Finally, we should remark that this approach may be applied only if the statistical weights, p_M, are nonnegative, which is not always fulfilled in practical applications. For example, if one wants to calculate a linear absorption spectrum it is sufficient to propagate a first-order perturbative term, $\Delta\rho$, which is due to the interaction with an electromagnetic field [38]. $\Delta\rho$ is not positive and has in fact a vanishing trace. Of course the actual state of the system is described by a positive density operator $\rho_0 + \Delta\rho$, where ρ_0 denotes the equilibrium state of the system before excitation; however, if $\Delta\rho$ is chosen as the initial condition the linear mean-field approach cannot sensibly be applied.

Furthermore, our approach can easily be generalised by choosing the wavefunction as $\Psi = (p_1^\alpha \Psi_1, p_2^\alpha \Psi_2, \ldots)^{\mathrm{T}}$, $\alpha > 0$, and applying the DFMVP for wavefunctions Eq. (2), analogously to the above line of argument. For $\alpha = 1$ this leads to the variational principle [Eqs. (79), (80)], and for $\alpha = 1/2$ to the variational principle [Eqs. (86), (87)]. One can conclude that $\mathrm{Tr}\{\rho^{2\alpha} H\}$ is conserved by this approach and that the usual variational principle for wavefunctions is obtained if the state is pure. However, we consider the cases $\alpha = 1/2$ and $\alpha = 1$ to be the most relevant ones.

6 Open systems

Large quantum systems are often divided into a small subsystem and an environment. From a physical point of view this is sensible if the subsystem interacts only weakly with the environment and if one is interested only in the dynamics of the former. In principle the subsystems dynamics is contained in the dynamics of the large system. If ρ is the density operator of the whole system the state of the subsystem, ρ_s, is given by taking the partial trace of ρ over the degrees of freedom of the environment, $\rho_s = \mathrm{Tr_e}\{\rho\}$. The time evolution of ρ is given by the Liouville–von Neumann equation, which means that the whole system is closed. From the Liouville–von Neumann equation one can derive an equation of motion for ρ_s, known as a generalised master equation [39–41]. This equation simplifies to a so-called Markovian master equation if the time scales of the subsystem and the environment are well separated, if the correlation time of the latter is negligible and if the environment couples only weakly or is at rather high temperature [26, 28, 41–43]. The time evolution of the subsystem is then influenced by dissipative effects leading to the irreversible dynamics of an open system.

From a formal point of view the irreversible dynamics of an open system should be given by a dynamical semigroup [29]. If one introduces an additional artificial witness system which does not interact with the system, however, this semigroup should not only be positive but also completely positive [29]. This means the following. If ρ_s is the density operator of the open system and ρ_w is that of the witness system $\rho_s \otimes \rho_w$ should be positive for any given dimensionality of the witness system. The requirement of complete positivity formally leads to the equation of motion Eq. (11) mentioned in Sect. 3

$$\dot{\rho}_s = -i[H, \rho_s] + \sum_j \left(V_j \rho_s V_j^\dagger - \frac{1}{2} V_j^\dagger V_j \rho_s - \frac{1}{2} \rho_s V_j^\dagger V_j \right) \ , \tag{107}$$

where the operators V_j, which are not further specified at this point, induce dissipation [29–31]. This equation is very similar to those derived in the Markovian limit, but not all of the latter share its special structure. The different equations of motion for open systems are still being discussed in the literature and from our point of view the question which of these is most appropriate is still open. We will discuss later only the form Eq. (107) but we emphasise that other forms of the dissipative operator may be used within our formalism as well.

Concerning the DFMVP, the investigation of open systems is, in general, more difficult than the investigation of closed ones since each of the various equations of motion has a more complicated structure than the Liouville–von Neumann equation [Eqs. (9), (10)]. The only result we obtained concerns the type of Eq. (107).

Proposition 8: For type 2 density operators Eq. (107) leads to $\mathrm{Tr}\{\dot{\rho}\} \leq 0$.

Proof: Defining the projector

$$P = \sum_J |\Phi_J\rangle\langle\Phi_J| \tag{108}$$

we obtain

$$\begin{aligned}\mathrm{Tr}\{\dot\rho\} = \mathrm{Tr}\{\dot{\mathbf{B}}\} &= \sum_J \langle\Phi_J|\mathscr{L}(\rho)|\Phi_J\rangle = \mathrm{Tr}\{P\mathscr{L}(\rho)\}\\ &= \sum_j \mathrm{Tr}\Big\{PV_j\rho V_j^\dagger - \frac{1}{2}PV_j^\dagger V_j\rho\\ &\quad -\frac{1}{2}P\rho V_j^\dagger V_j\Big\}\\ &= \sum_j \mathrm{Tr}\Big\{V_j^\dagger PV_j\rho\Big\} - \mathrm{Tr}\Big\{V_j^\dagger V_j\rho\Big\}\\ &= -\sum_j \mathrm{Tr}\Big\{(1-P)V_j\rho V_j^\dagger(1-P)\Big\}\\ &\le 0\ ,\end{aligned} \tag{109}$$

since $P\rho = \rho P = \rho$ by construction. The first of the equations follows because of the constraints [Eqs. (43), (44)].

Note that the possible decrease in $\mathrm{Tr}\{\rho\}$ is due to representing ρ within the finite incomplete basis set $\{\Phi_J\}$. The decrease in $\mathrm{Tr}\{\rho\}$ was observed previously in a numerical application [21].

7 Summary and conclusion

We introduced MCTDH-like expansions of density operators which may be used in numerical treatments of the dynamics of closed and open quantum systems [25]. We investigated their equations of motion which are based on the DFMVP. Starting first with an arbitrary parameterised form of the density operator, ρ, we investigated the application of the DFMVP in Sect. 3. We derived there a rather general criterion under which conditions the equations of motion conserve the hermiticity of ρ. It shows that an inappropriate parameterisation of ρ may lead to unphysical results.

We then introduced in Sect. 4 two MCTDH-like types of parameterised density operators, referred to as type 1 and 2. The latter type has recently been investigated by us numerically [25]. The first type is an expansion in terms of products of one-dimensional density operators. The second type is an expansion in terms of ket-bra products of wavefunctions which may be parameterised in an arbitrary way. However, special attention was given to the form of the Hartree products of one-dimensional wavefunctions as it is used in the MCTDH algorithm for wavefunctions [7–12]. For both types we showed that the hermiticity of ρ is conserved by the equations of motion. Further details can be found in Ref. [25], where we also discuss the numerical performance.

In Sect. 5 we investigated the implications of the DFMVP for closed systems and, in particular, obtained a number of interesting results for type 2 density operators. One of the main results for closed systems is that a pure state remains pure and that $\mathrm{Tr}\{\rho\}$ is conserved by the approximate propagation scheme. Both properties are not automatically fulfilled for other types of parameterised density operators, for example, type 1. We showed further that (for closed systems) the DFMVP applied to type 2 density operators is equivalent to a generalised version of the DFMVP for wavefunctions. Motivated by this result we introduced a modified version of this generalisation from which alternative equations of motion for type 2 density operators can be derived. For this second approach a pure state also remains pure and $\mathrm{Tr}\{\rho\}$ is also conserved. The difference between both approaches is that while the former conserves $\mathrm{Tr}\{\rho^2 H\}$ the latter conserves $\mathrm{Tr}\{\rho H\}$. The main reason for this difference is that the DFMVP for density operators makes use of the Hilbert–Schmidt scalar product and ρ enters quadratically. This sheds some light on the problems reported by McLachlan [6] and Heller [4] in applying the variational principle to a similar type of density operators. However, the second approach cannot be used in all practical applications, and a recent numerical study [25] has shown that the convergence properties of the linear mean-field approach are not as good as for the first one.

Finally, we discussed open systems, which, in general, are more difficult to study formally than closed ones. The only result we obtained concerns a Lindblad dissipative operator type leading to a completely positive semigroup evolution of the open system. We showed that for type 2 density operators $\mathrm{Tr}\{\rho\}$ may decrease due to the representation of ρ within a finite incomplete basis set. This effect was recently observed in a numerical application [21].

We close this article by making a remark on practical applications. The DFMVP usually yields an approximation $\dot\rho$ which converges to the exact solution if the parameterisation is improved. Any constant of motion which fails to be conserved, such as the mean energy for closed systems, can be used to measure the accuracy of the approximation. In following this strategy one thus obtains an internal error control.

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Appendix: generalised constraints for type 1 and 2 density operators

For type 1 density operators the constraints are given by

$$\left\langle \sigma_\mu^{(\kappa)} \middle| \sigma_\nu^{(\kappa)} \right\rangle = \delta_{\mu\nu} \tag{A1}$$

$$\left\langle \sigma_\mu^{(\kappa)} \middle| \dot\sigma_\nu^{(\kappa)} \right\rangle = 0\ . \tag{A2}$$

Each SPDO $\sigma_\mu^{(\kappa)}$ is an element of the Hilbert space of Hilbert–Schmidt operators, $\mathscr{S}_2^{(\kappa)}$, corresponding to the wavefunction Hilbert space, $\mathscr{H}_\kappa$, introduced in Sect. 4. As mentioned in Sect. 5 operators acting on $\mathscr{S}_2^{(\kappa)}$ can be classified in the same manner as operators acting on $\mathscr{H}_\kappa$. For example, an operator $\mathscr{G}^{(\kappa)} = [g^{(\kappa)}, \cdot]$ is self-adjoint with respect to the Hilbert–Schmidt scalar product if $g^{(\kappa)}$ is a self-adjoint (linear) operator acting on $\mathscr{H}_\kappa$. With the help of such operators one can formulate the generalised constraint

$$\left\langle \sigma_\mu^{(\kappa)} \middle| \dot{\sigma}_\nu^{(\kappa)} \right\rangle = -i \left\langle \sigma_\mu^{(\kappa)} \middle| \mathscr{G}^{(\kappa)} \sigma_\nu^{(\kappa)} \right\rangle \ . \tag{A3}$$

The actual choice of the operators $\mathscr{G}^{(\kappa)}$ is relevant in practical applications and may simplify the numerical treatment but does not affect the accuracy of the representation of the density operator. Defining

$$\tilde{\sigma}_\nu^{(\kappa)} = \dot{\sigma}_\nu^{(\kappa)} + i\mathscr{G}^{(\kappa)}\sigma_\nu^{(\kappa)} \tag{A4}$$

$$\tilde{\rho} = \dot{\rho} + i\mathscr{G}\rho, \quad \mathscr{G} = \sum_{\kappa=1}^{f} \mathscr{G}^{(\kappa)} \ , \tag{A5}$$

one can use

$$\mathrm{Tr}\left\{\delta\rho^\dagger(\dot{\rho} - \mathscr{L}(\rho))\right\} = \mathrm{Tr}\left\{\delta\rho^\dagger(\tilde{\rho} - \tilde{\mathscr{L}}(\rho))\right\} = 0, \quad \tilde{\mathscr{L}} = \mathscr{L} + i\mathscr{G} \ , \tag{A6}$$

to derive equations of motion for the $\tilde{\sigma}_\nu^{(\kappa)}$ in the same manner as for the $\dot{\sigma}_\nu^{(\kappa)}$ if $\mathscr{G}^{(\kappa)} = 0$ for all κ, since

$$\left\langle \sigma_\mu^{(\kappa)} \middle| \tilde{\sigma}_\nu^{(\kappa)} \right\rangle = 0 \ . \tag{A7}$$

The explicit derivation is given in Ref. [25], and the final result is

$$\dot{B}_{\mathscr{T}} = \langle \Omega_{\mathscr{T}} | (\mathscr{L} + i\mathscr{G})\rho \rangle \tag{A8}$$

$$\dot{\boldsymbol{\sigma}}^{(\kappa)} = -i\mathscr{G}^{(\kappa)}\boldsymbol{\sigma}^{(\kappa)} + \left(1 - \mathscr{P}^{(\kappa)}\right)\left(\mathscr{D}^{(\kappa)}\right)^{-1} \langle \mathscr{L} + i\mathscr{G} \rangle^{(\kappa)} \boldsymbol{\sigma}^{(\kappa)} \ . \tag{A9}$$

All quantities occurring in this set of equations are correspondingly defined as in Sect. 4.

For type 2 density operators the constraints are given by

$$\langle \Phi_J | \Phi_L \rangle = \delta_{JL} \tag{A10}$$

$$\langle \Phi_J | \dot{\Phi}_L \rangle = 0 \ . \tag{A11}$$

In the same manner as previously one can formulate the generalised constraint

$$\langle \Phi_J | \dot{\Phi}_L \rangle = -i \langle \Phi_J | G | \Phi_L \rangle \ , \tag{A12}$$

where G is a self-adjoint but otherwise arbitrary operator acting on $\mathscr{H}$. Defining

$$\tilde{\Phi}_L = \dot{\Phi}_L + iG\Phi_L \tag{A13}$$

$$\tilde{\rho} = \dot{\rho} + i\mathscr{G}\rho, \quad \mathscr{G}\rho = [G, \rho] \ , \tag{A14}$$

one can use again Eq. (A6) to derive equations of motion for the $\tilde{\Phi}_L$, taking into account that

$$\langle \Phi_J | \tilde{\Phi}_L \rangle = 0 \quad \forall J, L \ . \tag{A15}$$

Now we especially consider the MCTDH expansion of ρ in SPFs [c.f. Eq. (21)] introduced in Sect. 4. The constraint operator is given by $G = g^{(1)} + g^{(2)} + \cdots + g^{(f)}$, where $g^{(\kappa)}$, $1 \le \kappa \le f$, is a self-adjoint constraint operator acting exclusively on the κth degree of freedom. As previously the actual choice of the constraint operators is relevant in practical applications and may simplify the numerical treatment but does not affect the accuracy of the representation of the density operator. Applying the DFMVP for density operators (Eq. 13) the resulting equations of motion read

$$\dot{B}_{J,L} = \langle \Phi_J | (\mathscr{L} + i\mathscr{G})(\rho) | \Phi_L \rangle \tag{A16}$$

$$\dot{\boldsymbol{\varphi}}^{(\kappa)} = -ig^{(\kappa)}\boldsymbol{\varphi}^{(\kappa)} + \left(1 - P^{(\kappa)}\right)\mathrm{Tr}\{(\mathscr{L} + i\mathscr{G})(\rho)\rho\}_\kappa \times \left(\mathscr{D}^{(2),(\kappa)}\right)^{-1} \boldsymbol{\varphi}^{(\kappa)} \ . \tag{A17}$$

If the linear mean-field approach introduced in Sect. 5.2 is used one obtains instead of Eq. (A17)

$$\dot{\boldsymbol{\varphi}}^{(\kappa)} = -ig^{(\kappa)}\boldsymbol{\varphi}^{(\kappa)} + \left(1 - P^{(\kappa)}\right)\mathrm{Tr}\{(\mathscr{L} + i\mathscr{G})(\rho)\}_\kappa \times \left(\mathscr{D}^{(1),(\kappa)}\right)^{-1} \boldsymbol{\varphi}^{(\kappa)} \ . \tag{A18}$$

The explicit derivation of the equations of motion and a more detailed discussion are given in [25]. Furthermore, all quantities occurring in this set of equations are correspondingly defined as in Sect. 4.

Finally we want to remark that all results for type 1 and 2 density operators remain valid for these generalised constraints and that the proofs require only minor modifications.

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