Quantum molecular dynamics: Propagating wavepackets and density operators using the Multi-configuration time-dependent Hartree (MCTDH) method

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Abstract

Quantum molecular dynamics describe the time-evolution of a chemical system at the atomic level by directly solving the Schrödinger equation. Time-dependent methods, exemplified by wavepacket propagation, are by now developed to a point where they provide an important insight into the mechanism of many fundamental processes. Of these methods, the most versatile and efficient is probably the multi-configuration time-dependent Hartree (MCTDH) method. The form of the wavefunction used leads to a particularly compact description of the system, and it is possible to run either qualitative, cheap, or accurate, expensive, calculations within the same framework. MCTDH has now shown that it is able to treat systems much larger than other wavepacket propagation methods, and benchmark calculations on systems with up to 24 degrees of freedom have been made. In contrast, standard methods can rarely treat more than 4-6 degrees of freedom. In the following, we review the basic theory of MCTDH. Recent advances are included, such as the development of the method for treating the time-evolution of density operators.

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1 Introduction

Quantum molecular dynamics models the time-evolution of a chemical system by directly solving the Schrödinger equation, and thus aims to provide complete information at an atomic level. For many processes computer simulations using these methods are essential to understand the measurements made. Typical examples are found in molecular beam and femtochemistry experiments, where the fundamental steps of chemical change and reactivity are being probed.

The pictures from classical molecular dynamics simulations are by now well known to chemists. Particularly in the fields of bio- and organic chemistry, these methods have helped to highlight the dynamical nature of molecular interactions. In these simulations, the nuclei are treated as classical particles, and the molecule has a definite nuclear configuration at each point in time. In contrast, the nuclei in quantum molecular dynamics are represented by a wavefunction. The resulting picture is quite different, and the system flows across a potential energy surface, spreading out through configuration space in a complicated way including interference effects. Regions of high density indicate where the system is likely to be. In many simple situations the two pictures lead to a similar result, but in some cases the classical picture will be qualitatively incorrect.

Experimental information about molecular dynamics typically comes from spectra and reaction cross-sections. The former use light to probe what happens after a process is initiated, while the latter give the probability of a system moving from one quantum state to another during a reaction. The early studies typically used a time-independent picture to characterize the molecular dynamics in terms of the states of the system occupied. For example, a spectrum can be analyzed in terms of the eigenvalues of the Hamiltonian, and the calculation of Franck-Condon factors. Time-independent scattering theory is also able to deliver reaction cross-sections.

Time-dependent approaches to quantum molecular dynamics have in recent times become more popular. They add to the understanding of the dynamics and are numerically competitive, if not superior. They are particularly useful for studying scattering or half-scattering (e. g. photodissociation) problems as the complicated scattering boundary conditions do not appear in the time-dependent picture. Time-dependent approaches are also very useful for investigating very dense, not fully resolved spectra, e. g. vibronic spectra of polyatomic molecules when the Born-Oppenheimer potential energy surfaces exhibit a conical intersection. A time-dependent approach is usually not the first choice for accurately computing individual eigen-energies, but with the advent of the filtering method [1–4], the time-dependent approach became competitive even for this problem. Finally, a time dependent approach is unavoidable, when the Hamiltonian itself is time-dependent.

The direct solution of the time-dependent Schrödinger equation leads to wavepacket propagation methods [5–9]. The system is represented in its initial state by a wavepacket, a non-stationary superposition of eigenstates. The time-evolution of this wavepacket is then calculated using powerful numerical methods. Not only can all the required information be extracted from the evolving wavepacket, but it provides a very pictorial description of the process of interest. Unfortunately this standard method suffers from its need of computer resources, which scales exponentially with the number of degrees of freedom in the system. This typically precludes the treatment of systems with more than 4 - 6 degrees of freedom, and forces us to search for approximate methods.

Retaining the conceptual simplicity of wavepacket propagation, but attacking the poor scaling of the standard method leads us to the multiconfiguration time-dependent Hartree (MCTDH) method [10–15]. The power of the method lies in its flexibility and theoretically solid basis. The wavefunction is expanded in a set of time-dependent basis functions. Using a variational principle, equations of motion are obtained for these functions, known as single-particle functions. The basis thus follows the evolving wavepacket, which results in a very compact representation. Importantly, the result converges on the exact result as the basis is increased in size. In the other limit of a single configuration of basis functions is the well-known approximation time-dependent Hartree (TDH), or time-dependent self-consistent field (TDSCF), method [16, 17]. MCTDH is thus able to span a range of accuracies.

The method also provides a good starting point for further approximations. For example, in a recent development, which will not be treated further in this article, it has been suggested that replacing some of the fully flexible single-particle functions of the standard MCTDH method by either Gaussian functions [18] or localized sinc functions [19] may provide a more efficient, but more approximate, way to treat large molecular systems.

The method has been applied successfully to a number of phenomena such as direct photodissociation [11, 20–23], photodissociation off a surface [24–27], photo-absorption [13, 28–30], and pre-dissociation [26, 31, 32]. It has been used to calculate photo-electron [33–35] and resonance Raman spectra [36]. It has also been applied to compute cross-sections of both reactive scattering [37–41] and inelastic molecule-surface scattering [42–47] events. Reactions rates have also been calculated directly using a flux correlation function [48–58]. Other studies include the electron transfer along a conjugated chain [59], and resonant excitation by electron impact [60]. As it is a time-dependent method, including a time-dependent Hamiltonian is a trivial matter. An example of the sort of process that can then be studied is laser-driven proton transfer [61] Finally, combined with filter diagonalization, it has been used to calculate bound-state spectra [62, 63].

In a number of cases the method has been applied to non-adiabatic systems, i.e. those in which radiationless transitions can occur between electronic states due to the breakdown of the Born-Oppenheimer approximation. These are systems in which many degrees of freedom are present, and the potential energy surfaces are strongly anharmonic. Using the vibronic coupling model Hamiltonian [64], the MCTDH method has been able to perform high quality calculations on systems with a set of coupled electronic states and up to 24 degrees of freedom explicitely included [13, 29, 33–35]. In this way we have been able to examine the validity of the reduced dimensionality models used by most researchers in this field. To further demonstrate the applicability of the method to large systems, it should be mentioned that in a recent study MCTDH has been applied to the spin-boson problem including 80 degrees of freedom [65], and to the multi-dimensional Henon-Heiles model, a standard test problem for semi-classical and other approximate methods, including up to 32-dimensions [66].

The evolution of a wavefunction describes the evolution of a particular, well defined initial state. A system at finite temperature, however, is an incoherent mixture of very many thermally excited states. The density operator formalism allows one to correctly describe such 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, thus allowing the description of *open* quantum systems and their non-equilibrium dynamics [67]. The wavefunction formalism is not appropriate for such situations since, even if the system is initially in a pure state, it soon becomes a statistical mixture due to the influence of the environment.

The numerical treatment of density operators is more difficult than the treatment of wavefunctions since the dimensionality of the system formally doubles, squaring the effort for time propagation. The number of systems that can be investigated by numerically exact methods is thus rather restricted since it is normally not possible to treat more than two or three degrees of freedom. The MCTDH scheme has recently been extended to propagate density operators [68–70], and the first applications indicate that the method will be much more efficient than standard approaches [71].

In this article we review the theory of the method, including all the latest developments. Details of the basic theory have been the subject of a recent review [15], and only an overview will be given in Sec. 2. The application of the method to density operators is, however, still new. Named here ρMCTDH to distinguish it from the usual method which applies to wavefunctions, it will be described in some detail in Sec. 3. Other new developments include ways of generating an initial wavepacket for a range of physical processes, and for evaluating the results from a calculation, taking the special form of the MCTDH wavefunction into account. These will be discussed in Secs. 4 and 5. Of particular interest is a method of generating excited state nuclear eigenfunctions using a relaxation (imaginary time propagation) methods in Sec. 4.2.

2 MCTDH for wavefunctions

2.1 The time-dependent picture and the standard method

Our aim is to solve the time-dependent Schrödinger equation

$$i\dot{\Psi} = H\,\Psi \tag{1}$$

(we use a unit system with $\hbar = 1$ throughout) by representing the wavefunction and Hamiltonian with a basis set expansion. The most straightforward way to solve Eq. (1) is to take a one-dimensional time-independent basis set $\{\chi_j^{(\kappa)}\}$ for each degree of freedom κ and expand wavefunction in the direct product basis set, i. e.

$$\Psi(Q_1, \ldots, Q_f, t) = \sum_{j_1=1}^{N_1} \cdots \sum_{j_f=1}^{N_f} C_{j_1 \ldots j_f}(t) \prod_{\kappa=1}^{f} \chi_{j_\kappa}^{(\kappa)}(Q_\kappa)\,, \tag{2}$$

where f specifies the number of degrees of freedom, $Q_1, \ldots, Q_f$ are the nuclear coordinates, $C_{j_1 \ldots j_f}$ denote the time-dependent expansion coefficients, and N_κ denote the number of basis functions used for representing the κ degree of freedom.

The equations of motion for $C_{j_1 \ldots j_f}(t)$ can be derived from the Dirac-Frenkel variational principle [16, 72]

$$\langle \delta\Psi \,|\, H - i\frac{\partial}{\partial t} \,|\, \Psi \rangle = 0\,, \tag{3}$$

leading to

$$i\dot{C}_J = \sum_L H_{JL} C_L\,, \tag{4}$$

where we have established the multi-index $J = j_1 \dots j_f$ (and analogously for L). $H_{JL} = \langle \chi^{(1)}_{j_1} \dots \chi^{(f)}_{j_f} | H | \chi^{(1)}_{l_1} \dots \chi^{(f)}_{l_f} \rangle$ is the matrix representation of the Hamiltonian given in the product basis set.

To allow an efficient and accurate evaluation of the action of the Hamiltonian H on the wavefunction Ψ, one usually replaces the basis functions by a *discrete variable representation* (DVR) [15, 73–75]. If one utilizes the fact that the potential energy is diagonal on a DVR grid and that the kinetic energy part of H can be written in tensor form, the computational effort necessary to evaluate the right hand side of Eq. (4) becomes proportional to fN^{f+1}. Here we have assumed for simplicity that the same number $N = N_1 = \dots = N_f$ of basis functions (or grid points) is employed for each degree of freedom. Similarly, the memory requirement is $3 \times N^f \times 16$ Bytes, as a propagation algorithm requires at least three wavefunctions in central memory (RAM) and a complex word needs 16 Bytes. This scaling behavior, both for effort and memory, generally restricts the standard method to systems with not more than five or six degrees of freedom: for example, if $N = 32$ and $f = 6$ this amounts to 48 GB. If large grids are required, even a 4D calculation can become a difficult task.

2.2 The MCTDH equations of motion

From what is outlined above it is clear that the standard method is not capable of treating large systems. In the MCTDH scheme [10–15], one therefore employs an intermediate, smaller, but now time-dependent basis of so-called *single-particle functions* (SPFs). The *ansatz* for the MCTDH-wavefunction reads

$$\begin{aligned} \Psi(Q_1, \dots, Q_f, t) &= \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}(t) \prod_{\kappa=1}^{f} \varphi^{(\kappa)}_{j_\kappa}(Q_\kappa, t) \\ &= \sum_J A_J \, \Phi_J \end{aligned} \qquad (5)$$

with $n_\kappa < N_\kappa$. Here the configuration, or Hartree-product, Φ_J is a f-dimensional product of SPFs, implicitly defined by Eq. (5). The $A_J \equiv A_{j_1 \dots j_f}$ denote the MCTDH expansion coefficients and the $\varphi^{(\kappa)}_{j_\kappa}$ are the SPFs, which in turn are represented as linear combinations of the primitive basis

$$\varphi^{(\kappa)}_{j_\kappa}(Q_\kappa, t) = \sum_{i_\kappa=1}^{N_\kappa} c^{(\kappa)}_{i_\kappa \, j_\kappa}(t) \, \chi^{(\kappa)}_{i_\kappa}(Q_\kappa) \, . \qquad (6)$$

Since both the coefficients and the SPFs are time-dependent, the wavefunction representation (5) is not unique. Uniquely defined equations of motion can be obtained by imposing additional constraints on the SPFs [11, 12, 14, 15]. Hereby it can be achieved that initially orthonormal SPFs remain orthonormal for all times. The constraints read

$$\begin{aligned} \langle\varphi_j^{(\kappa)}(0)|\varphi_l^{(\kappa)}(0)\rangle &= \delta_{jl} && (7)\\ \langle\varphi_j^{(\kappa)}(t)|\dot{\varphi}_l^{(\kappa)}(t)\rangle &= -i\langle\varphi_j^{(\kappa)}(t)|g^{(\kappa)}|\varphi_l^{(\kappa)}(t)\rangle\ , && (8) \end{aligned}$$

were $g^{(\kappa)}$ denotes a constraint operator. The constraint operators are hermitian but otherwise arbitrary and should be chosen such that the equations of motion are easy to integrate.

In order to write down the equations of motion for the SPFs and coefficients in a concise way, it is necessary to introduce the *single-hole functions*

$$\Psi_l^{(\kappa)} = \langle\varphi_l^{(\kappa)}|\Psi\rangle = \sum_J^{\kappa} A_{J_l^\kappa} \prod_{\kappa'\neq\kappa} \varphi_{j_{\kappa'}}^{(\kappa')}\ , \tag{9}$$

where J_l^κ denotes a composite index J with the κth entry set at l, and $\sum_J^\kappa$ is the sum over the indices for all degrees of freedom excluding the κth. The single-hole functions allow us to write the total wavefunction as

$$\Psi = \sum_l \varphi_l^{(\kappa)} \Psi_l^{(\kappa)} \tag{10}$$

for any degree of freedom κ. This expansion is used when deriving the equations of motion for the SPFs.

Next we define the *mean field*

$$\langle H\rangle_{jl}^{(\kappa)} = \langle\Psi_j^{(\kappa)}\,|\,H\,|\,\Psi_l^{(\kappa)}\rangle \tag{11}$$

and *density* matrices

$$\rho_{jl}^{(\kappa)} = \langle\Psi_j^{(\kappa)}\,|\,\Psi_l^{(\kappa)}\rangle = \sum_J^{\kappa} A^*_{J_j^\kappa} A_{J_l^\kappa}\ . \tag{12}$$

Note that the mean-field matrix elements are operators on the κth degree of freedom. Finally, we define the MCTDH *projector*

$$P^{(\kappa)} = \sum_{j=1}^{n_\kappa} |\,\varphi_j^{(\kappa)}\rangle\langle\varphi_j^{(\kappa)}\,|\ , \tag{13}$$

and split the Hamiltonian into correlated and separable terms

$$H = \sum_{\kappa=1}^{f} h^{(\kappa)} + H_{\mathrm{R}} \; , \tag{14}$$

where $h^{(\kappa)}$ acts only on the κ th degree of freedom and residual part, H_{R}, includes all the correlations between the degrees of freedom.

The MCTDH equations of motion are derived by applying the Dirac-Frenkel variational principle, Eq. (3), to the *ansatz* Eq. (5). After some algebra one obtains [11,12,15]

$$\begin{aligned} i\dot{A}_J &= \sum_L \langle \Phi_J | H_R | \Phi_L \rangle \, A_L + \sum_{\kappa=1}^{f} \sum_{l=1}^{n_\kappa} (h^{(\kappa)}_{j_\kappa l} - g^{(\kappa)}_{j_\kappa l}) \, A_{J^\kappa_l} \; , & (15) \\ i\dot{\boldsymbol{\varphi}}^{(\kappa)} &= g^{(\kappa)} \mathbf{1}_{n_\kappa} \boldsymbol{\varphi}^{(\kappa)} + \left(1 - P^{(\kappa)}\right) \times \\ & \quad \left[\left(\boldsymbol{\rho}^{(\kappa)}\right)^{-1} \langle \mathbf{H}_{\mathrm{R}} \rangle^{(\kappa)} + (h^{(\kappa)} - g^{(\kappa)}) \mathbf{1}_{n_\kappa} \right] \boldsymbol{\varphi}^{(\kappa)} \; , & (16) \end{aligned}$$

where a vector notation has been adopted for the SPFs with

$$\boldsymbol{\varphi}^{(\kappa)} = \left(\varphi^{(\kappa)}_1, \ldots, \varphi^{(\kappa)}_{n_\kappa} \right)^T \; , \tag{17}$$

and where $\mathbf{1}_{n_\kappa}$ denotes the $n_\kappa \times n_\kappa$ unit matrix. $h^{(\kappa)}_{jl}$ and $g^{(\kappa)}_{jl}$ are the matrix elements of $h^{(\kappa)}$ and $g^{(\kappa)}$ with respect to the SPFs.

There are two obvious choices for the constraint operators $g^{(\kappa)}$, namely $g^{(\kappa)} = 0$ and $g^{(\kappa)} = h^{(\kappa)}$. The latter choice yields

$$\begin{aligned} i\dot{A}_J &= \sum_L \langle \Phi_J | H_{\mathrm{R}} | \Phi_L \rangle \, A_L \; , & (18) \\ i\dot{\boldsymbol{\varphi}}^{(\kappa)} &= \left[h^{(\kappa)} \mathbf{1}_{n_\kappa} + \left(1 - P^{(\kappa)}\right) \left(\boldsymbol{\rho}^{(\kappa)}\right)^{-1} \langle \mathbf{H}_{\mathrm{R}} \rangle^{(\kappa)} \right] \boldsymbol{\varphi}^{(\kappa)} \; , & (19) \end{aligned}$$

whereas the first choice yields

$$\begin{aligned} i\dot{A}_J &= \sum_L \langle \Phi_J | H_{\mathrm{R}} | \Phi_L \rangle \, A_L + \sum_{\kappa=1}^{f} \sum_{l=1}^{n_\kappa} h^{(\kappa)}_{j_\kappa l} \, A_{J^\kappa_l} \; , & (20) \\ i\dot{\boldsymbol{\varphi}}^{(\kappa)} &= \left(1 - P^{(\kappa)}\right) \left[h^{(\kappa)} \mathbf{1}_{n_\kappa} + \left(\boldsymbol{\rho}^{(\kappa)}\right)^{-1} \langle \mathbf{H}_{\mathrm{R}} \rangle^{(\kappa)} \right] \boldsymbol{\varphi}^{(\kappa)} \; . & (21) \end{aligned}$$

Finally, dropping the partitioning of the Hamiltonian, Eq. (14), and setting $H_R = H$, one may write the equations of motion for the choice $g^{(\kappa)} = 0$ rather compactly as

$$\begin{aligned} i\dot{A}_J &= \sum_L \langle \Phi_J \,|\, H \,|\, \Phi_L \rangle \, A_L \;, && (22) \\ i\dot{\boldsymbol{\varphi}}^{(\kappa)} &= \left(1 - P^{(\kappa)}\right) \left(\boldsymbol{\rho}^{(\kappa)}\right)^{-1} \langle \mathbf{H} \rangle^{(\kappa)} \boldsymbol{\varphi}^{(\kappa)} \;. && (23) \end{aligned}$$

Comparing Eq. (19) with (21) one notices that the two different choices for the constraints let the MCTDH projector appear at different positions. The MCTDH projector ensures that the part of the propagation of the total wavefunction, which is accomplished by the coefficients, is not re–done when propagating the SPFs.

It is important to understand that the choice of the constraints does not change the quality of the MCTDH expansion Eq. (5). The different wavefunctions obtained by propagating with different constraints are connected by unitary transformations among the SPFs and reverse transformations on the A–coefficients [15]. Other choices of the constraints, besides the two discussed, may be used for special purposes [15].

The MCTDH equations conserve the norm and, for time-independent Hamiltonians, the total energy. This follows directly from the variational principle [15]. MCTDH contains Time-Dependent Hartree (TDH) and the standard method as limiting cases. MCTDH simplifies to TDH when setting all $n_\kappa = 1$. Increasing the n_κ recovers more and more correlation, until finally, for $n_\kappa = N_\kappa$, the standard method is used.

2.3 Density matrices, natural orbitals, and natural populations

Let us define the reduced one-particle density operator in the usual manner as

$$\hat{\rho}^{(\kappa)} = \mathrm{Tr}\{\, |\, \Psi \rangle \langle \Psi \,|\, \}_\kappa \;, \tag{24}$$

where $\mathrm{Tr}\{\,\cdot\,\}_\kappa$ denotes the (partial) trace over all but the κ-th degree of freedom. The MCTDH density matrix is related to this operator through

$$\rho_{jl}^{(\kappa)} = \langle \varphi_l^{(\kappa)} \,|\, \hat{\rho}^{(\kappa)} \,|\, \varphi_j^{(\kappa)} \rangle \;. \tag{25}$$

Note that the indices are interchanged. The MCTDH density matrix is thus the transpose of the usual reduced one-particle density matrix.

Diagonalising the operator $\hat{\rho}^{(\kappa)}$ yields the *natural populations* and *natural orbitals* [10, 11, 76, 77], defined as the eigenvalues and eigenvectors of $\hat{\rho}^{(\kappa)}$. The natural orbitals are, of course, linear combinations of the SPFs. The natural populations characterize the contribution of the related natural orbitals to the representation of the wavefunction. Small natural populations indicate that the MCTDH expansion converges, and this provides an important internal check on the quality of the computed solution. (See e. g. Refs. [11, 20, 22, 27, 31, 37, 42, 43, 76] for examples). For vanishing eigenvalues, the hermitian and positive semi-definite density matrix will become singular. How to solve the resulting numerical problem is discussed e. g. in Refs. [11, 15].

2.4 Non-adiabatic systems, electronic states

The motion of the molecular nuclei may not evolve on a single Born-Oppenheimer potential energy surface, and a multi-state formulation may be necessary. In such an instance one often assumes a diabatic representation, but this is only for numerical convenience and not necessary in principle. The MCTDH algorithm can be applied straightforwardly to systems where more than one electronic state is included. One simply chooses one extra degree of freedom, the κ_eth say, to represent the electronic manifold [21, 78]. The coordinate Q_{κ_e} then labels the electronic states, taking only discrete values $Q_{\kappa_e} = 1, 2, \ldots, \sigma$, where σ is the number of electronic states under consideration. The number of single-particle functions for such an electronic mode is set to the number of states, i.e. $n_{\kappa_e} = \sigma$. The equations of motion (15 – 23) remain unchanged, treating nuclear and electronic modes on the same footing. This is called the *single-set formulation*, since only one set of SPFs is used for all the electronic states.

Because the motion on the included electronic potential energy surfaces can be vastly different, one may think of more efficient ways to include electronic states. The so-called *multi-set formulation* employs different sets of SPFs for each electronic state [24, 28]. In this formulation the wavefunction Ψ and the Hamiltonian H are expanded in the set $\{|\,\alpha\rangle\}$ of electronic states:

$$|\,\Psi\rangle = \sum_{\alpha=1}^{\sigma} \Psi^{(\alpha)}\,|\,\alpha\rangle \tag{26}$$

and

$$H = \sum_{\alpha,\beta=1}^{\sigma} |\,\alpha\rangle H^{(\alpha\beta)}\langle\beta\,|\,, \tag{27}$$

where each state function $\Psi^{(\alpha)}$ is expanded in MCTDH form (5). The derivation of the equations of motion corresponds to the single-set formalism, except that extra state labels have to be introduced on the various quantities such as constraint operators, mean fields and density matrices. For details see Refs. [15, 24, 28]. The computational effort of the single- and multi-set approach is analyzed and compared in Ref. [12].

2.5 Mode combination and numerical scaling

As discussed in Sec. 2.1 the standard method requires the storage of (at least) $3 \times N^f$ complex words. The storage of a single MCTDH wavefunction requires

$$\text{memory} \sim fnN \, + \, n^f \tag{28}$$

complex words, where – for the sake of simplicity – we have again assumed that each degree of freedom requires n SPFs and N grid-points to converge the wavefunction. The first part in the sum, fnN, accounts for the space needed to store the SPFs and the second part, n^f, accounts for the storage of the coefficient vector. To store the wavefunction, its derivative, and all the mean-fields etc, it was found that MCTDH requires a storage which approximately equals that of 12 MCTDH wavefunctions. An example will be illustrative. Let us assume that there are 12 degrees of freedom, and that 6 SPFs and 32 grid-points are needed for each degree of freedom to ensure convergence. Hence $f = 12, n = 6, N = 32$. The standard method would require 5×10^{10} GB, demonstrating that this method is totally inappropriate. MCTDH, on the other hand, would require 390 GB, which is 8 orders of magnitude smaller, but still much too big to fit on todays workstations. If one analyzes the wavefunction storage, one finds that the SPFs take only $fnN = 2304$ words, whereas storage of the coefficient vector requires $n^f = 2.2 \times 10^9$ words. It is thus the exponential growth of the A-vector, which eventually lets MCTDH become infeasible for sufficiently large numbers of degrees of freedom. Fortunately, there is a (partial) solution to this problem: *mode combination.*

The memory requirement of the A-vector can be reduced substantially if single-particle functions are used that describe a set of degrees of freedom, rather than just one. The wavefunction ansatz, Eq. (5), is then rewritten as a multi-configuration over p generalized "particles",

$$\Psi(q_1, \ldots, q_p, t) = \sum_{j_1=1}^{\tilde{n}_1} \cdots \sum_{j_p=1}^{\tilde{n}_p} A_{j_1 \ldots j_p}(t) \prod_{\tilde{\kappa}=1}^{p} \varphi_{j_{\tilde{\kappa}}}^{(\tilde{\kappa})}(q_{\tilde{\kappa}}, t) \, , \tag{29}$$

where $q_{\tilde{\kappa}} = (Q_{\kappa_1}, Q_{\kappa_2}, \ldots, Q_{\kappa_d})$ is the set of coordinates combined together in a single particle, described by $\tilde{n}_{\tilde{\kappa}}$ SPFs. Upon combination the primitive grid increases: $\tilde{N}_{\tilde{\kappa}} = N_{\kappa_1} \times N_{\kappa_2} \times \ldots \times N_{\kappa_d}$. The length of the A–vector, however, shrinks, because $\tilde{n}$ will be smaller than the product of the associated n. This is because the correlation among the combined modes is now already taken care of on the single-particle level. We have found that, as a rule of thumb, one usually need to set $\tilde{n}$ to the sum of the associated n to ensure convergence.

To investigate the memory requirement for combined modes, we assume that always d degrees of freedom are combined. There are hence $p = f/d$ particles, the grid-size increases to $\tilde{N} = N^d$, and the number of combined SPFs increases to $\tilde{n} = dn$. The memory requirement changes to

$$\begin{aligned} \text{memory} &\sim p\tilde{n}\tilde{N} + \tilde{n}^p \\ &\approx fnN^d + n^{f/d} \,. \end{aligned} \tag{30}$$

To illustrate this equation, we return to the example discussed above. With $d = 2$ follows $p = 6$, $\tilde{N} = 1024$, and $\tilde{n} = 12$. The memory requirement for the SPFs increases from 2304 to 73728 words, but the space needed to store one A–vector decreases from 2.2×10^9 to 3×10^6 words. The total memory required decreases dramatically from 390 GB to 560 MB. The first step, standard method to MCTDH, saved us 8 orders of magnitude in memory requirement (RAM), the second step, MCTDH to MCTDH with combined modes, brought us another three orders. Like the standard wavepacket method, MCTDH is plagued with exponential scaling, i. e. its memory requirement grows as b^f with the number of degrees of freedom f. The base b, however, is much smaller in MCTDH, making MCTDH suitable to attack larger problems [13, 29, 33–35, 65, 66]. For the three methods discussed, the base b equals N, n, and $\tilde{n} \approx (dn)^{(1/d)}$ (or 32, 6, and 3.46 in the example), respectively. In one particular case [13] the base was as small as $b = 1.83$.

In a practical situation one is confronted with the question of which modes to combine into a particle. If there are modes which are more strongly coupled to each other than to the rest of the modes, one should combine these strongly coupled modes. As the correlation among these modes is now treated on the single-particle level, rather low numbers $\tilde{n}_{\tilde{\kappa}}$ of multi–mode SPFs suffice for convergence and $\tilde{n}$ may become considerably smaller than dn. Often, however, it is difficult to decide a priory which modes are strongly coupled to each other. In this case one may take a pragmatic view, based on memory considerations, and follow the rules: 1) Combine modes such, that the sizes of the combined grids are roughly equal to each other.

2) The space taken by the SPFs should be similar to but not larger than the space consumed by the A–vector.

2.6 Product representation of the potential

The solution of the MCTDH equations of motion requires the evaluation of the Hamiltonian matrix $\langle \Phi_J \,|\, H_\mathrm{R} \,|\, \Phi_L \rangle$ and the mean fields $\langle \mathbf{H}_\mathrm{R} \rangle$ at each time step of the integration. These are formally f and f-1 dimensional integrals. Doing the integrals by multi-dimensional quadrature over the primitive grid would slow down MCTDH such that it would not be competitive.

The multi-dimensional integrations can be circumvented if the Hamiltonian is written as a sum of products of single-particle operators,

$$H = \sum_{r=1}^{s} c_r \prod_{\kappa=1}^{f} h_r^{(\kappa)} \,, \tag{31}$$

with expansion coefficients c_r. Using Eq. (31) the matrix elements can be expanded as

$$\langle \Phi_J \,|\, H \,|\, \Phi_L \rangle = \sum_{r=1}^{s} c_r \prod_{\kappa=1}^{f} \langle \varphi_{j_\kappa}^{(\kappa)} \,|\, h_r^{(\kappa)} \,|\, \varphi_{l_\kappa}^{(\kappa)} \rangle \,, \tag{32}$$

and similarly for the mean fields (see Ref. [11, 15]). Note that only one-dimensional integrals are now required. (With mode-combination, d–dimensional integrals may appear).

The kinetic energy operator normally has the required form (31). Often, however, the potential energy operator does not have the necessary structure, and it must be fitted to the product form. A convenient, systematic, and efficient approach to obtain an optimal product representation is described in Refs. [15, 79, 80]. Note that it is important to keep the number of expansion terms, s, as small as possible, because the computation time increases linearly with s.

The expansion of the potential in a product form can be avoided by adopting the correlated DVR (CDVR) of U. Manthe [81]. This uses a time-dependent DVR based on the SPFs to evaluate the multi-dimensional integrals without recourse to the full primitive grid. The method however suffers in that it has no internal error control (see Ref. [15] for a discussion). We hope that CDVR can be developed to overcome this problem, as it represents a very important step in increasing the generality of the method.

2.7 The constant mean-field (CMF) integrator

The MCTDH equations of motion, Eqs. (15, 16), are strongly coupled and non-linear. As a result they cannot be solved using the powerful integration schemes developed for linear equations, such as those used in the standard method [82]. A significant step forward in the application of the MCTDH method was made in the development of the constant mean-field (CMF) integrator.

The motivation behind the CMF integration scheme is that the matrix elements $\langle \Phi_J \mid H \mid \Phi_L \rangle$ and the product of the inverse density with the mean-field matrices generally change much slower in time than the MCTDH coefficients and the SPFs. For that reason it is possible to use a wider meshed time discretization for the propagation of the former quantities than for the latter ones with only a minor loss of accuracy. In other words, during the integration of the equations of motion (22) and (23) one may hold the Hamiltonian matrix elements, the density matrices, and the mean-field matrices constant for some time τ (hence the name).

Doing so, the the large set of coupled equations of motions (22,23) is split into $f + 1$ smaller sets which are uncoupled from each other over the time–step τ. The first set of equations is similar to (22), but, as the matrix elements are now constant, it turns into a linear differential equation. The other f sets of equations are similar to (23), but, as the inverse density and the mean-field matrices are now constant, the differential equations for the different degrees of freedom, κ, decouple from each other (and from the equation for the coefficients). Because of this decoupling one may use different step–sizes and even different integration routines for each set of equations. For the – now linear – set of equations for the coefficients a short iterative Lanczos (SIL) integrator [83] is usually used. For the – still non-linear – sets of equations for the SPFs we usually adopt a Bulirsch-Stoer or Runge-Kutta integrator.

In order to be efficient, the CMF-integrator algorithm has to be more complicated than outlined above. A predictor–corrector approach is used, which removes errors linear in τ and provides an automatic step–size control for the CMF–step τ. With these modifications [12, 15] the CMF–integrator has become an important ingredient to MCTDH. The use of the CMF–integrator speeds up the calculation by typically one order of magnitude.

2.8 Selected configurations (S-MCTDH)

The discussion on scaling in Sec. 2.5 shows that MCTDH has unfortunately not broken the exponential scaling of the standard wavepacket propagation method. Its success is achieved by using the SPFs to lower the base of the exponent, and by using multi-mode functions to change the effective dimensionality of a problem. In this and the next section, we look at two possible ways to fight the exponential scaling and to make MCTDH applicable to even larger systems.

The exponential scaling is simply due to the use of a direct product basis - configurations using all possible combinations of the basis functions are included. In an analogy to electronic structure calculations MCTDH can be called a full-configuration interaction (CI) method. For large systems, many millions of configurations may be generated that are negligible in importance for the description of the wavefunction, covering regions of space not occupied by the system. The S-MCTDH method aims to select and propagate only the important configurations [84].

To select a set of configurations from the full-CI set, the configuration space $\{J\}$, represented by the indices attached to the coefficients, A_J, is divided into two spaces $\{D\}$ and $\{R\}$, where the former are for the configurations to be included in, and the latter for those to be excluded from, the calculation. Assuming that $A_J(t_0) = 0 \quad \text{for} \quad J \in \{R\}$, we thus require that

$$i\dot{A}_J = 0; \quad \text{for} \quad J \in \{R\} \quad . \tag{33}$$

To meet these conditions, the operator $H - \sum_\kappa g^{(\kappa)}$ in Eq. (15) is replaced by its projection onto the space of the included configurations, $\{D\}$. Defining the time-dependent projector,

$$\hat{D} = \sum_{J \in \{D\}} \mid \Phi_J \rangle \langle \Phi_J \mid \quad , \tag{34}$$

the time-derivative of the expansion coefficients is then

$$i\dot{A}_J = \sum_L \langle \Phi_J \,|\, \hat{D}(H - \sum_{\kappa=1}^{p} g^{(\kappa)})\hat{D} \,|\, \Phi_L \rangle A_L \quad . \tag{35}$$

This equation is obviously zero for $J \in \{R\}$.

The S-MCTDH method is based on this change in the time-derivatives of the wavefunction expansion coefficients. The time-derivatives of the SPFs retain the form of the full-CI solution, Eq. (16), and these functions evolve in the mean-fields and density matrices formed from the wavefunction constrained to lie in the included configuration space. It can be shown that the system is now being propagated by the effective Hamiltonian

$$H_{\text{eff}} = H - G \quad , \tag{36}$$

where using the projector onto the excluded space, $\hat{R}$,

$$G = \hat{R}\,(H - \sum_{\kappa=1}^{p} g^{(\kappa)}) \quad . \tag{37}$$

This equation defines the space of redundant configurations. It is simply the space orthogonal to the result of the operation of $H - \sum_\kappa g^{(\kappa)}$ on the wavefunction.

How should the constraint operator, $g^{(\kappa)}$, be chosen? In the usual MCTDH method, it plays only a minor role: as mentioned in Sec. 2.2 different representations of the SPFs are connected by unitary transformations and different choices affect only the numerics. In S-MCTDH the representation chosen is crucial. Different $g^{(\kappa)}$ will result both in a different operator and a different excluded space. This will thus change the convergence, i.e. the number of redundant configurations that can be excluded from the calculation.

In Ref. [84] a natural orbital representation was used, in which the SPFs evolve so that the density matrices remain diagonal (see Sec. 2.3). As a result, an importance can be attached to each function, and products of unimportant functions can be ignored. In the 24-dimensional example studied, the largest MCTDH calculation made used 2,771,440 configurations. The spectrum obtained from an S-MCTDH calculation choosing just the 13,023 most important configurations was virtually indistinguishable. The problems in the method, however, are the extra book-keeping required to keep track of the indices, and improvements in the present algorithm are required to enable the full power of this approach to be used.

2.9 Cascading

The cascading approach is similar in spirit to S-MCTDH, discussed in the last section. In essence, cascading selects linear combinations of configurations rather than configurations itself. As cascading is fully based on an variational principle, it is expected to be more efficient than S-MCTDH. However, cascading is a much more complicated algorithm and has not been implemented yet.

One important step in going to large systems was the introduction of mode combination (see section 2.5). This, however, quickly reaches a limit because multi–dimensional SPFs have to be propagated. To go further, we thus need a method able to efficiently propagate multi-dimensional wavepackets. Of course we have such a method: MCTDH. The idea is thus to use MCTDH to propagate highly combined SPFs of the original MCTDH expansion. One may continue and use again MCTDH to propagate the (second layer) SPFs used to expand the original (first layer) SPFs, and so on. In this way one cascades down until one arrives at SPFs the dimension of which is small enough to be propagated conventionally. (The notation *first layer* and *second layer* was suggested by H. Wang).

Alternatively one may imagine performing a (standard) MCTDH calculation on a large system. This leads to an enormously long A–vector, which cannot be propagated conventionally. However, one may propagate it with MCTDH and, similar to above, cascades down until a a manageable size is reached. Fortunately, both approaches yield exactly the same set of working equations.

In the following we will discuss one–step cascading, which is expected to be the most important approximation out of the cascading family. It is fairly obvious how the working equations have to be generalized to cover two–step or three–step cascading.

We assume that the wavefunction is expanded in MCTDH form Eq. (5), and – for sake of simplicity – we will assume the constraint $g^{(\kappa)} = 0$ and discard the partitioning of the Hamiltonian, Eq. (14). The equations of motions hence are given by Eqs. (22,23). We split the composite index J into pieces

$$\begin{aligned} J &= (J_1, \cdots, J_p) \\ J_\beta &= (j_{\alpha_{\beta-1}+1}, \cdots, j_{\alpha_\beta}) \end{aligned} \tag{38}$$

where $\beta = 1, \cdots, p$ and where p denotes the number of *particles*, or first-layer degrees of freedom. The numbers α define which degrees of freedom go into one particle. Note, $\alpha_0 = 0$ and $\alpha_p = f$ by definition. With this nomenclature we write the A–vector as

$$A_J = \sum_{k_1}^{m_1} \cdots \sum_{k_p}^{m_p} B_{k_1 \cdots k_p} C^{(1)}_{k_1 J_1} \cdots C^{(p)}_{k_p J_p} \ , \tag{39}$$

define the partial configurations

$$\Phi_{J_\beta} = \prod_{\kappa=\alpha_{\beta-1}+1}^{\alpha_\beta} \varphi^{(\kappa)}_{j_\kappa} \ , \tag{40}$$

and the first-layer SPFs

$$\theta_k^{(\beta)} = \sum_{J_\beta} C_{kJ_\beta}^{(\beta)} \, \Phi_{J_\beta} \; . \tag{41}$$

The total wavefunction expanded in second layer SPFs is given by Eqs. (5,39), but expanded in first layer SPFs it reads

$$\begin{aligned} \Psi &= \sum_{k_1=1}^{m_1} \cdots \sum_{k_f=1}^{m_p} B_{k_1 \ldots k_p}(t) \; \prod_{\beta=1}^{p} \theta_{k_\beta}^{(\beta)} \\ &= \sum_K B_K \, \Theta_K \; , \end{aligned} \tag{42}$$

which implicitly defines the composite index K and the first-layer configuration Θ_K.

We proceed by introducing the first layer single-hole functions

$$\tilde{\Psi}_k^{(\beta)} = \langle \theta_k^{(\beta)} \, | \, \Psi \rangle \; , \tag{43}$$

where a more explicit equation can be easily derived (compare with Eq. (9)). The definition of the second layer single-hole functions, $\Psi_j^{(\kappa)}$, is still given by Eq. (9). The first layer single-hole functions allow us to define first layer density matrices and mean-fields

$$\tilde{\rho}_{kk'}^{(\beta)} = \langle \tilde{\Psi}_k^{(\beta)} \, | \, \tilde{\Psi}_{k'}^{(\beta)} \rangle = \sum_K^{\beta} B^*_{K_k^\beta} B_{K_{k'}^\beta} \; , \tag{44}$$

and

$$\langle \tilde{H} \rangle_{kJ_\beta k' J'_\beta}^{(\beta)} = \langle \tilde{\Psi}_k^{(\beta)} \, \Phi_{J_\beta} \, | \, H \, | \, \tilde{\Psi}_{k'}^{(\beta)} \, \Phi_{J'_\beta} \rangle \; , \tag{45}$$

and the first layer MCTDH projector

$$\tilde{P}_{J_\beta J'_\beta}^{(\beta)} = \sum_{k=1}^{m_\beta} C_{kJ_\beta}^{(\beta)} \, C_{kJ'_\beta}^{(\beta)*} \; . \tag{46}$$

The second layer mean–field, density matrix, and projector are the "original" ones, i. e. they are given by Eqs. (11,12,13). Note that the second layer mean–field, Eq. (11), is an operator, whereas the first layer mean–field, Eq. (45), is a number.

Using again the Dirac-Frenkel variational principle, Eq. (3), one arrives after some algebra at the one–step cascading equations of motion

$$i\dot{B}_K = \sum_{K'} \langle \Theta_K \, | \, H \, | \, \Theta_{K'} \rangle \, B_{K'} \; , \tag{47}$$

$$i\dot{C}^{(\beta)}_{kJ_\beta} = \sum_{J'_\beta J''_\beta k' k''} \left(\delta_{J'_\beta J''_\beta} - \tilde{P}^{(\beta)}_{J'_\beta J''_\beta}\right) \left(\tilde{\boldsymbol{\rho}}^{(\beta)-1}\right)_{kk'} \langle \tilde{H} \rangle^{(\beta)}_{k' J'_\beta k'' J''_\beta} C^{(\beta)}_{k'' J''_\beta} \,, \tag{48}$$

$$i\dot{\varphi}^{(\kappa)}_j = \sum_{lm} \left(1 - P^{(\kappa)}\right) \left(\boldsymbol{\rho}^{(\kappa)-1}\right)_{jl} \langle H \rangle^{(\kappa)}_{lm} \, \varphi^{(\kappa)}_m \,. \tag{49}$$

Note that the equation of motion for the second layer SPFs, Eq. (49), is precisely the "old" equation of motion (23). The equation of motion for the first layer SPFs is implicitly given by Eq. (48), i. e. by the equation of motion for their expansion coefficients. Note the evident formal similarity between Eqs. (49) and (48). In fact, Eq. (49) becomes very similar to Eq. (48) when writing it for the primitive basis expansion coefficients $c^{(\kappa)}_{i_\kappa\, j_\kappa}(t)$ (cf. Eq. (6)) rather than for the SPF $\varphi^{(\kappa)}_j$ itself. Finally, the equation of motion for the B coefficients is structurally very similar to Eq. (22).

Let us discuss an example to demonstrate the potential of one–step cascading. Assume that there are $f = 25$ degrees of freedom, and that $n = 10$ SPFs are required for each degree of freedom. In a conventional MCTDH approach there would be 10^{25} coefficients, requiring 1.5×10^{20} GB. Such a calculation is, of course, impossible. Using one–step cascading and combining 5 degrees of freedom into one particle such that there are $p = 5$ particles and assuming that $m = 25$ first layer SPFs per particle are sufficient for convergence, one finds that the B and C coefficients require 149 MB and 191 MB, respectively. The space required for the second layer SPFs is rather small. Even if a huge primitive grid of 10,000 points is used, only 39 MB are needed. Thus one total wavefunction takes less than 380 MB and the whole calculation is expected to consume less than 8 GB, feasible on a modern work station. The second layer SPFs may (and in fact should) already make use of mode combination. As a huge primitive grid of 10,000 points was assumed, we may presume that such a grid carries (on the average) four–dimensional SPFs. Hence a calculation with 100 degrees of freedom seems to be possible with one–step cascading.

3 ρMCTDH for density operators

3.1 Wavefunctions and density operators

The evolution of a wavefunction describes the evolution of a particular, well defined initial state. A system at finite temperature, however, is an incoherent mixture of very many thermally excited states, $|\Psi_n\rangle$. A correct description of such a statistical mixture can be made using the density operator

$$\rho = \sum_n p_n \, |\Psi_n\rangle\langle\Psi_n| \quad , \tag{50}$$

where $0 \leq p_n \leq 1$ are the occupation probabilities which add up to 1. (The density operator ρ should not be confused with the MCTDH one-particle reduced density, for which – in order to be consistent with the literature – we have used the same symbol). The most important advantage of the density operator formalism, however, is the possibility to include the effects of an environment on the system dynamics, thus allowing the description of *open* quantum systems and their non-equilibrium dynamics [67]. The wavefunction formalism is not appropriate for such situations since, even if the system is initially in a pure state (i. e. $\rho = |\Psi\rangle\langle\Psi|$), it soon becomes a statistical mixture due to the influence of the environment.

The time–evolution of a density operator is given by a differential equation of first order

$$i\dot{\rho} = \mathcal{L}(\rho) \tag{51}$$

where $\mathcal{L}$ is a linear super-operator. For closed systems the latter reads (Liouville–von Neumann equation)

$$\mathcal{L}(\rho) = [H, \rho] \tag{52}$$

where H is the Hamiltonian of the system. This equation is equivalent to the Schrödinger equation for wavefunctions, and leads to a unitary evolution of ρ. For open systems a number of approaches for defining $\mathcal{L}$ exist, in particular those that account for the interaction with the environment within the Markov approximation [85,86]. One of the prominent approaches in this context refers to the Lindblad form [87–89],

$$\mathcal{L}(\rho) = [H, \rho] + i \sum_j \left(V_j \rho V_j^\dagger - \frac{1}{2} V_j^\dagger V_j \rho - \frac{1}{2} \rho V_j^\dagger V_j \right) \tag{53}$$

which implies that the time evolution is completely positive. Other well-known expressions are due to Redfield [90] and Caldeira and Leggett [91] who proposed a perturbative treatment of the interaction and a bath at high temperature.

In this section we develop the ρMCTDH method, which is an extension of the MCTDH method to the propagation of density operators. A density operator is not uniquely defined by a ρMCTDH *ansatz*, and two different approaches have been investigated. In the first, known as type I, single-particle density operators are used to replace the single-particle functions of the wavepacket version. In the type II variant, the single-particle density operators are themselves represented by a product of single-particle functions. The *ansatz* used will be denoted in brackets, e.g. ρMCTDH(I) for the method using the type I basis.

3.2 Type I density operators

We generalize the MCTDH *ansatz* Eq. (5) to density operators

$$\rho(Q_1,\ldots,Q_f,Q'_1,\ldots,Q'_f,t) = \sum_{\tau_1=1}^{n_1}\cdots\sum_{\tau_f=1}^{n_f} B_{\tau_1\ldots\tau_f}(t)\prod_{\kappa=1}^{f}\sigma_{\tau_\kappa}^{(\kappa)}(Q_\kappa,Q'_\kappa,t) \tag{54}$$

where the $B_{\tau_1\ldots\tau_f}$ denote the ρMCTDH expansion coefficients, which are now called B rather than A to avoid confusion with the wavefunction formalism. The $\sigma_{\tau_\kappa}^{(\kappa)}$ are so-called *single-particle density operators* (SPDOs), analogous to the SPFs in the wavefunction scheme (see Section 2.2). A density operator has to be hermitian. To ensure this property we require that the coefficients are real and the SPDOs are hermitian

$$B_{\tau_1\ldots\tau_f} = B^*_{\tau_1\ldots\tau_f}\,, \quad \sigma_{\tau_\kappa}^{(\kappa)} = \sigma_{\tau_\kappa}^{(\kappa)\,\dagger}\,. \tag{55}$$

As shown in Ref. [70], the ρMCTDH(I) equations of motion conserve these properties.

To derive the equations of motion one needs a Hilbert space structure and in particular a scalar product. For this purpose we employ the Hilbert-Schmidt scalar product [92],

$$\langle\langle A\,|\,B\rangle\rangle = Tr\{A^\dagger B\}\,. \tag{56}$$

Using this scalar product, one may transfer all properties that usually apply for wavefunctions, such as orthonormality etc., to density operators. In the following operators and super-operators appear, and it is important to distinguish between them. For example, the operator $[H,\rho]$ is obviously anti-hermitian, but the super-operator $\mathcal{L} = [H,\cdot]$ is hermitian [69, 92]!

As in MCTDH for wavefunctions, the representation of the density operator (54) is not unique and constraints are needed to ensure unique, singularity free equations of motion. The constraints, which imply that the

SPDOs remain orthonormal, read

$$\begin{aligned} \Big\langle\Big\langle \sigma_\mu^{(\kappa)}(0) \Big| \sigma_\nu^{(\kappa)}(0) \Big\rangle\Big\rangle &= \delta_{\mu\nu} && (57) \\ \Big\langle\Big\langle \sigma_\mu^{(\kappa)}(t) \Big| \dot{\sigma}_\nu^{(\kappa)}(t) \Big\rangle\Big\rangle &= -i \Big\langle\Big\langle \sigma_\mu^{(\kappa)}(t) \Big| \mathcal{G}^{(\kappa)}\, \sigma_\nu^{(\kappa)}(t) \Big\rangle\Big\rangle . && (58) \end{aligned}$$

Here the *constraint super-operator* $\mathcal{G}^{(\kappa)}$ is a self-adjoint, but otherwise arbitrary, super-operator acting exclusively on the κ-th degree of freedom. In particular one may set $\mathcal{G}^{(\kappa)} = 0$. For further reference we introduce the total constraint super-operator

$$\mathcal{G} = \sum_{\kappa=1}^{f} \mathcal{G}^{(\kappa)} \tag{59}$$

which is just the sum of the individual constraint super operators.

The derivation of the equations of motion is very similar to the wave-function case. We need to define *single-hole density operators*

$$\Pi_\nu^{(\kappa)} = \langle\langle \sigma_\nu^{(\kappa)} | \rho \rangle\rangle = \sum_{\mathcal{T}}^{\kappa} B_{\mathcal{T}_\nu^\kappa} \prod_{\kappa' \neq \kappa} \sigma_{\tau_{\kappa'}}^{(\kappa')} \quad , \tag{60}$$

with which we define reduced density matrices (now called $\mathcal{D}$, as ρ is already used)

$$\begin{aligned} \mathcal{D}_{\mu\nu}^{(\kappa)} &= \Big\langle\Big\langle \Pi_\mu^{(\kappa)} \Big| \Pi_\nu^{(\kappa)} \Big\rangle\Big\rangle \\ &= \langle\langle \sigma_\nu \mid \ \mathrm{Tr}\{\, \rho^\dagger \rho\}_\kappa \mid \sigma_\mu \rangle\rangle \\ &= \sum_{\mathcal{T}}^{\kappa} B^*_{\mathcal{T}_\mu^\kappa}\, B_{\mathcal{T}_\nu^\kappa} \ , && (61) \end{aligned}$$

and mean-field Liouvillian super-operators

$$\langle \mathcal{L} - \mathcal{G} \rangle_{\mu\nu}^{(\kappa)} = \Big\langle\Big\langle \Pi_\mu^{(\kappa)} \Big| (\mathcal{L} - \mathcal{G}) \Pi_\nu^{(\kappa)} \Big\rangle\Big\rangle \ . \tag{62}$$

Finally, we define the ρMCTDH(I) projector

$$\mathcal{P}^{(\kappa)} = \sum_{\nu=1}^{n_\kappa} \Big| \sigma_\nu^{(\kappa)} \Big\rangle\Big\rangle \Big\langle\Big\langle \sigma_\nu^{(\kappa)} \Big| \ , \tag{63}$$

and the Hartree product

$$\Omega_{\mathcal{T}} = \prod_{\kappa=1}^{f} \sigma_{\tau_\kappa}^{(\kappa)} \ . \tag{64}$$

(These equations should be compared with Eqs. (9-13) and (24,25), where the nomenclature is explained.)

With the above definitions we can formulate the equations of motion

$$i\dot{B}_{\mathcal{T}} = \sum_{\mathcal{T}'} \langle\langle \Omega_{\mathcal{T}} \,|\, (\mathcal{L} - \mathcal{G})\Omega_{\mathcal{T}'} \rangle\rangle \, B_{\mathcal{T}'} \tag{65}$$

$$i\dot{\boldsymbol{\sigma}}^{(\kappa)} = \mathcal{G}^{(\kappa)}\boldsymbol{\sigma}^{(\kappa)} + \left(1 - \mathcal{P}^{(\kappa)}\right)\left(\boldsymbol{\mathcal{D}}^{(\kappa)}\right)^{-1} \langle\, \boldsymbol{\mathcal{L}} - \boldsymbol{\mathcal{G}}\,\rangle^{(\kappa)} \boldsymbol{\sigma}^{(\kappa)} \,. \tag{66}$$

Note the obvious similarity of these equations of motion with the Eqs. (15,16), in particular when H_{R} is set to H and the $h^{(\kappa)}$ vanish. The separation, Eq. (14), is useful for density propagation as well, but for sake of simplicity we will not further discuss it here.

3.3 Type II density operators

The SPDOs can also be written as ket–bra products of wavefunctions. Doing so, the algorithm for density operators becomes even more similar to the one for wavefunctions. One interprets the index τ_κ as composite index $\tau_\kappa = (j_\kappa, l_\kappa)$, and similarly $\mathcal{T} = (J, L)$. Setting

$$\sigma_{\tau_\kappa}^{(\kappa)}(Q_\kappa, Q'_\kappa, t) = \left|\, \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) \right\rangle \left\langle \varphi_{l_\kappa}^{(\kappa)}(Q'_\kappa, t) \right| \tag{67}$$

and

$$B_{\tau_1 \ldots \tau_f} = B_{j_1 \ldots j_f, l_1 \ldots l_f} = B^*_{l_1 \ldots l_f, j_1 \ldots j_f} \,, \tag{68}$$

one arrives at the type II density operator expansion

$$\rho(Q_1, \ldots, Q_f, Q'_1, \ldots, Q'_f, t) = \sum_{j_1, l_1 = 1}^{n_1} \cdots \sum_{j_f, l_f = 1}^{n_f} B_{j_1 \ldots j_f, l_1 \ldots l_f}(t) \prod_{\kappa=1}^{f} \left|\, \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) \right\rangle \left\langle \varphi_{l_\kappa}^{(\kappa)}(Q'_\kappa, t) \right| . \tag{69}$$

The hermiticity of B, Eq. (68), ensures that ρ is hermitian. The hermiticity is conserved during the propagation [70].

The constraints (58) must be translated into constraints for the SPFs, which requires the constraint super-operator to be given as

$$\mathcal{G}^{(\kappa)} = [g^{(\kappa)}, \,\cdot\,] \,, \tag{70}$$

where the constraint operators are similar to those of Eq. (8). In fact, using Eq. (70) one arrives at Eqs. (7,8), i. e. at the constraint equations for SPFs.

The ρMCTDH(II) equations of motion for propagating type II density operators now read [69, 70]

$$i\dot{B}_{J,L} = \langle \Phi_J \,|\, (\mathcal{L} - \mathcal{G})(\rho) \,|\, \Phi_L \rangle \,, \tag{71}$$

and

$$i\dot{\boldsymbol{\varphi}}^{(\kappa)} = g^{(\kappa)}\boldsymbol{\varphi}^{(\kappa)} + \left(1 - P^{(\kappa)}\right) \mathrm{Tr}\{(\mathcal{L} - \mathcal{G})(\rho)\rho\}_\kappa \left(\boldsymbol{\mathcal{D}}^{(2),(\kappa)}\right)^{-1} \boldsymbol{\varphi}^{(\kappa)} \,, \tag{72}$$

where the reduced single-particle density matrix is given by

$$\mathcal{D}^{(2),(\kappa)}_{jl} = \left\langle \varphi^{(\kappa)}_l \middle| \mathrm{Tr}\left\{\rho^2\right\}_\kappa \middle| \varphi^{(\kappa)}_j \right\rangle = \sum_L \sum_J^{\kappa} B^*_{L,J^\kappa_l}\, B_{L,J^\kappa_j} \,. \tag{73}$$

It is illustrative to exemplify these equations for the simplest case, $\mathcal{L} = [H, \,\cdot\,]$ and $\mathcal{G} = 0$. The equations of motion can then be written as

$$i\dot{B}_{J,L} = \sum_K \langle \Phi_J \,| H |\, \Phi_K \rangle\, B_{K,L} \;-\; B_{J,K} \,\langle \Phi_K \mid H \mid \Phi_L \rangle \,, \tag{74}$$

and

$$\begin{aligned} i\dot{\varphi}^{(\kappa)}_m \;\; &= \;\; \left(1 - P^{(\kappa)}\right) \sum_{J,L,K} \left(\boldsymbol{\mathcal{D}}^{(2),(\kappa)}\right)^{-1}_{mk} B_{J,L}\, B_{L,K} \\ &\qquad \times \langle \Phi_{K^\kappa} \,| H |\, \Phi_{J^\kappa} \rangle \;\; | \varphi^{(\kappa)}_j \rangle \,, \end{aligned} \tag{75}$$

where Φ_{J^κ} denotes a Hartree product in which the SPF of the κ's degree of freedom is missing. The indices j and k are the κ th entry of the composite indices J and K, respectively. When deriving Eq. (75) we have discarded the contribution of the term $\mathrm{Tr}\{\rho H \rho\}_\kappa$ because it will be annihilated by the projector $(1 - P^{(\kappa)})$. Only the term $\mathrm{Tr}\{H\rho^2\}_\kappa$ is kept.

When the density is a pure state, $\rho = |\Psi\rangle\langle\Psi|$, the coefficient matrix factorizes, $B_{J,L} = A_J A^*_L$, where A denotes the MCTDH coefficient vector of Ψ. Inserting this separation into Eqs. (73,74,75) one recovers the MCTDH wavefunction equations of motion (22,23). Hence, the closed system propagation of a pure-state density operator using ρMCTDH(II) is equivalent to an MCTDH wavefunction propagation (i.e. identical SPFs, B coefficients of ρ factorize into A coefficients of Ψ).

3.4 Properties of ρMCTDH density operator propagation

MCTDH for wavefunctions conserves the total probability $\langle \Psi | \Psi \rangle$ and the total energy $\langle \Psi | \, H \, | \Psi \rangle$. This follows directly from the Dirac-Frenkel variational principle. Similarly, the variational principle ensures that $\mathrm{Tr}\{\rho^2\}$

and $\mathrm{Tr}\{\rho^2 H\}$ are conserved when density operators are propagated using ρMCTDH for a closed system. Unfortunately, these are not the total probability, $\mathrm{Tr}\{\rho\}$, and total energy, $\mathrm{Tr}\{\rho H\}$, but when the calculation converges, the latter quantities are rather well conserved. The lack of (exact) energy conservation made us think about using another variational principle [69,70], which does ensure exact energy conservation. However this so called *linear mean-field approach* was found to be less efficient and we do not discuss it here.

For closed systems and type II density operators one additionally may prove some interesting results [70].

1. $\mathrm{Tr}\{\rho^n\}$, $n = 1, 2, 3, \ldots$, is conserved.
2. A pure state remains pure.
3. Diagonalising the density and writing $\rho = \sum_M p_M \mid \Psi_M\rangle\langle\Psi_M \mid$ one finds that the Dirac-Frenkel variational principle applied to type II density operators is equivalent to

   $$\sum_M p_M^2 \langle \delta\Psi_M \mid i\dot{\Psi}_M - H\Psi_M\rangle = 0 \; . \tag{76}$$

   and $\dot{p}_M = 0$
4. If ρ is pure, ρMCTDH(II) propagation is equivalent to the MCTDH propagation of wavefunctions.

Point 1) tells us, that probability conservation is no problem (for type II densities and closed systems). Point 2) follows from 1), but is worth to be mentioning explicitely. Point 3) builds the bridge between type II density and wavepacket propagation. The variational principle applied to type II density operators is equivalent to a weighted sum over the variational principles applied to the eigenfunctions of ρ, where the weights are the *squares* of the eigenvalues of ρ. Point 4 follows from 3) and was already mentioned in the previous section.

It is more difficult to make formally exact statements on the density operator propagation of open systems. The only result we have, is the explanation of the loss of total probability. Defining the projector

$$\tilde{P} = \sum_J \mid \Phi_J\rangle\langle\Phi_J \mid \, , \tag{77}$$

which is the tensor product of all MCTDH projectors $P^{(\kappa)}$, and assuming a Lindblad–type dissipation, Eq. (53), one obtains

$$
\begin{aligned}
\mathrm{Tr}\{\dot{\rho}\} = Tr\{\dot{\boldsymbol{B}}\} &= \sum_J \langle \Phi_J \,|\, \mathcal{L}(\rho) \,|\, \Phi_J \rangle = Tr\{\tilde{P}\mathcal{L}(\rho)\} \\
&= \sum_j \mathrm{Tr}\left\{ \tilde{P} V_j \rho V_j^\dagger - \frac{1}{2}\tilde{P} V_j^\dagger V_j \rho - \frac{1}{2}\tilde{P}\rho V_j^\dagger V_j \right\} \\
&= \sum_j \mathrm{Tr}\left\{ V_j^\dagger \tilde{P} V_j \rho \right\} - \mathrm{Tr}\left\{ V_j^\dagger V_j \rho \right\} \\
&= -\sum_j \mathrm{Tr}\left\{ (1-\tilde{P}) V_j \rho V_j^\dagger (1-\tilde{P}) \right\} \\
&\leq 0 \,,
\end{aligned} \tag{78}
$$

since $\tilde{P}\rho = \rho\tilde{P} = \rho$ by construction. The very first of the equations follows because of the constraints (7,8), where $g^{(\kappa)} = 0$ was assumed for sake of simplicity. Note that the possible decrease of $\mathrm{Tr}\{\rho\}$ is due to representing ρ in the finite, incomplete basis set $\{\Phi_J\}$. This analysis offers a cure for the problem. One simply replaces V_j by $\tilde{P} V_j \tilde{P}$ when propagating the coefficients. (This is equivalent to replacing only the products $V_j^\dagger V_j$ by $V_j^\dagger \tilde{P} V_j$). This simple modification has shown to significantly improve the stability of type II density operator propagation for open systems.

We have introduced two types of ρMCTDH density operator expansions, but have not yet discussed which expansion is superior under given conditions. Consider an uncorrelated system at high temperature. The type I density operator propagation then becomes numerically exact with one single configuration. A type II propagation, on the other hand, would require many SPFs to correctly represent the thermal excitations. Going to the other extreme, a pure state and a strongly correlated system, one notices that type II now becomes much more efficient than type I. One needs more SPDOs for type I than SPFs for type II to account for the correlation, and it is more elaborate to propagate SPDOs than to propagate SPFs. To make the comparison more vivid, let us distinguish between correlation and mixing. In a coordinate representation the density operator is a $2f$-dimensional function $\rho(\mathbf{Q}, \mathbf{Q}')$ where $\mathbf{Q}$ are the coordinates of the f degrees of freedom of the system. If this function is non-separable with respect to the coordinates Q_κ and $Q_{\kappa'}$ of *different* degrees of freedom, $\kappa \neq \kappa'$, we speak of correlation between these degrees of freedom. On the other hand, if $\rho(\mathbf{Q}, \mathbf{Q}')$ is non-separable with respect to the coordinates Q_κ and Q'_κ of a *single* degree of freedom κ we speak of mixing in this degree of freedom. In particular, a pure state is unmixed in all degrees of freedom. Using this terminology one can express the different performance of type I and type II expansions as follows. The type I expansion is more efficient if there is more mixing than correlation, whereas the type II expansion is to be preferred if correlation is stronger than mixing.

4 Initial State

4.1 Hartree products

The time–dependent Schrödinger equation (1) is an initial value problem. The initial state, $\Psi(0)$, thus has to be supplied. Depending on the process to be described, the initial state may be fully determined, e. g. as an eigenstate of another Hamiltonian. In other situations there is some freedom of choice. As the wavepacket is to be propagated by MCTDH, the initial wavepacket must be supplied in MCTDH form. Fortunately, the initial wavepacket can often be given as a simple Hartree product, which trivially is in MCTDH form. To give an example: for an AB+C scattering event described in Jacobian coordinates R, r, and θ, one may chose as initial wavefunction a product of a Legendre polynomial in $\cos(\theta)$, to specify a particular initial rotational state j, a vibrational eigenfunction in r, to specify a particular initial vibrational state v, and a Gaussian function in R. The width and the momentum of the Gaussian determine the energy range to be covered.

In other cases, where a Hartree product may not be appropriate, one may start with an initial guess such as a Hartree product, and alter this to the desired function in MCTDH form. The problem is the incomplete nature of the basis provided by an initial guess set of SPFs. For the representation of a general function both the expansion coefficients and SPFs must be changed.

When a ground–state wavefunction is required, e. g. when photo-dissociation is studied, one may start with a Hartree product which is close to the ground–state and propagate it in negative imaginary time. It relaxes [93] to the ground–state and, as this relaxation is performed by MCTDH, the wavefunction is automatically in MCTDH form. A recent modification of this approach, which also allows the generation of excited states, is described in the following section. Finally, the initial wavefunction may be modified by applying an operator to it. This will be described in section 4.3.

4.2 Relaxation and improved relaxation

The generation of a ground–state wavefunction is conveniently done by energy relaxation [93]. An initial wavepacket, usually a Hartree product, is propagated in negative imaginary time by $H - E(t)$, where $E(t)$ denotes the expectation value of H. The formal solution of this propagation reads

$$\Psi(t) = \exp\left(\int_0^t E(t) - E_0 \, dt\right) \, e^{-(H-E_0)\,t} \, \Psi(0) \; , \tag{79}$$

where E_0 denotes the ground–state energy. The second exponential damps all eigenstate contributions, except for the ground–state one, and the first exponential ensures that $\Psi(t)$ stays normalized. Thus with increasing time, $\Psi(t)$ converges towards the ground–state.

Energy relaxation is not the most efficient way to produce a ground–state wavefunction, but here it is a very convenient way. As the relaxation is performed by MCTDH, the computed ground–state wavefunction is automatically in MCTDH form and may serve as an initial state of a subsequent propagation. For this purpose, the initial ground–state wavefunction is usually either placed on an excited electronic state, or is modified by applying an operator to it (see next section).

Energy relaxation can in principle also be used to produce excited states, by keeping $\Psi(t)$ orthogonal to already computed lower lying states. But this is rather cumbersome to do and there is a more efficient way. As we are now dealing with a time-independent problem, we will now employ the usual time-independent variational principle

$$\delta \left\{ \langle \Psi \,|\, H \,|\, \Psi \rangle - E \left(\langle \Psi \,|\, \Psi \rangle - 1 \right) \right\} = 0 \; , \tag{80}$$

where the eigen-energy E serves as Lagrange parameter. Employing the MCTDH form (5), keeping the SPFs fixed and varying the coefficients yields

$$\sum_L H_{JL} \, A_L = E \, A_J \; , \tag{81}$$

where H_{JL} denotes the matrix elements of H with respect to the configurations Φ_J. This is of course the standard way to find the energy and eigenfunction of a state, only here the basis is formed by the SPFs. As initially selected, however, these may not provide a good description of the desired eigenfunction.

To optimize the basis, a variation must be performed with respect to the SPFs. Writing the wavefunction as in Eq. (10), and introducing the

Lagrange parameters $\epsilon_{ij}^{(\kappa)}$ to keep the SPFs orthonormal, the variational principle reads

$$\delta \sum_{jl} \{ \langle \varphi_j^{(\kappa)} \, \Psi_j^{(\kappa)} \, | \, H \, | \, \varphi_l^{(\kappa)} \, \Psi_l^{(\kappa)} \rangle \; - \; \epsilon_{jl}^{(\kappa)} \, (\, \langle \varphi_j^{(\kappa)} \, | \, \varphi_l^{(\kappa)} \rangle - \delta_{jl} \,) \, \} = 0 \; . \tag{82}$$

Performing the variation yields

$$\sum_l \langle H \rangle_{jl}^{(\kappa)} \, \varphi_l^{(\kappa)} = \sum_l \, \epsilon_{jl}^{(\kappa)} \, \varphi_l^{(\kappa)} \; . \tag{83}$$

The $\epsilon_{jk}^{(\kappa)}$ may be determined by multiplication of Eq. (83) with $\langle \varphi_k^{(\kappa)} \, |$

$$\epsilon_{jk}^{(\kappa)} = \sum_l \langle \varphi_k^{(\kappa)} \, | \, \langle H \rangle_{jl}^{(\kappa)} \, | \, \varphi_l^{(\kappa)} \rangle \; . \tag{84}$$

Eqs. (83,84) can be transformed into

$$\left(1 - P^{(\kappa)} \right) \langle \mathbf{H} \rangle^{(\kappa)} \boldsymbol{\varphi}^{(\kappa)} = 0 \; , \tag{85}$$

or equivalently

$$\left(1 - P^{(\kappa)} \right) \left(\boldsymbol{\rho}^{(\kappa)} \right)^{-1} \langle \mathbf{H} \rangle^{(\kappa)} \boldsymbol{\varphi}^{(\kappa)} = 0 \; . \tag{86}$$

Comparing this equation with Eq. (23) one notices, that the left hand side of Eq. (86) is equal to $-\dot{\boldsymbol{\varphi}}^{(\kappa)}$ when propagating in negative imaginary time. Hence a relaxation converges towards the variational solutions (83,84) of the SPFs.

Our strategy to generate excited state eigenfunctions is thus as follows. Starting with some initial guess for the wavefunction, one first builds and diagonalizes $\mathbf{H}$ to obtain the expansion coefficients for the desired eigenfunction expressed in the initial SPF basis. The mean-fields are then built, and the SPFs optimized by relaxation over some short time interval. After that, the cycle is re-done till convergence is obtained. Always taking the n th eigenvector of the matrix $\mathbf{H}$ will lead to convergence towards the n th eigenstate of the Hamiltonian. The relaxation of the SPFs is a rather efficient method, and it may be more efficient than the iterative diagonalization [94, 95] conventionally used to solve Eqs. (83,84).

The dimension of the matrix $\mathbf{H}$ may become so large that a full diagonalization is not appropriate. Presently this method – called *improved relaxation* – is implemented with a Lanczos routine as diagonalizer. (The SIL integrator could easily be generalized to serve as diagonalizer as well). This works very well as long as the ground–state or some low–lying excited state is the target. Unfortunately, for higher lying states Lanczos performs very poorly and should be replaced by a Davidson routine. This is planned. However, already with the present implementation it was possible to compute the first 50 vibrational states of the CO_2 molecule, using the Hamiltonian of Ref. [62]. Additionally, we have computed the first few low–lying states of HONO.

4.3 Modifying the initial state by applying operators

When the initial excitation is an electronic excitation and the Condon approximation is assumed, the ground–state wavefunction is placed onto an excited electronic state without changing its form. This is easy to do. In other situations, e. g. when exciting by infrared light, the initial wavefunction is given as a product of an (dipole) operator and a wavefunction. Let us thus write the initial state as $D\tilde{\Psi}$, where D denotes some operator and $\tilde{\Psi}$ some wavefunction, usually a ground–state. The application of D on $\tilde{\Psi}$ is not straightforward, again because $D\tilde{\Psi}$ has to be represented in MCTDH form (5). The operation of D will change both the coefficients and the SPFs. To arrive at an optimal representation we employ again a variational principle and require

$$\langle \delta\Psi \,|\, \Psi - D\tilde{\Psi} \rangle = \delta \sum_{\kappa} \sum_{jl} \epsilon_{jl}^{(\kappa)} \left(\langle \varphi_j^{(\kappa)} \,|\, \varphi_l^{(\kappa)} \rangle - \delta_{jl} \right) \,, \tag{87}$$

where Ψ and $\tilde{\Psi}$ are assumed to be in MCTDH form (5) and D in product form (31). The right hand side of Eq. (87) is included to ensure the orthonormality of the SPFs of Ψ. The $\epsilon_{jl}^{(\kappa)}$ are Lagrange parameters.

Variation with respect to the coefficients yields

$$A_J = \sum_L \langle \Phi_J \,|\, D \,|\, \tilde{\Phi}_L \rangle \, \tilde{A}_L \,, \tag{88}$$

where it is assumed that both sets of SPFs are orthonormal. Variation with respect to the SPFs yields

$$\sum_l \left(\rho_{jl}^{(\kappa)} - \epsilon_{jl}^{(\kappa)} \right) \varphi_l^{(\kappa)} = \sum_l \langle \Psi_j^{(\kappa)} \,|\, D \,|\, \tilde{\Psi}_l^{(\kappa)} \rangle \, \tilde{\varphi}_l^{(\kappa)} \,. \tag{89}$$

Rather than to determine the values of the Lagrange parameters $\epsilon_{jl}^{(\kappa)}$, we drop the matrix $(\rho_{jl}^{(\kappa)} - \epsilon_{jl}^{(\kappa)})$ and Gram-Schmidt orthogonalize the thus obtained functions. This is legitimate as only the space spanned by the SPFs matters. Orthogonal transformations among the SPFs are accounted for by the coefficients.

Eq. (89) is not an explicit equation, because the SPFs to be determined are already needed when evaluating the mean–fields $\langle \Psi_j^{(\kappa)} \mid D \mid \tilde{\Psi}_l^{(\kappa)} \rangle$. The equations are thus to be solved iteratively. The iteration is started by setting

$$\begin{aligned} \varphi_j^{(\kappa)(0)} &= \tilde{\varphi}_j^{(\kappa)} && (90) \\ A_J^{(0)} &= \sum_L \langle \Phi_J^{(0)} \,|\, D \,|\, \tilde{\Phi}_L \rangle \, \tilde{A}_L \ , && (91) \end{aligned}$$

and then evaluating for $i = 0, 1, 2, \cdots$

$$a) \quad \varphi_j^{(\kappa)(i+1)} = \sum_l \langle \Psi_j^{(\kappa)(i)} \,|\, D \,|\, \tilde{\Psi}_l^{(\kappa)} \rangle \, \tilde{\varphi}_l^{(\kappa)} \ , \tag{92}$$

$b)$ Gram–Schmidt orthogonalize the SPFs

$$c) \quad A_J^{(i+1)} = \sum_L \langle \Phi_J^{(i+1)} \,|\, D \,|\, \tilde{\Phi}_L \rangle \, \tilde{A}_L \ . \tag{93}$$

We still need a criterion to detect convergence and to stop the iteration. The coefficients and the SPFs do not necessarily converge, because, as already emphasized, only the space spanned by the SPFs is of relevance. A convenient criterion is given by employing the MCTDH projector

$$\mathrm{Tr}\{ P^{(\kappa)(i)} P^{(\kappa)(i+1)} \hat{\rho}^{(\kappa)(i+1)} \} \ , \tag{94}$$

as this provides a measure of the similarity of the i-th and the $((i+1)$-th space. The MCTDH density operator is included to weight the weakly occupied orbitals accordingly. Introducing the overlap matrix

$$M_{jl} = \langle \varphi_j^{(\kappa)(i+1)} \,|\, \varphi_l^{(\kappa)(i)} \rangle \ , \tag{95}$$

we hence stop the iteration if, for each κ,

$$\delta = 1 - \mathrm{Tr}\{ \mathbf{M}^\dagger \boldsymbol{\rho}^{\mathrm{T}} \mathbf{M} \} / \mathrm{Tr}\{ \boldsymbol{\rho} \} \tag{96}$$

is smaller than some threshold. δ vanishes when $P^{(\kappa)(i)}$ becomes equal to $P^{(\kappa)(i+1)}$, or, equivalently, when $\mathbf{M}$ becomes a unitary matrix. The transposed of the density matrix appears in Eq. (96) because of Eq. (25).

Turning from wavefunctions to density operators, we first note that one is usually interested in forming an initial density operator by the operation

$$\rho = -i[D, \tilde{\rho}] \tag{97}$$

as this is – similar to $D\tilde{\Psi}$ for wavefunctions – the first order contribution of an impulsive excitation $D(t) = D\delta(t)$. The variational principle now reads

$$\Big\langle\Big\langle \delta\rho \,\Big|\, \rho + i[D, \tilde{\rho}] \Big\rangle\Big\rangle = 0 \;, \tag{98}$$

where we have dropped the Lagrange parameters, because we will ensure the ortho-normality by explicit Gram–Schmidt orthogonalization. The derivations for type I and type II density operators are considerably more lengthy than in the wavefunction case and will not be sketched here. The final results read for type I:
Start the iteration with the initial values

$$\sigma_j^{(\kappa)(0)} = \tilde{\sigma}_j^{(\kappa)} \tag{99}$$

$$B_J^{(0)} = -i \sum_L \mathrm{Tr}\left\{ \Omega_J^{(0)} \, [D, \tilde{\Omega}_L] \right\} \tilde{B}_L \tag{100}$$

and evaluate for $l = 0, 1, 2, \cdots$

$$a) \quad \sigma_j^{(\kappa)(l+1)} = -i \, \mathrm{Tr}\Big\{ \Pi_j^{(\kappa)(l)} \, \big[D, \sum_m \tilde{\Pi}_m^{(\kappa)} \tilde{\sigma}_m^{(\kappa)} \big] \Big\}_\kappa \;, \tag{101}$$

$b)$ Gram–Schmidt orthogonalize the SPDOs

$$c) \qquad B_J^{(l+1)} = -i \sum_L \mathrm{Tr}\left\{ \Omega_J^{(l+1)} \, [D, \tilde{\Omega}_L] \right\} \tilde{B}_L \qquad . \tag{102}$$

Similarly we start the iteration for type II with the initial values:

$$\varphi_j^{(\kappa)(0)} = \tilde{\varphi}_j^{(\kappa)} \tag{103}$$

$$B_{J,L}^{(0)} = -i \, \langle \Phi_J^{(0)} \big| [D, \tilde{\rho}] \big| \Phi_L^{(0)} \rangle \tag{104}$$

and evaluate for $l = 0, 1, 2, \cdots$

$$a) \quad \varphi_j^{(\kappa)(l+1)} = -i \sum_L \sum_J{}^{\kappa} \langle \Phi_{J^\kappa}^{(l)} \big| [D, \tilde{\rho}] \big| \Phi_L^{(l)} \rangle \tag{105}$$

$b)$ Gram–Schmidt orthogonalize the SPFs

$$c) \qquad B_{J,L}^{(l+1)} = -i \, \langle \Phi_J^{(l+1)} \big| [D, \tilde{\rho}] \big| \Phi_L^{(l+1)} \rangle \qquad . \tag{106}$$

The actual working equations are obtained by expanding $\tilde{\rho}$ in MCTDH form.

5 Analysis

5.1 From time evolved wavefunctions to observables

MCTDH is an algorithm to solve the time–dependent Schrödinger equation. It thus provides us with the time evolved wavepacket $\Psi(t)$. This, however, is usually not what is finally desired. The quantities of interest are observables such as spectra, transition probabilities, cross-sections, etc. In any time–dependent approach an analysis step has to follow the propagation. Due to the special form of the MCTDH wavefunction, Eq. (5), one may have to re–design the analysis algorithm. For example, this special form does not allow the summation of different MCTDH wavefunctions, including wavefunctions at different times or from different calculations on the same system, because the SPFs will be different. On the other hand, the very compact representation of the MCTDH wavefunction may help to speed up the analysis. For instance, let $\Psi = \sum_J A_J \Phi_J$ and $\tilde{\Psi} = \sum_L \tilde{A}_L \tilde{\Phi}_L$ be two MCTDH wavefunctions, and let $\Omega = \sum_r^M c_r\, \omega_r^{(1)} \cdots \omega_r^{(f)}$ be an operator given in product form. Then the evaluation of the matrix element

$$\begin{aligned} \langle \Psi \,|\, \Omega \,|\, \tilde{\Psi} \rangle \;=\; & \sum_{r=1}^{M} c_r \sum_{j_1} \cdots \sum_{j_f} A^*_{j_1 \ldots j_f} \\ & \times \sum_{l_1} \langle \varphi^{(1)}_{j_1} \,|\, \omega^{(1)}_r \,|\, \tilde{\varphi}^{(1)}_{l_1} \rangle \cdots \sum_{l_f} \langle \varphi^{(f)}_{j_f} \,|\, \omega^{(f)}_r \,|\, \tilde{\varphi}^{(f)}_{l_f} \rangle \tilde{A}_{l_1 \ldots l_f} \end{aligned} \tag{107}$$

becomes very fast, as only one–dimensional integrals are required.

As sums of wavefunctions are not allowed, it is not possible to ($E \leftrightarrow t$) Fourier transform the MCTDH wavefunction. In practice this is no restriction, because the analysis algorithm can be formulated such that only Fourier transforms of matrix elements appear. In fact, it is almost always possible to re–formulate an analysis algorithm such that sums of wavefunctions do not appear. A very simple example may be illustrative. The norm of the difference between two wavefunctions, $\|\, \Psi - \tilde{\Psi} \,\|$, can be evaluated using

$$\|\, \Psi - \tilde{\Psi} \,\|^2 = \|\, \Psi \,\|^2 + \|\, \tilde{\Psi} \,\|^2 - 2\, \mathrm{Re}\, \langle \Psi \,|\, \tilde{\Psi} \rangle \,. \tag{108}$$

The three terms on the right hand side are all of type (107), with $\Omega = 1$.

Using the Heidelberg MCTDH package [96] the auto-correlation, $\langle \Psi(0) \mid \Psi(t) \rangle$, the cross-correlation, $\langle \tilde{\Psi} \mid \Psi(t) \rangle$, and time–dependent expectation values, $\langle \Psi(t) \mid \Omega \mid \Psi(t) \rangle$, may be calculated *on the fly*, i. e. one does not need to store the wavefunction. The correlation functions are then Fourier transformed or filter-analyzed [1–4, 62] to obtain spectra. For more details the reader is referred to the review [15] and the MCTDH User's Guide [97].

5.2 Flux analysis

To determine transition or reaction probabilities of a scattering event one may project the evolved wavepacket onto outgoing asymptotic states. A more efficient way is to determine the quantum flux (or the projected quantum flux) going through a surface which divides interior from asymptotic regions. The flux operator, which measures this quantum flux, is defined as the commutator of the Hamiltonian with a characteristic function of an asymptotic region

$$\hat{F} = i[H, \Theta] \ . \tag{109}$$

In an reactive scattering event there is more than one asymptotic region because there is more than one arrangement channel, but we will not indicate the dependence on the arrangement channel here. For the sake of simplicity we assume that the dividing surface is perpendicular to r, the coordinate of dissociation. Hence

$$\Theta = h(r - r_c) \ , \tag{110}$$

where h denotes the Heaviside-step-function and r_c is the point where the dividing surface cuts the r coordinate. The energy resolved quantum flux is defined as

$$F(E, \Psi) = 2\pi \, \langle\Psi|\delta(H - E)\, \hat{F}\, \delta(H - E)|\Psi\rangle \ , \tag{111}$$

where Ψ is the (initial) state under consideration. For further reference we define the energy distribution of the state Ψ

$$|\,\Delta(E)\,|^2 = \langle\Psi|\delta(H - E)|\Psi\rangle \ . \tag{112}$$

This energy distribution may, e. g., be evaluated by Fourier transform of the autocorrelation function. It can be shown [15, 98] that the flux and the energy distribution are connected trough the reaction probability $R(E)$

$$F(E, \Psi) = |\,\Delta(E)\,|^2 \;\; R(E) \ . \tag{113}$$

This equation was used to determine total, but initial state selected, reaction probabilities and cross–sections [38–41]. However, if there is only one arrangement channel, one finds $R(E) = 1$ and hence $F(E, \Psi) = |\,\Delta(E)\,|^2$. Thus, the evaluation of the (total) flux is in this case just an alternative way to compute the spectrum. However, the flux analysis allows the computation of a partial flux by introducing projectors onto internal fragment states. One merely replaces $\hat{F}$ in Eq. (111) by $P\hat{F}P$, where P denotes such a projector. Note that P commutes with $\hat{F}$, as it does not operate on the dissociative coordinate r. Using this formalism, one may determine the excitation cross-sections of an inelastic scattering event. See Ref. [47] for an example.

To derive working equations for evaluating the flux, we augment the Hamiltonian with a complex absorbing potential (CAP) [99–102]

$$H \rightarrow H - iW \ , \tag{114}$$

where W is a smooth positive function of r that vanishes for $r < r_c$. We replace the δ–functions in Eq. (111) by their Fourier representations and find after some arithmetic [15, 41, 98]

$$F(E, \Psi) = \frac{2}{\pi}\,\mathrm{Re} \int_0^T \left[g_W(\tau) + g_\Theta(\tau)\right] e^{iE\tau} d\tau \,. \tag{115}$$

The correlation functions g_W and g_Θ are defined as

$$g_W(\tau) = \int_0^{T-\tau} \langle \Psi(t) \mid PWP \mid \Psi(t+\tau) \rangle dt \tag{116}$$

and

$$g_\Theta(\tau) = \frac{1}{2}\,\langle \Psi(T-\tau) \mid P\Theta P \mid \Psi(T) \rangle \quad . \tag{117}$$

The symbol T denotes the final propagation time. Integrating the flux over all energies one obtains

$$\int F(E, \Psi)\, dE = 2 \int_0^T \langle \Psi(t) \mid PWP \mid \Psi(t) \rangle\, dt \,+\, \langle \Psi(T) \mid P\Theta P \mid \Psi(T) \rangle \tag{118}$$

which is the sum of the probability annihilated by the CAP and the one still present at time T in the asymptotic region.

Note that g_Θ vanishes for $T \rightarrow \infty$ since $\Psi(T)$ vanishes because of the CAP. Thus g_Θ may be dropped (and, in fact, has been ignored in earlier calculations), but its inclusion [41] makes the flux converge faster with increasing T. The formula for g_Θ allows a vivid interpretation. Assume that one is not using CAPs but is working with very long, almost infinite grids. Then Eqs. (115, 117) tells us that the flux is proportional to the Fourier transform of the autocorrelation function of the wavepacket projected onto the asymptotic region under consideration.

The time–consuming step of the flux analysis is the evaluation of the matrix elements (116). These are fortunately of form (107) and can thus be done efficiently. The flux analysis requires that the wavefunction is stored for several intermediate times. As the MCTDH wavefunction is very compact, it is usual no problem to store hundreds of wavefunctions. For more details on the flux analysis see [15, 41, 98].

Flux analysis of MCTDH wavefunctions has been used to evaluate initial state selected total reaction cross-sections [38–41], and to determine diffraction and rotational state resolved transition probabilities of inelastic molecule–surface scattering [47]. The flux analysis as presented here has also been used by other groups on non–MCTDH wavefunctions, e. g. to study charge–exchange in ion–atom collisions [103]. The present form of flux analysis should not be confused with the flux analysis based on flux–flux–correlation functions [104, 105] and flux eigenstates (although there are some connections). The latter method has been used extensively in the group of U. Manthe to determine reaction rates [48–58].

6 Concluding Remarks and Outlook

Over the last decade, the MCTDH method has established itself as a very efficient and general algorithm for wavepacket propagation studies. Its basic feature is the use of a variational time-dependent basis set that results in an extremely compact wavefunction, with efficient convergence on the exact solution. While it may be applied to study study small systems accurately, the full power of the method is uncovered when turning to large systems. In particular, it is able to provide quantitative results when the primitive basis set cannot fit into memory, and as a result has set a few benchmarks that are outside the capabilities of other methods (for example Refs. [13, 29, 33–35, 65, 66]).

Although MCTDH suffers from the exponential scaling typical of wavepacket propagation methods, the base to which it scales is considerably lower than the base to which the standard method scales. The resources required can be further minimized by the use of combined modes, rather than the one-dimensional single-particle functions used in the early calculations. The effort for the propagation can in this way be balanced between that required for the wavefunction expansion coefficients and that required for the multi-dimensional SPFs. Even so, in typical applications MCTDH will be limited to 15-30 degrees of freedom, although 80 degrees of freedom have been treated for the spin-boson case [65].

There are several strategies to enable MCTDH to go to even larger systems. MCTDH as defined above performs a (time-dependent) full CI in the active space, i.e. the space spanned by the SPFs. Selecting the most important configurations is a way to make MCTDH smaller and faster and thus enabling the treatment of larger systems. This version of MCTDH, called S-MCTDH, has been successfully tested [84]. Another approach tackles the bottleneck provided by the propagation of many-dimensional SPFs. This, the cascading method, recognizes that there is a method capable of propagating wavepackets of several dimensions: MCTDH. Thus, the idea is to use MCTDH to propagate the SPFs of an underlying MCTDH propagation. If cascading works as expected, it is likely that one can treat systems with more than 100 degrees of freedom.

With the extension of the method to density operators in the ρMCTDH algorithm, the advantages of the compact functional form can be brought to use in another field of theoretical chemistry, that dealing with open and mixed systems. This is an area of great importance, dealing with realistic problems past the idealized form of a single pure state represented by a wavefunction. The study of density operators is, however, hampered by the dimensionality of the problem, which at the moment restricts studies to small models far away from systems of chemical interest. It is to be hoped that the application of ρMCTDH here will help to advance this field of research significantly.

Finally, one of the key ingredients for a successful computational method is an efficient and easy to use program. This is particularly true of a difficult to implement algorithm, such as MCTDH. The program we are developing, the Heidelberg MCTDH package, is now used by a number of groups. Details of the program, and how to obtain it, are given in App. A.

7 Acknowledgments

The very first MCTDH program was written by Uwe Manthe as part of his PhD work in Heidelberg. Over the years several graduate students, postdocs and visitors have made contributions to the MCTDH package. We list them in chronological order: A. Jäckle, M. Beck, M. Ehara, M.-C. Heitz, A. Raab, S. Wefing, S. Sukiasyan, C. Cattarius, F. Gatti, and F. Otto. We are very, very grateful to all of them!

HDM would like to thank C. Cattarius for providing the “operate” formulas for density operators and H. Wang for many fruitful discussions on “cascading” during a visit to Berkeley, 2001. H. Wang independently had developed ideas which were very similar to cascading. Last but not least, HDM would like to thank L.S. Cederbaum for his strong support of the MCTDH project.

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

A The Heidelberg MCTDH Package

The Heidelberg MCTDH package is a set of programs for multi-dimensional quantum dynamics, and can do much more than wavefunction (or density operator) propagation using the MCTDH algorithm. For example, numerically exact propagations are also possible using a short-iterative Lanczos integrator. As a by-product of the improved relaxation method, it is also possible to generate a desired eigenfunction of an operator, and for smaller systems the spectrum of a Hamiltonian may be obtained by Lanczos diagonalization of a Hamiltonian in a DVR basis.

The package consists of more than 40 programs, the largest and most important of which is called simply *mctdh*. Using keyword input read from text files, it is able to set up a system using a range of DVRs or FFT for the primitive basis, form an initial wavefunction (density operator), and propagate this wavefunction (density operator) in time. Perhaps one of the most powerful features of the program is that it uses a text input to generate the operator. In fact, if the operator has a simple analytic form, it is often possible to implement it without having to touch the code. Routines coding for more complicated functions can also be linked to the program. If potential functions are not in MCTDH form, there is the *potfit* program to make the transformation. It is also possible to use the CDVR method, or even to use the potential as it is, of course with resulting inefficient propagation. Time-dependent Hamiltonians can also be used.

Other important programs of the package are a set of analysis tools. These include *filter*, which performs a filter analysis of the autocorrelation function, and *flux*, which does the flux analysis. Various programs plot one– and two–dimensional graphs of the wavefunction and the potential energy surface, and simple movies can be made. Other programs can be used to check the convergence of a calculation, generate a spectrum from the autocorrelation function, etc. All plotting uses the freely available Gnuplot program, often driven using interactive menus.

The package consists of more than 200,000 lines of (mainly FORTRAN 77) code. The documentation consists of both on-line documentation (in HTML) the MCTDH User's Guide (in LaTeX). The installation is performed by convenient installation scripts. We have run MCTDH on DEC–alpha, IBM–RS6000, Cray, Sun, Silicon Graphics and HP computers, and in par-

ticular on Linux–PC's. The Heidelberg MCTDH package is available to interested researchers. For more details see:
http://www.pci.uni-heidelberg.de/tc/usr/mctdh/

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