



Multilayer Multiconfiguration Time-Dependent Hartree Theory

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ABSTRACT: Multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) theory is a rigorous and powerful method to simulate quantum dynamics in complex many-body systems. This approach extends the original MCTDH theory of Meyer, Manthe, and Cederbaum to include dynamically contracted layers in a recursive way, within which the equations of motion are determined from the Dirac–Frenkel variational principle. This paper presents the general derivation of the theory and analyzes the important features that make the ML-MCTDH method numerically efficient. Furthermore, we discuss the generalization of the theory to treat many-body identical particles (fermions or bosons) as well as calculating energy eigenstates via the improved relaxation method.

$$\begin{aligned}
 |\Psi(t)\rangle &= \sum_{j_1} \dots \sum_{j_p} A_{j_1 \dots j_p}(t) \prod_{\kappa=1}^p |\varphi_{j_\kappa}^{(\kappa)}(t)\rangle \\
 |\varphi_{j_\kappa}^{(\kappa)}(t)\rangle &= \sum_{i_1} \dots \sum_{i_{Q(\kappa)}} B_{i_1 \dots i_{Q(\kappa)}}^{\kappa, j_\kappa}(t) \prod_{q=1}^{Q(\kappa)} |v_{i_q}^{(\kappa, q)}(t)\rangle \\
 |v_{i_q}^{(\kappa, q)}(t)\rangle &= \sum_{\alpha_1} \dots \sum_{\alpha_{M(\kappa, q)}} C_{\alpha_1 \dots \alpha_{M(\kappa, q)}}^{\kappa, q, i_q}(t) \prod_{\gamma=1}^{M(\kappa, q)} |\xi_{\alpha_\gamma}^{(\kappa, q, \gamma)}(t)\rangle \\
 &\dots
 \end{aligned}$$

I. INTRODUCTION

A central issue in theoretical physical chemistry is the accurate description of many-body quantum effects for complex systems. The task is particularly challenging in the field of chemical reaction dynamics, where the system is often out of equilibrium and many quantum states participate in the overall process. For small gas phase reactions a brute-force approach may be adopted where the total wave function is expanded in static basis functions/configurations that completely span the Hilbert space of the problem (“complete” in a sense of numerical convergence.) Owing to advances in both numerical algorithms and computer technology, considerable progress has been made in the past few decades in carrying out such calculations—from treating 2–4 degrees of freedoms in the 80s of the last century to 10–12 degrees of freedom at present. However, most of the methods developed in this context are not directly applicable to reactions in larger systems. The primary difficulty inherent in these conventional, full configurational approaches is the rapid growth of the number of basis functions versus the size of the system. This “curse of dimensionality” when data are analyzed and organized in high-dimensional spaces is not limited to chemical dynamics but occurs in various other fields, e.g., numerical analysis and data mining. A practical approach to go beyond more than a few degrees of freedom must then follow a different route.

In conventional quantum wave packet methods little attention has been paid to the nature of the problem. Be it strongly correlated or weakly coupled, in classical or quantum regimes, the same strategy is adopted to lay out the full basis functions, followed by the quantum simulation. This seems to be a waste if one considers the possibility of taking advantage of some special forms of the Hamiltonian that often occur in physics and chemistry as well as making valid approximations in appropriate physical regimes. According to this philosophy, current methodology developments for studying reaction

dynamics in more complex systems can be roughly divided into two major classes, approximate and numerically exact. Approaches in the first category include, for example, mixed quantum-classical^{1–12} and semiclassical approaches.^{13–18} The advantages of these approximate methods are their generality and ease of application. In principle, they can be used to treat any form of analytic potential functions or even *ab initio* potential energy surfaces generated on the fly. Therefore, such approaches are becoming increasingly more popular in modern computational chemistry. Another important type of approximate methods is quantum perturbation theory that usually describes the reduced dynamics of a subsystem.^{19–24} Stemming from physics, these approaches usually possess clear physical pictures and require relatively less computation such that they are easily applicable for the purpose of interpreting experimental observations.

The second class of methods concentrate on the numerically exact solution of certain types of problems, e.g., many physical models in condensed phase physics and chemistry. Examples are numerical path integral approaches^{25–29} using the Feynman–Vernon influence functional,³⁰ numerical renormalization group theory,^{31–33} multiconfiguration time-dependent Hartree (MCTDH) theory,^{34–37} and the numerically exact self-consistent hybrid method.^{38–40} Complementary to the approximate approaches, these methods aim at providing accurate results for physically motivated models whose parameters may be obtained from electronic structure calculations, classical molecular dynamics simulations, and/or experiments. Accurate simulations on these model systems may be regarded as “numerical experiments” with reliable results, which is often the first step in developing a general theory for

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describing the underlying processes. It should be noted that approximate methods also use models, e.g., force fields, affordable electronic structure theories, etc. Efforts are made to improve (i) the accuracy of approximate theories or (ii) the flexibility of models in the numerically exact treatment; so that the two classes of theories may converge one day.

The purpose of this Feature Article is to discuss the current state of the numerically exact method we have been developing, multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) theory.⁴¹ This is a method for studying time-dependent quantum dynamics that, on one hand, is a rigorous variational approach and, on the other hand, is very effective such that it is applicable to complex many-body problems with hundreds to thousands of degrees of freedom. The key feature of ML-MCTDH theory is its flexible, hierarchical form of the trial wave function used to construct the variational functional. This has greatly increased the efficiency of a time-dependent variational calculation without any sacrifice of theoretical rigor. Although the form of the wave function in ML-MCTDH was originally proposed on the basis of physical intuition, recent developments in applied mathematics appear to justify this choice. Furthermore, ML-MCTDH theory is readily generalizable to treat systems of identical particles despite the fact that the Hartree (tensor) product form is used to represent a configuration in the calculation. This is achieved by using occupation-number states in the second quantized representation.⁴² Finally, the ML-MCTDH wave function is not limited to quantum dynamics simulations but is also applicable to obtain energy eigenstates and other thermodynamic quantities.^{43–47}

In the following sections major aspects of ML-MCTDH theory will be reviewed. To put it in broader perspective, we first present the conventional basis set approach to time-dependent quantum dynamics from a variational point of view. Second, we go through the derivation of the MCTDH method and analyze its strength over the conventional approach and its bottleneck for treating even more complex systems. Third, we discuss ML-MCTDH theory and its numerical implementation. Fourth, we discuss the generalization of ML-MCTDH to treat systems of identical particles. Then, we illustrate the application of the ML-MCTDH method to calculate energy eigenstates. Finally, we conclude with a discussion of the scaling of ML-MCTDH theory.

II. VARIATIONAL FORMULATION OF WAVE PACKET PROPAGATION

A. Conventional Approach Using Static Configurations. The numerical solution to the time-dependent Schrödinger equation using a basis set approach can be obtained from the Dirac–Frenkel variational principle⁴⁸ (in this paper we use atomic units in which $\hbar = 1$)

$$\langle \delta\Psi(t) | i\hbar \frac{\partial}{\partial t} - \hat{H} | \Psi(t) \rangle = 0 \quad (\text{II.1})$$

In conventional methods the wave function is expanded linearly via a set of numerically complete, time-independent configurations

$$\begin{aligned} |\Psi(t)\rangle &= \sum_{j_1} \sum_{j_2} \dots \sum_{j_f} A_{j_1 j_2 \dots j_f}(t) \prod_{\nu=1}^f |\phi_{j_\nu}^{(\nu)}\rangle \\ &\equiv \sum_J A_J(t) |\Phi_J\rangle \end{aligned} \quad (\text{II.2})$$

where J is multidimensional index that collects all combinations of j_1, j_2, \dots, j_f . Without loss of generality, the basis functions for each dimension can be chosen to be orthonormal (non-orthogonal basis sets can always be brought to orthonormal using, e.g., Löwdin procedure,⁴⁹ or equivalently involving an overlap matrix in the equations of motion)

$$\langle \phi_n^{(\nu)} | \phi_m^{(\nu)} \rangle = \delta_{nm} \quad (\text{II.3a})$$

For the multidimensional problem this results in orthonormal static configurations

$$\langle \Phi_L | \Phi_J \rangle = \delta_{LJ} \quad (\text{II.3b})$$

Because the configurations $|\Phi_J\rangle$ are time-independent, the variation and time derivative of the wave function only operate on the expansion coefficients

$$\delta|\Psi(t)\rangle = \sum_J \delta A_J(t) |\Phi_J\rangle \quad (\text{II.4a})$$

$$\frac{\partial}{\partial t} |\Psi(t)\rangle = \sum_J \dot{A}_J(t) |\Phi_J\rangle \quad (\text{II.4b})$$

which, upon substitution into eq II.1 and application of the orthonormality constraint of eq II.3, gives the standard expression for the equation of motion

$$i\dot{A}_J(t) = \langle \Phi_J | \hat{H} | \Psi(t) \rangle = \sum_L \langle \Phi_J | \hat{H} | \Phi_L \rangle A_L(t) \quad (\text{II.5})$$

Equation II.5 is essentially what is used in all conventional approaches to propagate time-dependent wave packets. In this straightforward but brute-force approach, the number of time-independent configurations grows exponentially versus the number of degrees of freedom. In other words, if there were n basis functions per degree of freedom, expression II.2 would require n^f configurations. One may improve the situation somewhat by, e.g., (i) choosing an appropriate coordinate system to better capture the physics of the problem such that the number of basis functions n is reduced, (ii) applying some a priori criteria to remove physically irrelevant configurations, for example, those that are too high in energy or too far in space, (iii) using a better time propagator to reduce the number of Hamiltonian operations on the wave function, and (iv) employing techniques in applied linear algebra such as the fast Fourier transform (FFT) or sparse matrix-vector multiplication schemes to efficiently handle each Hamiltonian operation on the wave function. However, the fact that the configurations are static in this approach and only the expansion coefficients are varied, which inevitably leads to exponential scaling of the number of variational parameters, prohibits its applicability to larger systems.

The limitation of the simple expansion scheme in eq II.2 can be understood by considering a completely uncorrelated case; that is, there are f separable degrees of freedom. In this case it is well-known that the solution to the time-dependent Schrödinger equation has the form of a Hartree product, $|\Psi(t)\rangle = \prod_{\nu=1}^f |\phi^{(\nu)}(t)\rangle$. Thus, wave function $|\Psi(t)\rangle$ is completely specified by $\sim n \times f$ parameters. However, even in this uncorrelated case, the expansion in II.2 still requires n^f terms, suggesting that most parameters are composite in nature. This example shows that expansion II.2, though formally “correct”, does not exploit any physical simplicity that a given problem may possess. It is then not surprising that such a method is not applicable to complex systems with many degrees of freedom.

Thus, it is natural to consider a more flexible approach to describe dynamics in a reduced, but nevertheless numerically converged, parameter space. From the above simple example a reasonable proposal would be to start from the single Hartree description for the completely uncorrelated dynamics and gradually add more time-dependent configurations as correlation becomes stronger. This is the conceptual basis of the multiconfiguration time-dependent Hartree (MCTDH) approach pioneered by Meyer, Manthe, and Cederbaum.^{34–37}

B. Multiconfiguration Time-Dependent Hartree Theory. Within the MCTDH method^{34–37} for systems of distinguishable particles or for situations where the exchange symmetry of identical particles has been built into the Hamiltonian explicitly, the wave function is expanded in *time-dependent* configurations

$$|\Psi(t)\rangle = \sum_J A_J(t) |\Phi_J(t)\rangle \equiv \sum_J A_J(t) \prod_{\kappa=1}^p |\varphi_J^{(\kappa)}(t)\rangle \quad (\text{II.6})$$

Each configuration $|\Phi_J(t)\rangle$ has the form of a direct or Hartree product of single particle functions (SPFs) $|\varphi_J^{(\kappa)}(t)\rangle$. The major difference between this and the expansion in the conventional approach, eq II.2, is that the configurations (orbitals) are also allowed to vary in the variational procedure. With this ansatz, the Dirac–Frenkel variational principle leads to two separate variations:

$$\langle \delta\Psi(t) | \text{li} \frac{\partial}{\partial t} - \hat{H} | \Psi(t) \rangle_{\text{coefficients}} = 0 \quad (\text{II.7a})$$

$$\langle \delta\Psi(t) | \text{li} \frac{\partial}{\partial t} - \hat{H} | \Psi(t) \rangle_{\text{orbitals}} = 0 \quad (\text{II.7b})$$

where in eq II.7a only the expansion coefficients and in eq II.7b only the orbitals are varied.

Before and after the introduction of the MCTDH method, expansions in the form of eq II.6 have been proposed repeatedly to simulate quantum dynamics in large systems (e.g., a product of coherent states or Gaussians with variational parameters). This is similar to the valence bond or multiconfiguration approaches in early electronic structure theories.⁵⁰ In mathematics, expansion II.6 corresponds to decomposing a tensor of order p . For a second-order ($p = 2$) tensor, i.e., a matrix, eq II.6 is the well-known singular value decomposition (SVD) that has been used extensively in least-squares and data compression. Naturally for $p > 2$ the decomposition is called multilinear or higher order SVD. The specific form of II.6 is called the CANDECOMP–PARAFAC (CP) decomposition.^{51,52} Unfortunately, the CP decomposition does not enforce orthogonality of the configurations $|\Phi_J(t)\rangle$ in eq II.6, and in fact, an orthogonal decomposition in the form of II.6 may not even exist. This presents severe difficulties for carrying out practical simulations. For example, if one substitutes eq II.6 into the Dirac–Frenkel variational principle, one would get a very complicated set of nonlinear differential equations that essentially have no practical use.

Thus, in many situations it is desirable to enforce orthogonality in a tensor decomposition. For this purpose Meyer, Manthe, and Cederbaum^{34,35} proposed a more general form of the wave function to guarantee existence of an orthogonal decomposition,

$$|\Psi(t)\rangle = \sum_{i_1} \sum_{i_2} \dots \sum_{i_p} A_{i_1 i_2 \dots i_p}(t) \prod_{\kappa=1}^p |\varphi_{i_\kappa}^{(\kappa)}(t)\rangle \quad (\text{II.8})$$

That is, the summation is over all combinations of the SPFs $|\varphi_{i_\kappa}^{(\kappa)}(t)\rangle$ for $\kappa = 1, 2, \dots, p$ single particle (SP) groups (an overall order- p tensor). The upper limit in each summation \sum_{i_κ} restricts the subspace spanned by the SPFs $|\varphi_{i_\kappa}^{(\kappa)}(t)\rangle$ in the κ th SP group.

The tensor decomposition in eq II.8 is usually called the Tucker form⁵³ or N-way SVD, which finds a wide range of applications⁵⁴ apart from MCTDH. The expansion has several advantages over eq II.6. First, it allows one to impose orthonormality constraints, which results in MCTDH equations of motion (*vide infra*) that are easy to implement. Another advantage is that it facilitates the multilayer generalization to be discussed later.

Due to the form of the wave function in II.8, the orthogonality can be imposed by requiring additional constraints such that the SPFs are orthonormal at any time

$$\langle \varphi_n^{(\kappa)}(t) | \varphi_m^{(\kappa)}(t) \rangle = \delta_{nm} \quad (\text{II.9})$$

In the form of differential equations, this gives

$$\langle \varphi_n^{(\kappa)}(0) | \varphi_m^{(\kappa)}(0) \rangle = \delta_{nm} \quad (\text{II.10a})$$

$$\langle \varphi_n^{(\kappa)}(t) | \text{li} \frac{\partial}{\partial t} \varphi_m^{(\kappa)}(t) \rangle = \langle \varphi_n^{(\kappa)}(t) | \hat{h}_\kappa | \varphi_m^{(\kappa)}(t) \rangle \quad (\text{II.10b})$$

where \hat{h}_κ is required to be Hermitian but otherwise arbitrary. A different choice may result in different stepsize in time integration but does not affect the quality of the multiconfigurational expansion of the wave function. For simplicity we set $\hat{h}_\kappa = 0$ hereafter. This gives the differential orthonormality condition

$$\langle \varphi_n^{(\kappa)}(0) | \varphi_m^{(\kappa)}(0) \rangle = \delta_{nm} \quad (\text{II.11a})$$

$$\langle \varphi_n^{(\kappa)}(t) | \frac{\partial}{\partial t} \varphi_m^{(\kappa)}(t) \rangle \equiv \langle \varphi_n^{(\kappa)}(t) | \dot{\varphi}_m^{(\kappa)}(t) \rangle = 0 \quad (\text{II.11b})$$

With these constraints, the variations in eq II.7 lead to the MCTDH equations of motion^{34–37}

$$i\dot{A}_J(t) = \langle \Phi_J(t) | \hat{H} | \Psi(t) \rangle = \sum_L \langle \Phi_J(t) | \hat{H} | \Phi_L(t) \rangle A_L(t) \quad (\text{II.12a})$$

$$i\text{li} \dot{\underline{\varphi}}^{(\kappa)}(t) = [1 - \hat{P}^{(\kappa)}(t)] [\hat{\rho}^{(\kappa)}(t)]^{-1} \langle \hat{H}^{(\kappa)}(t) | \underline{\varphi}^{(\kappa)}(t) \rangle \quad (\text{II.12b})$$

Equation II.12a bears some similarity to eq II.5, except that the Hamiltonian matrix $H_{JL}(t) \equiv \langle \Phi_J(t) | \hat{H} | \Phi_L(t) \rangle$ now becomes time-dependent. Equation II.12b describes the time evolution of the SPFs that are not present in the conventional method. Other notations defined in SP space κ are as follows: $|\underline{\varphi}^{(\kappa)}(t)\rangle = \{|\varphi_1^{(\kappa)}(t)\rangle, |\varphi_2^{(\kappa)}(t)\rangle, \dots\}^T$ denotes the column vector of all the SPFs for the κ th SP group, $\langle \hat{H}^{(\kappa)}(t) |$ is the matrix of the mean-field operator, $\hat{\rho}^{(\kappa)}(t)$ is the reduced density matrix,

$$\langle \hat{H}^{(\kappa)}(t) | = \langle \Psi_n^{(\kappa)}(t) | \hat{H} | \Psi_m^{(\kappa)}(t) \rangle \quad (\text{II.13a})$$

$$\rho_{nm}^{(\kappa)}(t) = \langle \Psi_n^{(\kappa)}(t) | \Psi_m^{(\kappa)}(t) \rangle \quad (\text{II.13b})$$

and $P^{(\kappa)}(t)$ is the single particle space projection operator,

$$P^{(\kappa)}(t) = \sum_m |\varphi_m^{(\kappa)}(t)\rangle \langle \varphi_m^{(\kappa)}(t)| \quad (\text{II.14})$$

In the expressions above, the single hole function $|\Psi_n^{(\kappa)}(t)\rangle$ is defined as^{34–37}

$$|\Psi_n^{(\kappa)}(t)\rangle = \sum_{j_1} \dots \sum_{j_{k-1}} \sum_{j_{k+1}} \dots \sum_{j_p} A_{j_1 \dots j_{k-1} n_{j_{k+1}} \dots j_p}(t) \prod_{\lambda \neq \kappa}^p |\varphi_{j_\lambda}^{(\lambda)}(t)\rangle \quad (\text{II.15a})$$

so that

$$|\Psi(t)\rangle = \sum_n |\varphi_n^{(\kappa)}(t)\rangle |\Psi_n^{(\kappa)}(t)\rangle \quad (\text{II.15b})$$

One may solve the above coupled ordinary differential equations (ODEs) II.12a and II.12b simultaneously using any ODE integrator or an integrator specifically tailored to MCTDH.^{34–37,55} In practice, a few technical improvements can be made to enhance the efficiency and reliability of the method. First, it is customary to subtract the expectation energy $\bar{E} = \langle \Psi | \hat{H} | \Psi \rangle$ from the Hamiltonian. This removes the irrelevant phase oscillation in the time evolution and does not alter any physical quantity evaluated using both bra and ket. Second, the time-dependent projection operator $1 - \hat{P}^{(\kappa)}(t)$ keeps the SPFs orthonormal at all time. However, a naive implementation does not serve this purpose due to numerical roundoff error.³⁶ Motivated by a trick used in numerical Gram–Schmidt orthogonalizations,⁵⁶ a mathematically equivalent form

$$[1 - \hat{P}^{(\kappa)}(t)]^2 = [1 - \hat{P}^{(\kappa)}(t)] \quad (\text{II.16})$$

can be used in eq II.12b to remedy the deficiency. Third, $[\hat{P}^{(\kappa)}(t)]^{-1}$ denotes a regularized pseudoinverse. It casts the implicit equations for the SPFs

$$i \sum_m \rho_{nm}^{(\kappa)}(t) |\dot{\varphi}_m^{(\kappa)}(t)\rangle = [1 - \hat{P}^{(\kappa)}(t)] \sum_m \langle \hat{H} \rangle_{nm}^{(\kappa)}(t) |\varphi_m^{(\kappa)}(t)\rangle \quad (\text{II.17})$$

in the form of eq II.12b, which is based on the variation of the SPFs

$$\begin{aligned} i \langle \delta \varphi_n^{(\kappa)}(t) | \sum_m \rho_{nm}^{(\kappa)}(t) |\dot{\varphi}_m^{(\kappa)}(t)\rangle \\ = \langle \delta \varphi_n^{(\kappa)}(t) | [1 - \hat{P}^{(\kappa)}(t)] \sum_m \langle \hat{H} \rangle_{nm}^{(\kappa)}(t) |\varphi_m^{(\kappa)}(t)\rangle \end{aligned} \quad (\text{II.18})$$

The pseudoinverse needs to be handled with care. Even though some redundant SPFs do not contribute to the wave function initially, they need to be updated quickly to make contributions later.

The MCTDH expansion in eq II.8 resembles the full configurational expression in eq II.2. As a result, the overall number of time-dependent configurations still scales exponentially versus the total number of SP groups p . The reason why MCTDH is a significant improvement is 2-fold: (i) the required number of dynamically optimized SPFs in MCTDH is usually much smaller than the number of static basis functions in the conventional approach and (ii) an SP group may combine several physical degrees of freedom so that the number of SP groups (p) is usually much less than the dimensionality of the problem (f). This renders the overall computational effort in MCTDH increase more slowly as the number of degrees of freedom increases. Therefore, the MCTDH method is able to handle quite large molecular systems in a numerically

converged fashion.^{38,39,41,57–69} From its design, MCTDH recovers the single Hartree limit naturally for an uncorrelated system and systematically requires more configurations as correlation become stronger.

In MCTDH, the SPFs still need to be expressed by some primitive basis functions. Much the same as in the conventional approach, this is done by performing another multidimensional expansion in an SP subspace

$$\begin{aligned} |\varphi_n^{(\kappa)}(t)\rangle &= \sum_I B_I^{\kappa,n}(t) |u_I^\kappa\rangle \\ &\equiv \sum_{i_1} \sum_{i_2} \dots \sum_{i_{F(\kappa)}} B_{i_1 i_2 \dots i_{F(\kappa)}}^{\kappa,n}(t) \prod_{q=1}^{F(\kappa)} |\varphi_{i_q}^{\kappa,q}\rangle \end{aligned} \quad (\text{II.19})$$

where $F(\kappa)$ specifies the number of Cartesian degrees of freedom in the κ th SP group, such that $\sum_{\kappa=1}^p F(\kappa) = f$, and $|\varphi_{i_q}^{\kappa,q}\rangle$ denotes a (time-independent) primitive basis function for the q th coordinate in this SP. That is, we are using conventional approach to express each SPF. The full configurational-type expansion of the SPFs in eq II.19 is usually limited to a few (~ 10) degrees of freedom, and the multiconfigurational expansion of the wave function in eq II.8 typically has less than ten SP groups. Therefore, most MCTDH applications are limited to systems with a few tens of degrees of freedom (which is already much beyond the conventional approach). Sometimes further improvement is possible by employing static basis set contraction techniques,^{38,39,41,60,66,67} but that only brings the limit of the MCTDH method to treat ~ 100 degrees of freedom.

ML-MCTDH theory⁴¹ successfully circumvents the bottleneck of the MCTDH method by using a hierarchical, dynamic contraction of the basis functions that constitute the original SPFs. This gives a flexible representation of the overall wave function and opens up new avenues for significantly increasing the number of degrees that can be treated by a numerically exact simulation method.

C. Multilayer Formulation of Multiconfiguration Time-Dependent Hartree Theory. Within the original MCTDH approach, the SPFs are expressed in static primitive basis functions and the variation terminates at this level. However, things do not have to stop here. Instead, each SPF $|\varphi_{j_\kappa}^{(\kappa)}(t)\rangle$ can again go through a time-dependent multiconfiguration expansion, creating another level in the hierarchy. That is, the full configurational-type expression of an SPF in eq II.19 is replaced by another *time-dependent* multiconfigurational expansion in the Tucker format

$$\begin{aligned} |\varphi_n^{(\kappa)}(t)\rangle &= \sum_I B_I^{\kappa,n}(t) |u_I^\kappa(t)\rangle \\ &\equiv \sum_{i_1} \sum_{i_2} \dots \sum_{i_{Q(\kappa)}} B_{i_1 i_2 \dots i_{Q(\kappa)}}^{\kappa,n}(t) \prod_{q=1}^{Q(\kappa)} |v_{i_q}^{\kappa,q}(t)\rangle \end{aligned} \quad (\text{II.20})$$

One may use arguments similar to those in MCTDH to show that this is an optimal choice because it essentially uses MCTDH to handle each SPF. This hierarchy can be continued to include an arbitrary number of layers. We thus named this approach multilayer MCTDH or ML-MCTDH.⁴¹ Below we derive the equations of motion for a two-layer implementation and then extend the derivation to infinite layers using mathematical induction. For notation purposes, we refer the

SP introduced previously as the level one (L1) SP. Each L1-SP then contains several level two (L2) SPs, and each L2-SP contains several level 3 (L3) SPs, and so on. Combining eq II.8 for the L1 expansion of the wave function $|\Psi(t)\rangle$ and eq II.20 for the L2 expansion of an L1-SP function $|\varphi_n^{(\kappa)}(t)\rangle$, the overall wave function for the two-layer ML-MCTDH reads

$$|\Psi(t)\rangle = \sum_{j_1} \sum_{j_2} \dots \sum_{j_p} A_{j_1 j_2 \dots j_p}(t) \times \prod_{\kappa=1}^p \left[\sum_{i_1} \sum_{i_2} \dots \sum_{i_{Q(\kappa)}} B_{i_1 i_2 \dots i_{Q(\kappa)}}^{\kappa, j_\kappa}(t) \prod_{q=1}^{Q(\kappa)} |v_{i_q}^{(\kappa, q)}(t)\rangle \right] \quad (\text{II.21})$$

where $Q(\kappa)$ is the number of L2-SP groups in the κ th L1-SP group and $|v_{i_q}^{(\kappa, q)}(t)\rangle$ denotes an L2-SPF in the q th L2-SP group. Both are contained within the upper κ th L1-SP group. Now the Dirac–Frenkel variational principle can be separated into three parts for the overall wave function

$$\langle \delta \Psi(t) | i \frac{\partial}{\partial t} - \hat{H} | \Psi(t) \rangle_{\text{top coefficients}} = 0 \quad (\text{II.22a})$$

$$\langle \delta \Psi(t) | i \frac{\partial}{\partial t} - \hat{H} | \Psi(t) \rangle_{\text{L1 SPFs}} = 0 \quad (\text{II.22b})$$

$$\langle \delta \Psi(t) | i \frac{\partial}{\partial t} - \hat{H} | \Psi(t) \rangle_{\text{L2 SPFs}} = 0 \quad (\text{II.22c})$$

That is variation with respect to the L1 expansion coefficients $A_j(t)$ in eq II.6, variation with respect to the L2 expansion coefficients $B_i^{\kappa, n}(t)$ in eq II.20, and variation of the L2-SPFs $|v_{i_q}^{(\kappa, q)}(t)\rangle$ in eq II.20. The first two have already been obtained when the MCTDH equations of motion, eqs II.12a and II.12b, were derived

$$i \dot{A}_j(t) = \sum_L \langle \Phi_j(t) | \hat{H} | \Phi_L(t) \rangle A_L(t) \quad (\text{II.23a})$$

$$i \dot{\underline{\varphi}}^{(\kappa)}(t) \rangle_{\text{L2 coefficients}} = [1 - \hat{P}^{(\kappa)}(t)] [\hat{\rho}^{(\kappa)}(t)]^{-1} \langle \hat{H} \rangle^{(\kappa)}(t) | \underline{\varphi}^{(\kappa)}(t) \rangle \quad (\text{II.23b})$$

For simplicity we use a short-hand notation such that the overhead dot on the left-hand side of eq II.23b means that the time derivative is only taken with respect to the L2 expansion coefficients $B_i^{\kappa, n}$ and does not act on the L2 configuration $|u_i^{\kappa}(t)\rangle = \prod_{q=1}^{Q(\kappa)} |v_{i_q}^{(\kappa, q)}(t)\rangle$ in eq II.20. In ML-MCTDH the configurations $|\Phi_j(t)\rangle$, the Hamiltonian matrix $H_{jL}(t) = \langle \Phi_j(t) | \hat{H} | \Phi_L(t) \rangle$, the L1 mean-field operator $\langle \hat{H} \rangle^{(\kappa)}(t)$, and the L1-SPFs $|\underline{\varphi}^{(\kappa)}(t)\rangle$, all depend on the L2-SPFs $|v_{i_q}^{(\kappa, q)}(t)\rangle$. Therefore, they need explicit reference to the bottom layer SPFs and primitive basis functions and are more complicated to construct than in the original single-layer MCTDH method.

To perform variation of the L2-SPFs, we can define L2 single hole functions $|g_{n,r}^{(\kappa, q)}(t)\rangle$ analogous to those in eq II.15,

$$|\varphi_n^{(\kappa)}(t)\rangle = \sum_r |v_r^{(\kappa, q)}(t)\rangle |g_{n,r}^{(\kappa, q)}(t)\rangle \quad (\text{II.24})$$

Different from the original MCTDH notation, an L2 hole function $|g_{n,r}^{(\kappa, q)}(t)\rangle$ is related to a particular L1-SPF $|\varphi_n^{(\kappa)}(t)\rangle$ and thus depends on the index n , but the L2-SPFs $|v_r^{(\kappa, q)}(t)\rangle$ are the same for all the L1-SPFs in SP group κ and do not depend on n . Imposing the same orthonormal constraints for the L2-SPFs as done previously, cf. eq II.11

$$\langle v_r^{(\kappa, q)}(0) | v_s^{(\kappa, q)}(0) \rangle = \delta_{rs} \quad (\text{II.25a})$$

$$\langle v_r^{(\kappa, q)}(t) | \frac{\partial}{\partial t} v_s^{(\kappa, q)}(t) \rangle \equiv \langle v_r^{(\kappa, q)}(t) | \dot{v}_s^{(\kappa, q)}(t) \rangle = 0 \quad (\text{II.25b})$$

we obtain a similar orthonormality condition for the L2 configurations

$$\langle u_L^{\kappa}(0) | u_J^{\kappa}(0) \rangle = \delta_{LJ} \quad (\text{II.25c})$$

$$\langle u_L^{\kappa}(t) | \dot{u}_J^{\kappa}(t) \rangle = 0 \quad (\text{II.25d})$$

For ML-MCTDH with two layers, each L2-SPF is expanded in static configurations in the form of time-independent Hartree products

$$|v_r^{(\kappa, q)}(t)\rangle = \sum_{\alpha} C_{\alpha}^{\kappa, q, r}(t) |w_{\alpha}^{\kappa, q}\rangle \\ \equiv \sum_{\alpha_1} \sum_{\alpha_2} \dots \sum_{\alpha_{M(\kappa, q)}} C_{\alpha_1 \alpha_2 \dots \alpha_{M(\kappa, q)}}^{\kappa, q, r}(t) \prod_{\tau=1}^{M(\kappa, q)} |\phi_{\alpha_{\tau}}^{\kappa, q, r}\rangle \quad (\text{II.26})$$

where $M(\kappa, q)$ denotes the dimensionality for the q th L2-SP group under the κ th L1-SP group, and $|\phi_{\alpha_{\tau}}^{\kappa, q, r}\rangle$ denotes the α_{τ} th primitive basis function for the r th degree of freedom within this particular L2-SP group. Variation of the L2-SPFs $|\delta v_r^{(\kappa, q)}(t)\rangle$ leads to the implicit working equation as⁴¹

$$i \sum_s \mathbf{Q}_{rs}^{\kappa, q}(t) |v_s^{(\kappa, q)}(t)\rangle = (1 - \hat{P}_{L2}^{\kappa, q}(t)) \sum_s \langle \hat{H}(t) \rangle_{rs}^{\kappa, q} |v_s^{(\kappa, q)}(t)\rangle \quad (\text{II.27})$$

where the overhead dot again denotes a time derivative with respect to the coefficient $C_{\alpha}^{\kappa, q, r}(t)$. Similar to eq II.23b an explicit form of the equation is given as

$$i \dot{\underline{v}}^{(\kappa, q)}(t) \rangle = [1 - \hat{P}_{L2}^{(\kappa, q)}(t)] [\hat{\mathbf{Q}}^{(\kappa, q)}(t)]^{-1} \langle \hat{H} \rangle^{(\kappa, q)}(t) | \underline{v}^{(\kappa, q)}(t) \rangle \quad (\text{II.28})$$

Again, $\underline{v}^{(\kappa, q)}(t) \rangle = \{|v_1^{(\kappa, q)}(t)\rangle, |v_2^{(\kappa, q)}(t)\rangle, \dots\}^T$ is the column vector of (the expansion coefficients of) all the L2-SPFs in (κ, q) and $\hat{P}_{L2}^{(\kappa, q)}(t) \equiv \sum_i |v_i^{(\kappa, q)}(t)\rangle \langle v_i^{(\kappa, q)}(t)|$ the projection operator in the same L2-SP subspace. The second-layer reduced density matrices and mean-field operators are given with the aid of the second-layer hole functions in eq II.24 and the first-layer reduced density matrices and mean-field operators are given in eq II.13

$$\mathbf{Q}_{rs}^{(\kappa, q)}(t) = \sum_n \sum_m \rho_{nm}^{(\kappa)}(t) \langle g_{n,r}^{(\kappa, q)}(t) | g_{m,s}^{(\kappa, q)}(t) \rangle \quad (\text{II.29a})$$

$$\langle \hat{H} \rangle_{rs}^{(\kappa, q)}(t) = \sum_n \sum_m \langle g_{n,r}^{(\kappa, q)}(t) | \langle \hat{H} \rangle_{nm}^{(\kappa)}(t) | g_{m,s}^{(\kappa, q)}(t) \rangle \quad (\text{II.29b})$$

Thus, the explicit equations of motion for the two-layer ML-MCTDH are given by eqs II.23a, II.23b, and II.28. One immediately realizes that the equation for the expansion coefficients of the second-layer SPFs, eq II.28, has exactly the same form as that for the first layer, eq II.23b. This motivates us to generalize ML-MCTDH to another layer by replacing the static basis configuration $|w_{\alpha}^{\kappa, q}\rangle$ in eq II.26 with the *time-dependent* configuration $|w_{\alpha}^{\kappa, q}(t)\rangle$, which introduces the third layer. This process can be recursively carried out to include an arbitrary number of layers, i.e.,

$$|\Psi(t)\rangle = \sum_{j_1} \sum_{j_2} \dots \sum_{j_p} A_{j_1 j_2 \dots j_p}(t) \prod_{\kappa=1}^p |\varphi_{j_\kappa}^{(\kappa)}(t)\rangle \quad (\text{II.30a})$$

$$|\varphi_{j_\kappa}^{(\kappa)}(t)\rangle = \sum_{i_1} \sum_{i_2} \dots \sum_{i_{Q(\kappa)}} B_{i_1 i_2 \dots i_{Q(\kappa)}}^{\kappa, j_\kappa}(t) \prod_{q=1}^{Q(\kappa)} |v_{i_q}^{(\kappa, q)}(t)\rangle \quad (\text{II.30b})$$

$$|v_{i_q}^{(\kappa, q)}(t)\rangle = \sum_{\alpha_1} \sum_{\alpha_2} \dots \sum_{\alpha_{M(\kappa, q)}} C_{\alpha_1 \alpha_2 \dots \alpha_{M(\kappa, q)}}^{\kappa, q, i_q}(t) \prod_{\gamma=1}^{M(\kappa, q)} |\xi_{\alpha_\gamma}^{(\kappa, q, \gamma)}(t)\rangle \quad (\text{II.30c})$$

...

and the equations of motion can be derived the same way as above for the two layer case using mathematical induction^{41,70}

$$i\hbar \dot{|\Psi(t)\rangle}_{L1 \text{ coefficients}} = \hat{H}(t)|\Psi(t)\rangle \quad (\text{II.31a})$$

$$i\hbar \dot{|\underline{\varphi}^{(\kappa)}(t)\rangle}_{L2 \text{ coefficients}} = [1 - \hat{P}^{(\kappa)}(t)][\hat{\rho}^{(\kappa)}(t)]^{-1} \langle \hat{H}^{(\kappa)}(t) | \underline{\varphi}^{(\kappa)}(t) \rangle \quad (\text{II.31b})$$

$$i\hbar \dot{|\underline{v}^{(\kappa, q)}(t)\rangle}_{L3 \text{ coefficients}} = [1 - \hat{P}_{L2}^{(\kappa, q)}(t)][\hat{\rho}_{L2}^{(\kappa, q)}(t)]^{-1} \langle \hat{H}_{L2}^{(\kappa, q)}(t) | \underline{v}^{(\kappa, q)}(t) \rangle \quad (\text{II.31c})$$

$$i\hbar \dot{|\underline{\xi}^{(\kappa, q, \gamma)}(t)\rangle}_{L4 \text{ coefficients}} = [1 - \hat{P}_{L3}^{(\kappa, q, \gamma)}(t)][\hat{\rho}_{L3}^{(\kappa, q, \gamma)}(t)]^{-1} \langle \hat{H}_{L3}^{(\kappa, q, \gamma)}(t) | \underline{\xi}^{(\kappa, q, \gamma)}(t) \rangle \quad (\text{II.31d})$$

...

where the reduced density matrices and mean-field operators are recursively defined as

$$\rho_{L2;rs}^{(\kappa, q)}(t) = \sum_n \sum_m \rho_{nm}^{(\kappa)}(t) \langle g_{L2;n,r}^{(\kappa, q)}(t) | g_{L2;m,s}^{(\kappa, q)}(t) \rangle \quad (\text{II.32a})$$

$$\rho_{L3;rs}^{(\kappa, q, \gamma)}(t) = \sum_n \sum_m \rho_{L2;nm}^{(\kappa, q)}(t) \langle g_{L3;n,r}^{(\kappa, q, \gamma)}(t) | g_{L3;m,s}^{(\kappa, q, \gamma)}(t) \rangle \quad (\text{II.32b})$$

...

$$\langle \hat{H}_{L2;rs}^{(\kappa, q)}(t) \rangle = \sum_n \sum_m \langle g_{L2;n,r}^{(\kappa, q)}(t) | \langle \hat{H}^{(\kappa)}(t) \rangle_{nm} | g_{L2;m,s}^{(\kappa, q)}(t) \rangle \quad (\text{II.33a})$$

$$\langle \hat{H}_{L3;rs}^{(\kappa, q, \gamma)}(t) \rangle = \sum_n \sum_m \langle g_{L3;n,r}^{(\kappa, q, \gamma)}(t) | \langle \hat{H}^{(\kappa)}(t) \rangle_{L2;nm} | g_{L3;m,s}^{(\kappa, q, \gamma)}(t) \rangle \quad (\text{II.33b})$$

...

as well as the SP-space projection operators for different layers

$$P^{(\kappa)}(t) = \sum_n |\varphi_n^{(\kappa)}(t)\rangle \langle \varphi_n^{(\kappa)}(t)| \quad (\text{II.34a})$$

$$\hat{P}_{L2}^{(\kappa, q)}(t) = \sum_n |v_n^{(\kappa, q)}(t)\rangle \langle v_n^{(\kappa, q)}(t)| \quad (\text{II.34b})$$

$$\hat{P}_{L3}^{(\kappa, q, \gamma)}(t) = \sum_n |\xi_n^{(\kappa, q, \gamma)}(t)\rangle \langle \xi_n^{(\kappa, q, \gamma)}(t)| \quad (\text{II.34c})$$

...

As indicated above, we have used the subscripts “L2”, “L3”, ... to denote the second, the third, and so on layers. Again, the short-hand notation used in eq II.31 follows the convention that an overhead dot means the time derivative on the left-hand side only operates on the expansion coefficients of a particular layer (denoted by the respective subscript). For example, the time derivative in eq II.31a operates only on the L1 expansion coefficients $A_{j_1 j_2 \dots j_p}(t)$, the time derivatives in eq II.31b are on the L2 expansion coefficients $B_{i_1 i_2 \dots i_{Q(\kappa)}}^{\kappa, j_\kappa}(t)$, and so on. The multilayer hierarchy terminates at the deepest level by expressing the SPFs in this layer in terms of static configurations. For an N -layer version, there are $N + 1$ levels of expansion coefficients because the SPFs in the deepest layer need to be expanded in time-independent basis functions/configurations. In this sense, the conventional wave packet propagation method is a “zero-layer” ML-MCTDH approach. (We note that in the work of Manthe et al.^{44–46,89–97} or Meyer et al.^{98–103} $L = 1$ is defined for the conventional wave packet method, whereas for MCTDH it is considered a “two-layer” approach, $L = 2$.)

Implementation of the ML-MCTDH approach follows a systematic streamlined procedure. On one hand, different pieces of the Hamiltonian in eq II.31 are built from the deepest layer L ; i.e., they are expressed in matrix representation within the time-independent primitive basis functions. These fundamental pieces of operators are gathered to build the Hamiltonian operators for the next level up ($L - 1$), in which the operators are in matrix representation with time-dependent SPFs as basis sets. This process goes on until the top layer is reached and the complete expansion of eq II.30 has been exhausted. This procedure is thus a “bottom-up” one. On the other hand, relations in eq II.32 suggest that reduced density matrices are built from the top layer first using the A coefficients and are recursively processed to the second layer, the third layer, ..., until reaching the deepest layer. This procedure is “top-down”.

The matrices of mean-field operators (eq II.33) contain information on both Hamiltonian operators and reduced density matrices at all levels. Thus, the procedure is a combination of the above two. One needs to use the bottom-up procedure to build the operator parts first and then express the matrix part together with the reduced density matrices according to the top-down procedure. Along the way time derivatives of the SPFs at all levels are obtained.

The introduction of the recursive, dynamically optimized layering scheme in the ML-MCTDH wave function provides a great deal of flexibility in the trial wave function, which results in a tremendous gain in one's ability to study large many-body quantum systems. This is demonstrated by many applications on simulating quantum dynamics of ultrafast electron transfer reactions in condensed phases.^{71–87} The ML-MCTDH work of Manthe has introduced an even more adaptive formulation based on a layered correlation discrete variable representation (CDVR).^{43,88} This important development potentially extends the applicability of ML-MCTDH theory to rather general systems described by a general form of the potential energy surface. ML-MCTDH has also been implemented in the popular Heidelberg MCTDH program package. The theory has been used extensively for studying polyatomic systems by Manthe and co-workers^{44–46,89–97} as well as Meyer and co-workers.^{98–103}

The form of the ML-MCTDH wave function in eq II.30 has also received much attention recently in applied mathe-

matics.¹⁰⁴ A generalization of the Tucker format for the tensor decomposition (that corresponds to the original MCTDH form), this type of expansion is naturally called the hierarchical Tucker form. It is also a more general form of the tree Tucker format, the tensor train format, or the sequential unfolding SVD. These names have been discussed in the literature¹⁰⁴ and have been shown to be identical or very similar to the earlier proposal of the ML-MCTDH expansion.⁴¹

III. MULTILAYER MULTICONFIGURATION TIME-DEPENDENT HARTREE THEORY IN SECOND QUANTIZATION REPRESENTATION

Despite its previous success, the original ML-MCTDH method was not directly applicable to studying systems of identical particles. This is because a Hartree product in the first quantized picture is only suitable to describe a configuration for a system of distinguishable particles. To handle systems of identical particles explicitly, additional constraints need to be imposed because the exchange symmetry is not accounted for in the Schrödinger equation or the Dirac–Frenkel variational principle. One strategy is to employ a properly symmetrized wave function, i.e., Slater determinants in a fermionic case or permanents in a bosonic case. This led to the MCTDHF^{105–107} and MCTDHB approaches¹⁰⁸ as well as their combinations.¹⁰⁹ However, this wave function-based symmetrization restricts the form of the tensor decomposition, which is only applicable to single layer MCTDH theory but is incompatible with ML-MCTDH—there is no obvious counterpart of a recursive, multilayer formulation if permanents/determinants are used to expand the wave function. As a result, the ability to treat much larger quantum systems numerically exactly was severely limited.

To overcome this limitation, we proposed a novel approach⁴² that follows a fundamentally different route to tackle quantum dynamics of identical particles—an operator-based method that employs the second quantization formalism of many-particle quantum theory. In the new approach the variation is carried out entirely in the abstract Fock space represented by the occupation number states. Thereby the burden of maintaining symmetries of indistinguishable particles in a variational calculation is completely shifted from wave functions to the algebraic properties of operators. As a result, the form of the Hartree product is retained, which makes ML-MCTDH theory formally complete. This unified ML-MCTDH theory has been developed over the past few years and has seen promising applications.^{110–114}

ML-MCTDH theory in the second quantized picture can be formulated for both bosons and fermions, with the latter being more difficult. Thus, we illustrate the procedure by considering a system of identical fermions. In the first quantized representation a Slater determinant $|\chi_{P_1}\chi_{P_2}\dots\chi_{P_N}\rangle$ describes an antisymmetric N -particle state by choosing N spin-orbitals out of the M orthonormal spin-adapted basis functions, $\{\chi_1(\mathbf{x}), \chi_2(\mathbf{x}), \dots, \chi_M(\mathbf{x})\}$. All possible Slater determinants in this form constitute the fermionic subspace of the N -particle Hilbert space, denoted by $H(M, N)$. The Fock space $F(M)$ is formed by considering an arbitrary number of particles up to M

$$F(M) = \mathcal{H}(M, 0) \oplus \mathcal{H}(M, 1) \oplus \mathcal{H}(M, 2) \oplus \dots \oplus \mathcal{H}(M, M) \quad (\text{III.1})$$

In second quantization a standard basis to represent the Fock space is the occupation number state

$$|\mathbf{n}\rangle \equiv |n_1, n_2, \dots, n_M\rangle \quad (\text{III.2})$$

where n_p can be either 1 if the one-particle state χ_p is occupied (i.e., appear in the original Slater determinant) or 0 if it is unoccupied (i.e., absent in the determinant). The total number of particles in $|\mathbf{n}\rangle$ is obtained by a simple sum $N = \sum_{p=1}^M n_p$. Thus, $H(M, N)$ contains all possible occupation-number states with N particles. Each of them is defined by acting a series of creation operators a_p^\dagger on the vacuum state, $|\mathbf{n}\rangle = \prod_{p=1}^M (a_p^\dagger)^{n_p} |\text{vac}\rangle$.

In contrast to a Slater determinant, an occupation-number state $|\mathbf{n}\rangle$ can be formally written as a Hartree product,¹¹⁵

$$|\mathbf{n}\rangle = \prod_{p=1}^M |n_p\rangle \equiv |n_1\rangle |n_2\rangle \dots |n_M\rangle \quad (\text{III.3})$$

One may then decompose the Fock space into M two-level subspaces

$$F(M) = f_1(1) \otimes f_2(1) \otimes \dots \otimes f_k(1) \otimes \dots \otimes f_M(1) \quad (\text{III.4a})$$

where $f_k(1)$ represents a single spin-orbital subspace with two possibilities/states: occupied or unoccupied. Bigger subspaces can be formed by grouping a few spin-orbitals together

$$F(M) = f_1(m_1) \otimes f_2(m_2) \otimes \dots \otimes f_k(m_k) \otimes \dots \otimes f_L(m_L) \\ M = \sum_{k=1}^L m_k \quad (\text{III.4b})$$

where $f_k(m_k)$ is a composite subspace with m_k spin-orbitals and has 2^{m_k} states.

The decomposition schemes in eqs III.4a and III.4b are conceptually different from that in eq III.1. The aim is no longer at handling an occupation-number vector in one step and treating it as a whole, unbreakable object like the original Slater determinant, but rather dealing with each subspace $f_k(m_k)$ defined by 2^{m_k} basis subvectors $\{\phi_{I_k}^{(k)}\}$, $I_k = 1, \dots, 2^{m_k}$. Although one may still link an occupation-number vector to these subvectors in the form of Hartree product

$$|\mathbf{n}\rangle = \prod_{k=1}^L |\phi_{I_k}^{(k)}\rangle \quad (\text{III.5})$$

this is hardly useful because most systems are correlated and the wave function cannot be expressed by only one occupation-number vector (single determinant in the first quantized picture). Instead, the wave function should be represented by a multiconfiguration expansion. The crucial point is that in a variational calculation each subvector in the k th subspace does not have to be one of these fixed basis vectors $\{\phi_{I_k}^{(k)}\}$ but may be a superposition of all of them. One may then express the overall wave function in the same multilayer form as in eq II.30. Take, for example, three explicit layers in eq II.30. An SPF in the deepest layer (third layer here) is expanded via such subvectors as

$$|\xi_{\alpha_\gamma}^{K, q, \gamma}(t)\rangle \\ = \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \sum_{n_{m(K, q, \gamma)}=0}^1 D_{n_1 n_2 \dots n_{m(K, q, \gamma)}}^{K, q, \gamma, \alpha_\gamma}(t) |n_1\rangle |n_2\rangle \dots |n_{m(K, q, \gamma)}\rangle \quad (\text{III.6})$$

This is much the same as in the ML-MCTDH approach described in the previous section where $|\Psi(t)\rangle$ in eq II.30 is built hierarchically from the optimal, time-dependent SPFs of the layered subspaces. All the machinery developed in ML-MCTDH theory can then be applied.

The real situation is slightly more complicated for fermions because the notion of an occupation-number state as a Hartree product is only formally true. To handle anticommutation relations of fermionic operators for identical particles, maintaining and keeping track of the order of the spin-orbitals in the Hartree product expression III.3 are required. One may choose an arbitrary initial sequence to arrange all these spin-orbitals, $\{|n_p\rangle\}$, $P = 1, 2, \dots, M$, but then the order cannot be changed in later operator algebra. The decomposition of the Fock space into composite subspaces, eq III.4b, needs to follow the same rules. For example, $f_1(m_1)$ needs to contain sequentially the first m_1 spin-orbitals ($P = 1, 2, \dots, m_1$) in the above arrangement; $f_2(m_2)$ contains the next m_2 spin-orbitals ($P = m_1 + 1, m_1 + 2, \dots, m_1 + m_2$); and so on. Details of the correct operation of the Hamiltonian operator in the second quantized framework will be given below.

Once the problem is cast into the second quantized representation, the Hamiltonian can be transformed accordingly employing fermionic creation/annihilation operators. This is a standard practice in the second quantization formalism.^{116,117} For instance, in common electronic structure theory the many-body Hamiltonian contains one-electron operator $h_1 = -(1/2)\nabla_1^2 - \sum_A (Z_A/r_{1A})$ and two-electron operator $h_2 = r_{12}^{-1}$. In the second quantized form the Hamiltonian is given by

$$\hat{H} = \sum_{ij} \langle ih_1 | j \rangle \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{ijkl} \langle ijkl | \rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \quad (\text{III.7})$$

where $\langle ih_1 | j \rangle$ and $\langle ijkl | \rangle$ are standard one- and two-electron integrals

$$\langle ih_1 | j \rangle \equiv \int d\mathbf{x}_1 \chi_i(\mathbf{x}_1)^* h_1(\mathbf{r}_1) \chi_j(\mathbf{x}_1) \quad (\text{III.8a})$$

$$\langle ijkl | \rangle \equiv \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i(\mathbf{x}_1)^* \chi_j(\mathbf{x}_2)^* \frac{1}{r_{12}} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) \quad (\text{III.8b})$$

The generalized method is thus a ML-MCTDH approach in the second quantization representation (SQR). The major difference is that in the second quantized form the fermionic creation/annihilation operators fulfill the anticommutation relations

$$\{a_p, a_Q^+\} \equiv a_p a_Q^+ + a_Q^+ a_p = \delta_{pQ} \\ \{a_p^+, a_Q^+\} = \{a_p, a_Q\} = 0 \quad (\text{III.9})$$

The symmetry of indistinguishable particles is thus realized by enforcing such algebraic properties of the operators.

The practical procedure can be illustrated by considering a single layer theory in the form of eq III.4b, where each SP group κ corresponds to a Fock subspace in III.4b

$$|\Psi(t)\rangle = \sum_{i_1} \sum_{i_2} \dots \sum_{i_L} A_{i_1 i_2 \dots i_L}(t) \prod_{\kappa=1}^L |\varphi_{i_\kappa}^{(\kappa)}(t)\rangle \quad (\text{III.10a})$$

$$|\varphi_{i_\kappa}^{(\kappa)}(t)\rangle = \sum_{I_\kappa=1}^{2^{m_\kappa}} B_{I_\kappa}^{\kappa, i_\kappa}(t) |\phi_{I_\kappa}^{(\kappa)}\rangle \\ \equiv \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \sum_{n_{m_\kappa}=0}^1 B_{n_1 n_2 \dots n_{m_\kappa}}^{\kappa, i_\kappa}(t) |n_1\rangle |n_2\rangle \dots |n_{m_\kappa}\rangle \quad (\text{III.10b})$$

We discuss the case of acting a fermionic creation operator $(a_\nu^{(\kappa)})^+$ on an SPF. The operation of an annihilation operator follows the same procedure. Taking into account the whole Fock space, the creation operator can be factorized into a product of operators

$$(a_\nu^{(\kappa)})^+ = \left(\prod_{\mu=1}^{\kappa-1} \hat{S}_\mu \right) (\tilde{a}_\nu^{(\kappa)})^+ \quad (\text{III.11})$$

where \hat{S}_μ ($\mu = 1, 2, \dots, \kappa - 1$) are a series of permutation sign operators that account for permuting $(a_\nu^{(\kappa)})^+$ from the first Fock subspace $\mu = 1$ to the second subspace $\mu = 2$, and then to the third $\mu = 3$, ..., until reaching the κ th subspace, and $(\tilde{a}_\nu^{(\kappa)})^+$ represents what is left, i.e., a reduced creation operator that deals with the anticommutation relation only in the κ th subspace. The operator-based anticommutation constraint (eq III.9) results in the following operations

$$(\tilde{a}_\nu^{(\kappa)})^+ |\varphi_{i_\kappa}^{(\kappa)}(t)\rangle = \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \sum_{n_{m_\kappa}=0}^1 \delta_{n_\nu, 0} \left[\prod_{q=1}^{\nu-1} (-1)^{n_q} \right] \\ \times B_{n_1 n_2 \dots n_{m_\kappa}}^{\kappa, i_\kappa}(t) |n_1\rangle |n_2\rangle \dots |1_\nu\rangle \dots |n_{m_\kappa}\rangle \quad (\text{III.12a})$$

$$\hat{S}_\mu |\varphi_{i_\mu}^{(\mu)}(t)\rangle = \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \sum_{n_{m_\mu}=0}^1 \left[\prod_{q=1}^{m_\mu} (-1)^{n_q} \right] \\ \times B_{n_1 n_2 \dots n_{m_\mu}}^{\mu, i_\mu}(t) |n_1\rangle |n_2\rangle \dots |n_{m_\mu}\rangle \quad (\text{III.12b})$$

In other words, $(\tilde{a}_\nu^{(\kappa)})^+$ would have been a regular creation operator in the κ th subspace if other subspaces did not exist. In another word, its operation in this subspace follows the same algebraic rules as those obeyed by a regular fermionic creation operator. However, one cannot ignore other subspaces prior to κ , and the role of the permutation sign operators \hat{S}_μ $\mu = 1, 2, \dots, \kappa - 1$ is to take care of this within the ML-MCTDH framework. This is a tedious task because all subspaces prior to κ need to be tracked, but it is necessary to enforce the fermionic anticommutation relation in the whole Fock space.

With respect to the formal procedure of treating identical fermions, there is little difference between the single layer MCTDH method described above and hierarchical ML-MCTDH. Similar to the recursive grouping of all degrees of freedom in regular ML-MCTDH, the second quantized ML-MCTDH-SQR decomposes the Fock space via a recursive, layered fashion. The spin-orbitals used here are pretty much the same as the coordinates in the first quantized representation. One expands the whole wave function recursively using these spin-orbitals as primitive basis states, in the form of eq II.30. Then one needs to factorize a fermionic creation or annihilation operator to a product of permutation sign operators and a reduced creation or annihilation operator, just as described above. The complication is that these permutation sign operators now have to be operated to all the prior Fock subspaces recursively in all layers. If we ignore

this somewhat challenging technical detail, we realize that the equations of motion have the same form in ML-MCTDH-SQR as those in ML-MCTDH discussed in the previous section. Thus, with the generalization to the second quantized representation, ML-MCTDH theory is formally complete.

It is now easy to extend ML-MCTDH-SQR theory to identical bosons. One applies the same second quantization procedure except that bosons do not obey the Pauli exclusion principle, and thus, their occupation numbers do not have an upper limit. The expression for an occupation-number state is obtained by acting a series of bosonic creation operators on the vacuum state

$$|n\rangle = \prod_{p=1}^M \frac{(\hat{a}_p^+)^{n_p}}{\sqrt{n_p!}} |vac\rangle \quad (\text{III.13})$$

Thereby, the bosonic creation/annihilation operators satisfy the commutation relation

$$[\hat{a}_p, \hat{a}_q^+] \equiv \hat{a}_p \hat{a}_q^+ - \hat{a}_q^+ \hat{a}_p = \delta_{pq} \quad (\text{III.14a})$$

$$[\hat{a}_p^+, \hat{a}_q^+] = [\hat{a}_p, \hat{a}_q] = 0 \quad (\text{III.14b})$$

Same as in the fermionic case, a bosonic occupation-number state $|n\rangle$ can also be treated as a Hartree product¹¹⁵

$$|n\rangle = \prod_{p=1}^M |n_p\rangle \equiv |n_1\rangle |n_2\rangle \dots |n_M\rangle \quad (\text{III.15})$$

This enables a similar multilayer hierarchical decomposition of the Fock space.

The practical implementation of ML-MCTDH-SQR theory for identical bosons is much simpler than that for identical fermions. This is because the commutation relations in eq III.14 are the same as those obeyed by distinguishable particles. Once the second quantized formalism is introduced, the ML-MCTDH-SQR method is exactly the same as ML-MCTDH discussed earlier.

For a mixture of identical bosons and fermions or several types of identical particles, ML-MCTDH theory is readily available in the second quantized form. After introducing the occupation-number states in the Fock space, one simply follows the anticommutation relation for fermionic operators and commutation relation for bosonic operators in the ML-MCTDH implementation. There is really nothing special here.

After the introduction of MCTDH theory, effort was made to generalize it to treat identical particles in the first quantized representation.^{105–108} Attempts have also been made to generalize the ML-MCTDH theory in the first quantized picture but failed. As mentioned previously, this is due to the fact that there is no obvious hierarchical expansion of the wave function if determinant/permanent forms are to be retained. Things are quite different in the second quantization representation where the wave function is expressed via occupation number basis in the abstract Fock space. Although formally the same set of exchange symmetry rules are enforced, second quantization does so by using operators instead of wave functions. The fact that this is a better choice can be understood from an important observation that in both phenomenological models and more fundamental theories, there is only a limited number of combinations of the creation/annihilation operators. For example, in electronic structure theory it is true that once Slater determinants are used, one does not need to worry about maintaining the exchange

symmetry for any types of operators. However, in this case only one- and two-electron operators are present. In the second quantized representation one only needs to deal with this subset of operators and never needs to worry about all, redundant possibilities of operator combinations. It is precisely this property that gains advantage for the second quantized form and allows a multilayer treatment.

IV. MULTILAYER IMPROVED RELAXATION

The applicability of ML-MCTDH theory is not only limited to simulating quantum dynamics. Similar to the previous formulation of MCTDH for calculating eigenstates of the Hamiltonian^{37,118,119} or the thermal flux operator,^{119,120} ML-MCTDH theory can be applied in the same way. This extension may be useful to generate a correlated initial state or to calculate a few lowest energy eigenstates under critical conditions so as to predict important thermodynamic properties of a large system.

A. Time-Independent Variation. To compute an energy eigenstate within the multilayer wave function ansatz (except that the coefficients are no longer time-dependent), eq II.30, it is natural to first consider the time-independent variation with the orthonormal constraints of the SPFs enforced by the method of Lagrange multipliers

$$\begin{aligned} \delta\{\langle\Psi|\hat{H}|\Psi\rangle - E(\langle\Psi|\Psi\rangle - 1) \\ - \sum_{\kappa=1}^p \sum_{j,l} \epsilon_{j,l}^{(\kappa)} (\langle\varphi_j^{(\kappa)}|\varphi_l^{(\kappa)}\rangle - \delta_{ij}) \\ - \sum_{\kappa=1}^p \sum_{q=1}^{Q(\kappa)} \sum_{j,l} \tilde{\epsilon}_{j,l}^{(\kappa,q)} (\langle v_j^{(\kappa,q)}|v_l^{(\kappa,q)}\rangle - \delta_{ij}) \\ - \sum_{\kappa=1}^p \sum_{q=1}^{Q(\kappa)} \sum_{\gamma=1}^{M(\kappa,q)} \sum_{j,l} \tilde{\tilde{\epsilon}}_{j,l}^{(\kappa,q,\gamma)} (\langle \xi_j^{(\kappa,q,\gamma)}|\xi_l^{(\kappa,q,\gamma)}\rangle - \delta_{ij}) \\ - \dots\} = 0 \end{aligned} \quad (\text{IV.1})$$

Here E is the Lagrange multiplier to keep the overall wave function normalized and $\epsilon_{j,l}^{(\kappa)}$, $\tilde{\epsilon}_{j,l}^{(\kappa,q)}$, $\tilde{\tilde{\epsilon}}_{j,l}^{(\kappa,q,\gamma)}$, etc. are Lagrange multipliers to keep the SPFs of the first, second, third, etc. layers orthonormal. To carry out the variation in eq IV.1, we assume that the expansion coefficients of all the layers, e.g., $A_{j_1 j_2 \dots j_p} B_{i_1 i_2 \dots i_{Q(\kappa)}} C_{\alpha_1 \alpha_2 \dots \alpha_{M(\kappa,q)}}$ etc. in eq II.30, are complex, so that their complex conjugates (bra) are varied independently (if they are real, the variations of bra and ket give the same result). Variation in the top layer gives the standard eigenequation

$$\sum_L H_{jL} A_L \equiv \sum_L \langle\Phi_j|\hat{H}|\Phi_L\rangle A_L = E A_j \quad (\text{IV.2})$$

whereas in the previous sections we have denoted a configuration $|\Phi_j\rangle$ as the Hartree product $|\Phi_j\rangle \equiv \prod_{\kappa=1}^p |\varphi_j^{(\kappa)}\rangle$ and used the collective index, $A_{j_1 j_2 \dots j_p} \equiv A_j$. Solving this eigenequation thus gives the eigenenergy E and the eigenvector $|\Psi\rangle = \sum_j A_j |\Phi_j\rangle$ in terms of the top layer expansion coefficients A_j and the SPFs of all the layers. Variation IV.1 with respect to the SPFs of all the layers, after eliminating all the Lagrange multipliers, gives

$$[1 - \hat{P}^{(\kappa)}] \langle\hat{H}\rangle^{(\kappa)} |\varphi_j^{(\kappa)}\rangle = 0 \quad (\text{IV.3a})$$

$$[1 - \hat{P}_{L2}^{(\kappa,q)}] \langle\hat{H}\rangle_{L2}^{(\kappa,q)} |v_j^{(\kappa,q)}\rangle = 0 \quad (\text{IV.3b})$$

$$[1 - \hat{P}_{L3}^{(\kappa,q,\gamma)}] \langle \hat{\mathcal{H}}_{L3}^{(\kappa,q,\gamma)} | \underline{\xi}^{(\kappa,q,\gamma)} \rangle = 0 \quad (\text{IV.3c})$$

...

where the notations are the same as in the previous ML-MCTDH formulation.

One may propose to solve the above set of equations, eqs IV.2 and IV.3, iteratively so that eventually the eigenenergy E and the eigenvector $\Psi = \sum_j A_j |\Phi_j\rangle$ can be obtained. However, just as in the early days of MCSCF theory,⁵⁰ the resulting equations are highly nonlinear to iterate and very difficult to converge. To get around this difficulty, the MCTDH “improved relaxation” method¹¹⁸ uses repeated, short imaginary time propagation to relax the SPFs, which is then combined with a Krylov subspace method to solve the eigenequation (IV.2). This is generalized in a straightforward way employing the ML-MCTDH method.⁴⁷

B. Improved Relaxation Employing ML-MCTDH.

Similar to the single layer MCTDH case as described in ref 118, the stationary solution in eq II.31 remains valid under any linear transformation. Thus, one may insert the pseudoinverse of the reduced density matrices $\hat{\rho}^{(\kappa)}$, $\hat{Q}_{L2}^{(\kappa,q)}$, $\hat{Q}_{L3}^{(\kappa,q,\gamma)}$, ..., to the equation of the corresponding layer

$$[1 - \hat{P}^{(\kappa)}][\hat{\rho}^{(\kappa)}]^{-1} \langle \hat{H}^{(\kappa)} | \underline{\varphi}^{(\kappa)} \rangle = 0 \quad (\text{IV.4a})$$

$$[1 - \hat{P}_{L2}^{(\kappa,q)}][\hat{Q}_{L2}^{(\kappa,q)}]^{-1} \langle \hat{\mathcal{H}}_{L2}^{(\kappa,q)} | \underline{\nu}^{(\kappa,q)} \rangle = 0 \quad (\text{IV.4b})$$

$$[1 - \hat{P}_{L3}^{(\kappa,q,\gamma)}][\hat{Q}_{L3}^{(\kappa,q,\gamma)}]^{-1} \langle \hat{\mathcal{H}}_{L3}^{(\kappa,q,\gamma)} | \underline{\xi}^{(\kappa,q,\gamma)} \rangle = 0 \quad (\text{IV.4c})$$

...

and realize that these are related to the imaginary time ($\tau = -it$) derivative of the SPFs,

$$|\underline{\varphi}^k(\tau)\rangle_{L2 \text{ coefficients}} = -[1 - \hat{P}^{(\kappa)}][\hat{\rho}^{(\kappa)}]^{-1} \langle \hat{H}^{(\kappa)} | \underline{\varphi}^{(\kappa)} \rangle \quad (\text{IV.5a})$$

$$|\underline{\nu}^{(\kappa,q)}(\tau)\rangle_{L3 \text{ coefficients}} = -[1 - \hat{P}_{L2}^{(\kappa,q)}][\hat{Q}_{L2}^{(\kappa,q)}]^{-1} \langle \hat{\mathcal{H}}_{L2}^{(\kappa,q)} | \underline{\nu}^{(\kappa,q)} \rangle \quad (\text{IV.5b})$$

$$|\underline{\xi}^{(\kappa,q,\gamma)}(\tau)\rangle_{L4 \text{ coefficients}} = -[1 - \hat{P}_{L3}^{(\kappa,q,\gamma)}][\hat{Q}_{L3}^{(\kappa,q,\gamma)}]^{-1} \langle \hat{\mathcal{H}}_{L3}^{(\kappa,q,\gamma)} | \underline{\xi}^{(\kappa,q,\gamma)} \rangle \quad (\text{IV.5c})$$

...

Thus, the approximate solution to eq IV.3 is to use the ML-MCTDH method to propagate the SPFs in imaginary time, applying eq IV.5, until the time derivatives are sufficiently small. This is then coupled to the solution of the top layer eigenequation (IV.2) in an iterative way.

In practice, the multilayer improved relaxation method employs a procedure similar to that discussed in ref 118. An initial guess can be generated by diagonalizing a zeroth-order Hamiltonian \hat{H}_0 and choosing an appropriate target (ground or excited) state. Besides the SPFs that are used to define this initial state, other SPFs are chosen randomly and orthogonalized. This constructs a multilayer wave function in the form of eq II.30. The wave function is relaxed over a short imaginary time to generate a correlated initial state. Then one proceeds to the iterations of multilayer improved relaxation as follows.

In each iteration step, the Hamiltonian matrix of the top layer is first constructed on the basis of the updated SPFs. Then this Hermitian matrix is diagonalized as shown in eq IV.2. Because

the matrix is often big in size and one is often only interested in a few eigenstates with extreme eigenvalues, an iterative solver such as a Krylov subspace method is desirable. We have employed an Arnoldi/Lanczos method on the Boltzmann operator⁴⁷ in spirit similar to the work of Manthe^{119,121} but only applying the Krylov iteration to the linear part of the top layer A -coefficients. One may also use Davidson's method as in the previous work by Meyer and co-workers¹¹⁸ with a preconditioner, e.g., Jacobi (diagonal), Gauss–Seidel, or symmetric successive over relaxation (SSOR)¹²² to accelerate the Krylov iteration. After the top layer Hamiltonian matrix is diagonalized, the A coefficients of the target eigenstate are fixed while the SPFs of all layers are relaxed over a certain imaginary time interval by solving eq IV.5. This completes one step of iteration. In the next step, the Hamiltonian matrix at the top layer is rebuilt using the relaxed SPFs and diagonalized again, followed by the imaginary time relaxation of the SPFs. This process is iterated until convergence, usually defined by the relative energy or density between two successive iterations, is achieved for the target state of interest.⁴⁷

For a large system with many degrees of freedom, it is practically impossible to solve for all the eigenstates. However, there is often physical significance in analyzing states with the lowest energies, e.g., the ground state and some low-lying excited states. This makes the multilayer improved relaxation approach a valuable tool. As an example, the multilayer improved relaxation method has been applied to computing the energy splitting for the lowest pair of eigenstates as well as the spin observables and entanglement entropy of the spin-boson model.⁴⁷ A large number of degrees of freedom, up to 10 000 bath modes, can be treated and thus the appropriate phase transition at a critical system–bath coupling strength may be predicted. Another important development for calculating the energy eigenstates is to use the (modified) Lanczos method directly within the ML-MCTDH framework.⁴⁴ Both approaches may be adapted in the second quantized framework, as described in the previous section, to treat identical fermions or bosons. This offers a very attractive alternative to the standard numerical renormalization group theory^{31–33} for studying thermodynamic properties of various physical models.

V. CONCLUDING REMARKS: EXPLOITING DYNAMICAL SIMPLICITY USING ML-MCTDH

In many respects, ML-MCTDH theory is a natural extension of the original MCTDH method. Thus, for several years the general idea had been informally discussed among various researchers in the field. The difficulty lies in the practical implementation of this somewhat sophisticated algorithm. It was also not so clear that the method would actually provide any significant benefits over the then already successful MCTDH method. In a certain sense this hesitation is justified. For some problems such as quantum scattering study of the $\text{H} + \text{H}_2$ reaction, the conventional wave packet method was so well developed, and the dimensionality small enough, that there was no need to apply MCTDH, let alone ML-MCTDH, to such reactions. However, as in many studies, the advantage of a method cannot be judged only by problems that have already been studied but should also be based on its potential to treat problems that are difficult or impossible for other methods. In 2003 the first implementation of ML-MCTDH was reported⁴¹ with an application to the spin-boson model. In that work up to 1000 degrees of freedom were treated in a numerically converged way, which was much larger than any systems that

had been treated by a quantum wave packet method. This generated a lot of interest in both methodology and software development for ML-MCTDH theory. In areas other than chemistry it has also been realized that this hierarchical tensor decomposition or “tensor train” format can be used to treat very large systems with good accuracy.¹⁰⁴

ML-MCTDH theory has been applied by us to the study of many different complex systems.^{41,44–47,71–84,86,87,89–103,110–113,123,124} A particularly important area for application of the method is condensed phase problems. Many interesting phenomena in this field require accurate (numerically exact) quantum descriptions across a broad range of physical parameter space and/or with anharmonic potential energy functions, but very often an effective method for such a purpose is lacking. ML-MCTDH theory has been successful in this regard, in particular for treating electron transfer reactions.^{71–87} Other research groups have also been active in developing ML-MCTDH. Development has been pursued by Manthe and co-workers to incorporate more general forms of potential energy surfaces as well as to obtain a recursive implementation of ML-MCTDH with an arbitrary number of layers.^{43,88} The method has also recently been implemented in the Heidelberg MCTDH package.⁸⁵

Due to the complexity of the ML-MCTDH algorithm it is difficult to give a general rule of thumb for the scaling of ML-MCTDH simulations versus the number of degrees of freedom. To provide a rough estimate, we make the following assumptions: (i) the numbers of single particle (SP) groups are the same for all layers; (ii) the numbers of single particle functions (SPFs) are the same for all the SP groups and for all layers, and this does not change as the number of degrees of freedom increases; (iii) the numbers of primitive basis functions are the same for all the degrees of freedom (obviously one may pick the largest number of basis functions for the sake of argument.) On the basis of these assumptions and counting the dominant floating point operations in the ML-MCTDH algorithm, an expression for the scaling of the method is

$$C(f) \exp[A + B \times f^{1/(L+1)}] \quad (\text{V.1})$$

where $C(f)$ is a polynomial pre-exponential factor that comes from the number of quantum mechanical operators as the number of degrees of freedom f increases, A and B are constants, and L is the number of layers in ML-MCTDH.

The expression above indicates that ML-MCTDH still has an exponential scaling for a fixed number of layers L . However, the exponent is no longer the number of degrees of freedom f but a smaller quantity $f^{1/(L+1)}$. In section II we noted that from the perspective of ML-MCTDH the conventional wave packet method is a “zeroth-layer” approach. Setting $L = 0$ in eq V.1 indeed recovers the usual exponential scaling of the computational effort with respect to the number of degrees of freedom f . For the original single layer MCTDH, $L = 1$, the scaling becomes $\exp[A + B\sqrt{f}]$; i.e., the exponent becomes the square root of f , which gives a slower increase of the computational effort versus the number of degrees of freedom. The scaling becomes more and more slow versus f as the number of layers increases. This is shown in Figure 1, where converged ML-MCTDH simulations were carried out for a model spin-boson problem used in an earlier test of the theory.⁴¹ For a small number of degrees of freedom, Figure 1a shows that including more layers in the ML-MCTDH simulation introduces a small

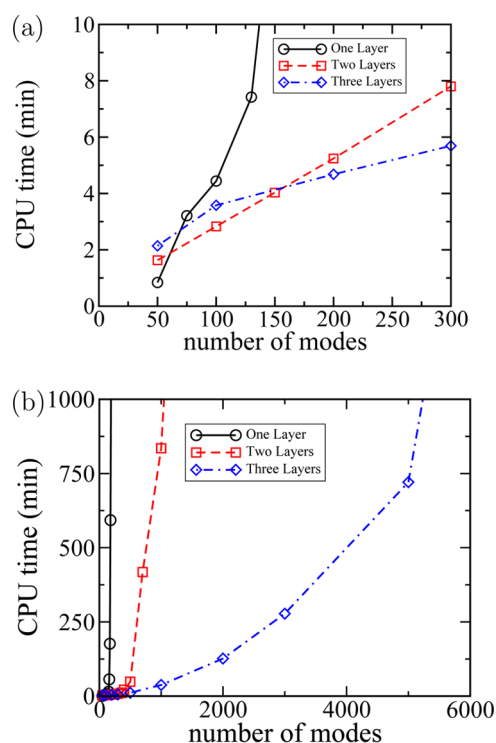


Figure 1. CPU time versus the number of degrees of freedom for a spin-boson model problem. The scaling behavior is shown for ML-MCTDH simulation with one, two, and three layers.

computational overhead. This is, however, not a significant factor due to the overall low CPU cost. As the number of degrees of freedom increases, more layers in ML-MCTDH quickly dominate the scaling behavior. As shown in Figure 1b, the CPU cost with one layer (i.e., the original MCTDH) scales sharply with respect to the number of degrees of freedom. Such scaling is much slower when three layers are used. Figure 2 includes a

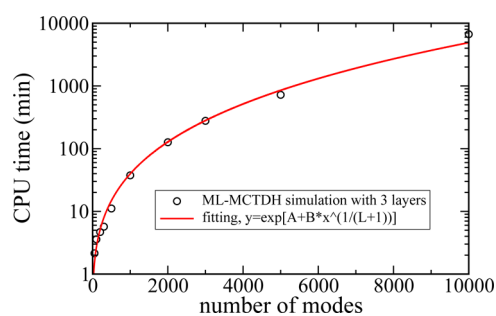


Figure 2. Same as Figure 1 but shows a fitting to the scaling in eq V.1 for ML-MCTDH simulation with three layers.

fit of the scaling to the estimate in eq V.1 and shows rather good agreement except for the last point with 10 000 modes (which is the limit of the three-layer calculation). In the limit that the number of layers L increases proportionally to the number of degrees of freedom, the above formula in fact implies an absence of the exponential scaling behavior, which has also been discussed earlier.⁸⁸

A question frequently encountered is why ML-MCTDH can simulate a much larger system than that which can be treated by the conventional full configurational wave packet method. Is it due to some significant approximations involved? The answer

is that if the results are converged, ML-MCTDH is as rigorous as any other wave packet method including the conventional method. The fact that a large system can be treated numerically exactly by the ML-MCTDH theory indicates that there is some dynamical simplicity inherent in the problem, that the problem is not exponentially hard. If we do not pay attention to such intrinsic simplicity and approach the problem by brute force, it will render many problems unsolvable. On the contrary, many problems in physics and chemistry are in fact solvable, and ML-MCTDH serves as an effective tool to exploit the dynamical simplicity in these problems.

The major hurdle for ML-MCTDH theory to reach an even broader community is the complexity in algorithm design and software development. This is partly due to the fact that methodology development is often less rewarding than creative applications of existing theories. It is also due to the fact that many mathematical aspects of the theory are less well understood. Another note is that ML-MCTDH theory is best suited to certain types of problems where the potential energy can be written as (a sum of) products, each containing only a few-body coordinates. Other types of problems are possible^{45,46,94,98} but somewhat restrictive in the size of the systems that can be treated. Nevertheless, ML-MCTDH theory has demonstrated great potential for accurate quantum dynamical simulations of many important problems and remains under very active development.

AUTHOR INFORMATION

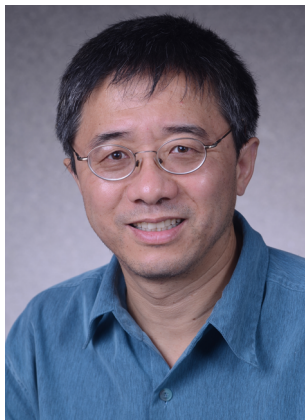
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Notes

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Biography



Haobin Wang obtained a B.Sc. from University of Science and Technology of China in 1991, majoring in Chemical Physics. In 1996, he received a Ph.D. in Chemistry from Wayne State University, Detroit, under the supervision of Professor William L. Hase. He then carried out postdoctoral work with Professor William H. Miller at University of California, Berkeley. He was an Assistant Professor of Chemistry at New Mexico State University from 2001 to 2006 and has been Professor there since 2011. In 2014, he joined the Chemistry Department of the University of Colorado—Denver. Dr. Wang's research has focused on developing accurate theoretical methods and practical computational techniques to simulate quantum dynamics for large many-body systems. His research interests also include developing classical and semiclassical methods for dynamical simulations.

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