The multi-configuration time-dependent Hartree (MCTDH) algorithm: an efficient method for propagating wavepackets of several dimensions

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The formal derivation of the multi-configuration time-dependent Hartree (MCTDH) method and its performance is briefly discussed and an outlook to possible future developments of MCTDH is given. For a more comprehensive overview on MCTDH see the review article *Physics Reports* **324** (2000) 1.

I. INTRODUCTION

Wavepacket propagation methods are an essential tool for understanding the molecular dynamics underlying many physical phenomena, especially those that occur on an ultrafast (subpicosecond) time scale. The standard method is the numerically exact solution of the time-dependent Schrödinger equation, representing the wavepacket and Hamiltonian in an appropriate basis. The method is however restricted by the numerical resources required, which grow exponentially with the number of degrees of freedom. As a result, studies of systems with more than six degrees of freedom are in general impossible.

In an attempt to remove this obstacle, approximate methods exemplified by the time-dependent Hartree (TDH) method have been developed. Here, the wavefunction is represented as a Hartree product of one-dimensional functions, and as a result the equations of motion for the wavepacket are a set of coupled one-dimensional equations. The effort required is thus significantly reduced, but at the cost that the correlation between the degrees of freedom is no longer treated correctly.

The multiconfiguration time-dependent Hartree (MCTDH) method [1–6] combines the benefits of these two extremes. As the name implies, the wavefunction is described by an expansion in Hartree products (configurations). Using this wavefunction ansatz and solving the time-dependent Schrödinger equation by a variational method leads to a set of coupled equations of motion for the expansion coefficients and for the functions used to build the Hartree products. The latter are known as single-particle functions. In the limit of convergence with respect to the number of configurations included, the results become numerically exact. An important feature of the method is that, due to its variational character, a small set of single-particle functions are in general sufficient to produce good results. The MCTDH equations of motion, while seemingly complex, thus require considerably less effort and memory than the standard method.

The method has been applied successfully to a number of phenomena such as photodissociation [2,7–9] and photo-absorption [4,10–13] spectra, pre-dissociation [14], resonance Raman spectra [15], and reactive [16–25] and molecule-surface [26–31] scattering. To demonstrate the applicability of the method to large systems, it should be mentioned that in one study we have performed a converged calculation on a system with two coupled electronic states and 24 nuclear degrees of freedom [4,10–12]. In a very recent study MCTDH has been applied to the spin-boson problem including 80 degrees of freedom [32].

The MCTDH scheme has recently been extended to propagate density operators [33,34]. First applications [35] proved to be very promising, but here we will not discuss the propagation of density operators any further.

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II. THE MULTI-CONFIGURATION TIME-DEPENDENT HARTREE METHOD

In any basis set based method the infinite-dimensional quantum mechanical Hilbert space is replaced by a numerical one with finite dimension. Assuming that a system has f degrees of freedom described by nuclear coordinates $Q_1, \ldots, Q_f$, this can be accomplished by establishing an $N_1 \times \ldots \times N_f$-dimensional time-independent orthonormal product basis set $\{\chi^{(1)}_{j_1}(Q_1) \ldots \chi^{(f)}_{j_f}(Q_f)\}$.

By expanding the Hamiltonian H in this basis one obtains the matrix representation of H:

$$H_{i_1 \ldots i_f j_1 \ldots j_f} = \langle \chi^{(1)}_{i_1} \ldots \chi^{(f)}_{i_f} \,|\, H \,|\, \chi^{(1)}_{j_1} \ldots \chi^{(f)}_{j_f} \rangle \,. \tag{1}$$

It is the quantum dynamics controlled by this matrix which we want to study. The artifacts possibly introduced by the finite dimensional product basis set (later called primitive basis or primitive grid) are not our present concern. To allow an efficient evaluation of the action of H on the functions $\chi^{(\kappa)}_{j_\kappa}$, one usually chooses them as the basis functions of a discrete variable representation (DVR) [36].

If the wavefunction is also expanded in the product basis set, the time-dependent Schrödinger equation simplifies to a set of equations of motion for the expansion coefficients. Solving these linear differential equations is called the standard, or numerically exact, propagation method.

The disadvantage of the standard propagation method lies in the computational labour, which grows exponentially with the number of degrees of freedom. For f=6 degrees of freedom and N=32 grid points in each degree of freedom one needs 48 GByte to hold three wavefunctions in memory. This makes it clear that the (brute force) standard method is not capable of treating large systems.

In the MCTDH scheme [1–6], one therefore employs a smaller, but now time-dependent, basis, i.e. the *ansatz* for the wavefunction reads

$$\Psi(Q_1, \ldots, Q_f, t) = \sum_{j_1=1}^{n_1} \ldots \sum_{j_f=1}^{n_f} A_{j_1 \ldots j_f}(t) \; \prod_{\kappa=1}^{f} \varphi^{(\kappa)}_{j_\kappa}(Q_\kappa, t) \,, \tag{2}$$

with $n_\kappa < N_\kappa$. Here the $A_{j_1 \ldots j_f}$ denote the MCTDH expansion coefficients and the $\varphi^{(\kappa)}_{j_\kappa}$ are the expansion functions for each degree of freedom, known as single-particle functions. The single-particle functions in turn are represented as linear combinations of the primitive basis

$$\varphi^{(\kappa)}_{j_\kappa}(Q_\kappa, t) = \sum_{i_\kappa=1}^{N_\kappa} c^{(\kappa)}_{i_\kappa \, j_\kappa}(t) \; \chi^{(\kappa)}_{i_\kappa}(Q_\kappa) \,. \tag{3}$$

Since both the coefficients and the single-particle functions are time-dependent, the wavefunction representation (2) is not unique. Uniquely defined equations of motion can be obtained by imposing additional constraints on the single-particle functions [2,3,5,6]. Hereby it can be achieved that initially orthonormal single-particle functions remain orthonormal for all times.

The MCTDH equations of motion are then derived by variationally optimizing the coefficients and single-particle functions employing the Dirac-Frenkel variational principle [37,38] $\langle \delta\Psi \,|\, H - i\,\partial/\partial t \,|\, \Psi \rangle = 0$ (NB we use a unit system with $\hbar = 1$ throughout), subject to the constraints mentioned above.

Before presenting the MCTDH working equations we simplify the notation by establishing the composite index J and the configurations Φ_J:

$$A_J = A_{j_1 \ldots j_f} \qquad \text{and} \qquad \Phi_J = \prod_{\kappa=1}^{f} \varphi^{(\kappa)}_{j_\kappa} \,, \tag{4}$$

and introduce the projector on the space spanned by the single-particle functions for the κth degree of freedom:

$$P^{(\kappa)} = \sum_{j=1}^{n_\kappa} |\, \varphi^{(\kappa)}_j \rangle \langle \varphi^{(\kappa)}_j \,| \;. \tag{5}$$

The *single-hole functions* $\Psi^{(\kappa)}_l$ are defined as the linear combination of Hartree products of $(f-1)$ single-particle functions that do not contain the single-particle functions for the coordinate Q_κ,

$$\Psi_l^{(\kappa)} = \langle \varphi_l^{(\kappa)} \mid \Psi \rangle$$
$$= \sum_J^{\kappa} A_{J_l^\kappa} \, \varphi_{j_1}^{(1)} \dots \varphi_{j_{\kappa-1}}^{(\kappa-1)} \varphi_{j_{\kappa+1}}^{(\kappa+1)} \dots \varphi_{j_f}^{(f)} \,, \tag{6}$$

where in the first line the integration runs only over Q_κ and where in the last line 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 enable us to define the *mean-fields*

$$\langle H \rangle_{jl}^{(\kappa)} = \langle \Psi_j^{(\kappa)} \,|\, H \,|\, \Psi_l^{(\kappa)} \rangle \tag{7}$$

and *density matrices*

$$\rho_{jl}^{(\kappa)} = \langle \Psi_j^{(\kappa)} \,|\, \Psi_l^{(\kappa)} \rangle = \sum_J^{\kappa} A_{J_j^\kappa}^* A_{J_l^\kappa} \,. \tag{8}$$

The MCTDH equations of motion resulting from the Dirac-Frenkel variational principle can be shown [2–6] to read

$$i\dot{A}_J = \sum_L \langle \Phi_J \,|\, H \,|\, \Phi_L \rangle A_L \,, \tag{9}$$

$$i\dot{\varphi}_j^{(\kappa)} = \sum_{lm} \left(1 - P^{(\kappa)}\right) \left(\rho^{(\kappa)^{-1}}\right)_{jl} \langle \mathbf{H} \rangle_{lm}^{(\kappa)} \varphi_m^{(\kappa)} \,. \tag{10}$$

These are the MCTDH equations of motion for the simplest choice of constraints. Slightly different (and sometimes more useful) equations of motion are obtained for alternative choices of constraints. For a further discussion of this point we refer the reader to the literature [2–6]. Due to the variational character of the single-particle basis, they optimally represent the evolving wavefunction, and the wavefunction *ansatz* (2) monotonically converges towards the numerically exact one as n_κ approaches N_κ.

The MCTDH equations of motion are a fairly complicated set of coupled non-linear differential equations. (Note that $\dot{A}$ depends on φ through $\langle \Phi_J \,|\, H \,|\, \Phi_L \rangle$ and $\dot{\varphi}$ depends on A through ρ and $\langle \mathbf{H} \rangle$). However, there are fewer equations as compared to the set of linear differential equations of the standard method. In fact, the number of equations is often smaller by several orders of magnitude. This is what makes MCTDH both small and fast.

III. IMPLEMENTATION AND PERFORMANCE OF THE METHOD

The solution of the MCTDH equations of motion requires the evaluation of the Hamiltonian matrix $\langle \Phi_J \mid H \mid \Phi_L \rangle$ and the mean fields $\langle \mathbf{H} \rangle$ 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 points 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,

$$H = \sum_{r=1}^{s} c_r \prod_{\kappa=1}^{f} h_r^{(\kappa)} \,, \tag{11}$$

with expansion coefficients c_r. Using Eq. (11) the matrix elements can be expanded as

$$\langle \Phi_J \,|\, H \,|\, \Phi_L \rangle = \sum_{r=1}^{s} c_r \prod_{\kappa=1}^{f} \langle \varphi_{j_\kappa}^{(\kappa)} \,|\, h_r^{(\kappa)} \,|\, \varphi_{l_\kappa}^{(\kappa)} \rangle \,, \tag{12}$$

and similarly for the mean fields (see Ref. [6]) Note that only one-dimensional integrals are used now.

The kinetic energy operator normally has the required form (11). 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. [6,39,40].

When the Hamiltonian is given in MCTDH product form and when the MCTDH equations of motion are propagated with the efficient constant mean field (CMF) integrator (see Refs. [3,6]) then there is a useful estimate of the MCTDH advantage over the standard method. The gain factors for memory and CPU-time are:

$$\text{gain(mem)} \approx \frac{1}{4}\left(\frac{N}{n}\right)^{f}, \tag{13}$$

$$\text{gain(CPU)} \approx \frac{1}{2s}\left(\frac{N}{n}\right)^{f+1}. \tag{14}$$

A more careful analysis shows that the expressions n^f and n^{f+1} should be interpreted as $(\prod_\kappa n_\kappa)$ and $f^{-1}(\sum_\kappa n_\kappa)(\prod_\kappa n_\kappa)$, respectively (and similarly for N^f and N^{f+1}). The symbol s denotes the number of Hamiltonian terms (see Eq. (11)). See Ref. [6] for a more comprehensive discussion of the gain-factors.

The expansion of the potential in a product form can be avoided by adopting the correlated DVR (CDVR) of U. Manthe [41]. This uses a time-dependent DVR based on the single-particle functions 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, and our experience with CDVR was rather mixed (see Ref. [6] 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.

Finally, we have to mention two important extensions of the MCTDH method as it is described above. The first one is the use of the multi-set formalism for the treatment of non-adiabatic processes. Here, different sets of single-particle functions are used to describe the wavepacket evolving in the various electronic states. This leads to a much more compact description of the wavefunction for these systems. The second one is the use of combined modes. By combined modes we mean that several degrees of freedom can be combined into a so-called MCTDH-particle. The relevant single-particle functions then describe multi-mode particles rather than a single degree of freedom. Combinations have been proven to be extremely useful when treating large systems (more than six degrees of freedom, say). For a further discussion of both the multi-set formalism and combined modes we refer the reader to Refs. [4,6] and references therein.

IV. CONCLUDING REMARKS AND OUTLOOK

MCTDH is a propagation algorithm suited to treat the quantum molecular dynamics of large systems. Although it has been applied successfully to 3D problems, the full power of MCTDH is uncovered only when turning to large systems, in particular when turning to systems the primitive product grid of which ceases to fit into the memory. On the other hand, MCTDH suffers from exponential scaling, although the base to which it scales is considerably lower than the base to which the standard method scales. In typical applications this will limit MCTDH to 15-30 degrees of freedom, although 80 degrees of freedom have been treated for the spin-boson case [32].

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 single-particle functions. 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 [42].

The use of combined modes has been proven to be very essential when treating large systems. However, when combining several degrees of freedom one has to propagate multi-dimensional single-particle functions. This may become very difficult when one wishes to combine more than three or four degrees of freedom. There are two possible solutions to this problem. In general a large system has several degrees of freedom which exhibit a rather simple dynamics. It may be thus sufficient to describe the motion within these degrees of freedom approximately and we proposed [43] to represent and propagate the corresponding single-particle functions in the spirit of Heller Gaussians [44]. This allows the use of highly combined (10 degrees of freedom, say) single-particle functions. The second possible approach to be mentioned makes use of the fact that there is a method capable of propagating wavepackets of several dimensions: MCTDH. Thus, the idea is to

use MCTDH to propagate the single-particle functions of an underlying MCTDH propagation. We call this approach cascading. If cascading works, it is likely that one can treat systems with more than 100 degrees of freedom.

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