Matrix product state formulation of the multiconfiguration time-dependent Hartree theory

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(Dated: August 6, 2018)

A matrix product state formulation of the multiconfiguration time-dependent Hartree (MPS-MCTDH) theory is presented. The Hilbert space that is spanned by the direct products of the phonon degree of freedoms, which is linearly parameterized in the MCTDH ansatz and thus results in an exponential increase of the computational cost, is parametrized by the MPS form. Equations of motion based on the Dirac-Frenkel time-dependent variational principle is derived by using the tangent space projection and the projector-splitting technique for the MPS, which have been recently developed. The mean-field operators, which appears in the equation of motion of the MCTDH single particle functions, are written in terms of the MPS form and efficiently evaluated by a sweep algorithm that is similar to the DMRG sweep. The efficiency and convergence of the MPS approximation to the MCTDH are demonstrated by quantum dynamics simulations of extended excitonic molecular systems.

Matrix product state (MPS) is one of the most successful tensor-network states (TNS) which encode quantum states in the exponentially growing Hilbert space of strongly correlated systems to a sequential product of tensors and was first introduced by White [1, 2] as an eigensolver named as the density-matrix renormalized group (DMRG) algorithm. Although the DMRG works best for one-dimensional Hamiltonians, it has been successfully extended to many fields of applications such as \textit{ab initio} Hamiltonian of quantum chemistry where all the degree of freedoms (DOFs), i.e. electrons, are coupled complexly through the Coulomb interaction [3, 4]. Extension to time-dependent simulations, i.e. time evolution of the MPS, has been also developed, such as the adaptive time-dependent DMRG (t-DMRG) [5, 6] and the time-evolving block-decimation (TEBD) algorithm [7]. The use of the Suzuki-Trotter decomposition by splitting the summation of terms of interactions in the Hamiltonian makes the methods particularly efficient, but in principle it works well for Hamiltonians consisting of local interactions, typically nearest neighbor interaction models.

Recently, time-evolution of the MPS wavefunction has been formulated within the Dirac-Frenkel time-dependent variational principle (TDVP) [8–10]. This method, in principle, is not restricted to any particular type of Hamiltonians and reasonably applicable to long-range interactions including two-dimensional systems. Efficiency of the method was, however, deteriorated by numerical instability problems arose from the highly nonlinear parametrization in the wavefunction ansatz. Very recently, Haegeman and co-workers have developed a novel method that circumvents those problems [11]. The method utilizes Lie-Trotter splitting of the tangent space projectors of different sites canonical form, which realizes an efficient and stable propagation of the MPS wavefunctions. The development of robust time evolution method based on the TDVP should significantly expand the applicability of the MPS to a variety of problems.

Time evolution methods based on the TDVP have great affinity for molecular quantum dynamics simulations, in which the interactions in the Hamiltonian are represented in the first quantization form. The basis function expansion of the wavefunctions allows us to efficiently evaluate the Hamiltonian matrix elements by analytical or numerical integrations in the real space. The multiconfiguration time-dependent Hartree (MCTDH) theory [12, 14] is the most widely used method in this field. In the method, variational space of a vibrational wavefunction is spanned by direct products of one-particle basis functions, of which the shapes are also regarded as variational parameters and evolved with time. While the use of variable one-particle basis significantly reduces the size of the Hilbert space, the number of linear parameters of the space still grows exponentially with the number of phonon modes. It is, therefore, natural to introduce TNS ansatzes instead of the linear parametrization, in fact the multi-layer formulation (ML-MCTDH), which corresponds to the hierarchical Tucker tensor decomposition [15], made a great success in particular for encoding a tremendous number of harmonic oscillators describing the bath modes that couple to one of the molecules [16].

In this letter, a MPS formulation of the MCTDH theory (MPS-MCTDH) is presented. It is expected to be applied to extended molecular systems where many phonons are strongly and complexly correlated via the electronic inter-state couplings as is often the case with molecular systems; thus, it is supposed to be complementary to the multi-layer formulation. In the MPS-MCTDH method, the molecular wavefunction is
parametrized as
\[ |\Psi\rangle = \sum_{\alpha} |\alpha\rangle |\Psi^{\alpha}\rangle = \sum_{\alpha} |\alpha\rangle \sum_{J} A^{(\alpha)}_{J} |\Phi^{\alpha}_{J}\rangle, \]  
(1)
where
\[ A^{(\alpha)}_{J}=\sum_{\tau_{1}\cdots\tau_{J-1}} a^{\alpha}_{\tau_{1}} a^{\alpha}_{\tau_{2}} \cdots a^{\alpha}_{\tau_{J-1}}, \]  
(2)
\[ |\Phi^{\alpha}_{J}\rangle \equiv |\varphi^{(1)}_{\alpha_{1}} \varphi^{(2)}_{\alpha_{2}} \cdots \varphi^{(f)}_{\alpha_{f}}\rangle, \]  
(3)
\[ \alpha \] denotes an electronic states in the multiset formalism and thus satisfies \( \langle \alpha | \beta \rangle = \delta_{\alpha \beta} \) \[21\], \( a^{\alpha}_{p-1} \) is a site function of the MPS, and \( \varphi^{(p)}_{\alpha_{p}} \) is a site basis states which is expressed as a linear combination of the primitive functions as \( \sum_{\tau} c_{\tau} \chi^{\tau}_{p}(Q_{\rho}) \) where \( c_{\tau} \) are variational parameters as well as the site functions \( a^{\alpha}_{p-1} \). In contrast to the linear coefficients \( A^{(\alpha)}_{J} \) of which the dimension grows rapidly as \( \sim O(n^{J}) \) where \( n \) is the number of the site basis per site \( j_{p} = 1 \cdots n \), the dimension of the MPS site functions \( \{ a^{\alpha}_{p-1} \} \) grows as only \( \sim O(m\rho^{2}f) \) where \( m \) is the bond dimension of each site functions, \( \tau_{p} = 1 \cdots m \). Note that the high-dimensional \( A^{(\alpha)}_{J} \) \( \sim O(n^{J}) \) are never explicitly constructed in the MPS-MCTDH method. In the current implementation, it is possible to combine several phonon modes into single site in the MPS, similarly to the multimode single-particle function \( Q_{\rho} = (q_{1}, q_{2}, \cdots) \) of the MCTDH method.

Time-evolution of the variational parameters based on the TDVP is formulated by using the tangent space projector \( \hat{P}_{\Psi} \)
\[ |\dot{\Psi}\rangle = -i \hat{P}_{\Psi} \hat{H} |\Psi\rangle. \]  
(4)
The tangent space projector acts as orthogonal projection for an arbitrary vector onto the tangent plane, i.e. within the variational space, at the current point \( \Psi(t) \); thus, the time-dependent Schrödinger equation is satisfied at the first-order with respect to all the variational parameters. The tangent space projector is expressed as a summation of subspace projectors that must be orthogonal to each other. As the subspace projectors for the MPS site coefficients, the author adopted the projector that imposes the left-gauge fixing condition developed in Ref [11]
\[ \hat{P}_{\text{MPS}} = \sum_{p=1}^{J} \sum_{\tau_{p-1} \cdots \tau_{p}} |\Psi_{\tau_{p-1}}^{L} \varphi^{(p)}_{\tau_{p}} \rangle \langle \Psi_{\tau_{p}}^{R} \varphi^{(p)}_{\tau_{p}} | |\Psi_{\tau_{p-1}}^{L} \rangle, \]  
(5)
and
\[ |\Psi_{\tau_{p}}^{L} \rangle \equiv \sum_{\tau_{1} \cdots \tau_{p-1}} L_{\tau_{p}}^{(1)} \cdots L_{\tau_{p-1}}^{(p)} |\varphi^{(1)}_{\tau_{p}} \cdots \varphi^{(p)}_{\tau_{p}}\rangle, \]
\[ |\Psi_{\tau_{p}}^{R} \rangle \equiv \sum_{\tau_{p+1} \cdots \tau_{J}} R_{\tau_{p+1}}^{(p+1)} \cdots R_{\tau_{J}}^{(J)} |\varphi^{(p+1)}_{\tau_{p+1}} \cdots \varphi^{(J)}_{\tau_{J}}\rangle, \]
where \( L_{\tau_{p-1}}^{(p)} \) and \( R_{\tau_{p+1}}^{(p+1)} \) denote the left-orthonormal and right-orthonormal site functions, respectively, appearing in the \( p \)-canonical form of MPS wavefunctions
\[ A^{(\alpha)}_{J} = \sum_{\tau_{1} \cdots \tau_{J}} L_{\tau_{1}}^{(1)} \cdots L_{\tau_{p-1}}^{(p)} C_{\tau_{p-1} \tau_{p}}^{\gamma} R_{\tau_{p+1}}^{(p+1)} \cdots R_{\tau_{J}}^{(J)}, \]
which can be transformed to the next site \( (p+1) \)-canonical form by using the relation
\[ \sum_{\tau_{p}} C_{\tau_{p-1} \tau_{p}}^{\gamma} R_{\tau_{p+1}}^{(p+1)} = \sum_{\tau_{p}} L_{\tau_{p-1} \tau_{p}}^{\gamma} \sigma_{\tau_{p}, \tau_{p-1}} R_{\tau_{p+1}}^{(p+1)} = \sum_{\tau_{p}} L_{\tau_{p-1} \tau_{p}}^{\gamma} C_{\tau_{p+1} \tau_{p}}^{\gamma+1}, \]
where
\[ \sigma_{\tau_{p}, \tau_{p-1}} \equiv \sum_{j_{p} \tau_{p-1}} L_{j_{p} \tau_{p-1}}^{(p)} C_{j_{p} \tau_{p-1}}^{(p+1)} \]
and
\[ |\Psi_{\tau_{p}}^{L} \rangle \equiv \sum_{\tau_{1} \cdots \tau_{p-1}} f_{\tau_{p-1}}^{(1)} \cdots f_{\tau_{p-1}}^{(p)} |\varphi^{(1)}_{\tau_{p}} \cdots \varphi^{(p)}_{\tau_{p}}\rangle, \]
for details refer to literature, e.g. Ref [21]. In the case of the MPS-MCTDH ansatz, this projector generates not only the variation of site functions of the MPS, but also the variation of site basis states, themselves. It should bring a complication for its formulation, thus a certain MCTDH gauge, \( \langle \varphi^{(p)}_{\tau} | \varphi^{(p)}_{\tau} \rangle = 0 \), is adopted, by which the variation of the site basis states generated by \( \hat{P}_{\text{MPS}} \) are vanished. The projector for the complementary space \( \hat{P}' \equiv \hat{P} - \hat{P}_{\text{MPS}} \), i.e. the site basis functions space, can be derived in the same way as Ref [22] except that the MCTDH coefficient is replaced by the MPS, and the Lie-Trotter splitting of the tangent space projectors should be done naturally for all the projector
\[ e^{\hat{P}' \hat{H}} \approx e^{\frac{i}{\hbar} \hat{P}' \hat{H}} e^{\hat{P}' \hat{R} \hat{H}} e^{\hat{P}' \hat{L} \hat{H}}. \]
(9)
Another way is to assume the constant mean-field (CMF) approximation [22], in which the mean-field operators and the integrals written in the site basis functions are frozen during each step of the propagation, and thus the time-evolution of the MPS site functions and the site basis functions are decoupled during the step intervals. The CMF integration method,
which was adopted in this work, becomes advantageous for extended systems where the computation of the mean-field operators and related operations are the most time-consuming steps.

Another issue of discussion for using the MPS form in the MCTDH theory is the construction of mean-field operators for single-particle functions \( \langle \varphi_j^{(p)} | \) expressed as

\[
\langle \hat{O} \rangle_{jk}^{\beta(\alpha)} = \langle \Psi_j^{(\alpha)} | \hat{O} | \Psi_k^{(\beta)} \rangle,
\]

where

\[
| \Psi_k^{(\beta)} (p) \rangle = \sum_{k_1} \cdots \sum_{k_{p-1}} \sum_{k_{p+1}} \cdots \sum_{k_f} A_{k_1 \cdots k_{p-1} k_{p+1} \cdots k_f} \langle \varphi_{k_1}^{(1)} \cdots \varphi_{k_{p-1}}^{(p-1)} \varphi_{k_{p+1}}^{(p+1)} \cdots \varphi_{k_f}^{(f)} \rangle.
\]

In general, phonon modes of molecular systems are complexly coupled through the potential energy surface created by the electronic-state; thus, there can be a \( f \)-body interaction \( V(Q_1, \ldots, Q_f) \) term in the Hamiltonian, but in many cases the \( f \)-body interaction is efficiently expanded by the \( n \)-mode coupling representation \[24\] and usually it is sufficient to truncate up to the fourth order expansion \[25\]. An efficient evaluation of three and four-body operators for MPS wavefunction by the DMRG sweep algorithm is presented in our previous work \[26\]. Alternatively, the \( f \)-body Hamiltonian are reduced to products of one-body operators of the single site basis \( \varphi^{(p)}(Q_p) \) in the MCTDH method \[13\] as

\[
\langle \varphi_j^{(1)} \cdots \varphi_j^{(f)} | \hat{O}^{(1 \cdots f)} | \varphi_{k_1}^{(1)} \cdots \varphi_{k_f}^{(f)} \rangle = \sum_{a} c_{a} \langle \varphi_{j_1}^{(a(1)} | \hat{O}^{(a(1)}_{\lambda_{p-1}} | \varphi_{k_1}^{(1)} \rangle \cdots \langle \varphi_{j_f}^{(a(f)} | \hat{O}^{(a(f)}_{\lambda_{p-1}} | \varphi_{k_f}^{(f)} \rangle.
\]

This product form is also very suitable for the MPS wavefunction. For example, a mean-field operator in the product form is decomposed as

\[
\langle \hat{O}_{a} \rangle_{jk}^{(p)} = \sum_{\lambda_{p-1},\lambda_{p}} \langle \varphi_{\lambda_{p-1}}^{(L)} | \hat{O}_{\lambda_{p-1}}^{(p-1)} | \varphi_{\lambda_{p}}^{(L)} \rangle \times \langle \varphi_{\lambda_{p}}^{(R)} | \hat{O}_{\lambda_{p}}^{(p+1 \cdots f)} | \varphi_{\lambda_{p-1}}^{(L)} \rangle C_{\lambda_{p-1}}^{(R)} C_{\lambda_{p}}^{(R)} \varphi_{\lambda_{p-1}}^{(p)}.
\]

The operators in the left and right blocks can be prepared easily in the same way as the DMRG algorithm, and the mean-field operators for the different sites \( p \) are constructed by the \( p \)-canonical form transformation along the MPS lattice.

To demonstrate the efficiency of the MPS-MCTDH method, exciton-phonon dynamics in the molecular aggregates were performed. The Hamiltonian adopted for the simulation is

\[
\hat{H} = \sum_{\alpha} \langle \alpha | \sum_{v} \frac{\omega_{v}^{a}}{2} \frac{\partial^{2}}{\partial Q_{v}^{2}} + \hat{Q}_{v} \rangle | \alpha \rangle \langle \alpha | J_{\alpha \beta},
\]

where \( \omega_{v}^{a} \) is the harmonic frequency of the phonon mode \( v \) on the diabatic electronic-state \( \alpha \), \( \kappa_{v}^{a} \) is the first-order coupling between the diabatic electronic-state \( \alpha \) and the phonon mode \( v \), and \( J_{\alpha \beta} \) for \( \alpha \neq \beta \) is the diabatic coupling between \( \alpha \) and \( \beta \) states and that for \( \alpha = \beta \) is the energy gaps between the states at the origin, \( Q_{v}=0 \) for all \( v \). The diabatic electronic-state of the molecular aggregate, \( | \alpha \rangle \), is characterized by the electronic state of each molecules; if the \( i \)-th molecule is in its excited-state, e.g. \( S_{1} \) state, while all the other molecules are in the ground state, the state is denoted by \( | i \rangle \). The parameters in the Hamiltonian, \( \omega_{v}^{a} \), \( \kappa_{v}^{a} \), and \( J_{\alpha \beta} \), can be quantitatively determined by \textit{ab initio} quantum chemical calculations to simulate real molecular systems. In the following, a single local vibrational mode per monomer is considered; thus the number of phonon DOFs is equal to the number of molecules and to the number of electronic states. The dimension for the site basis functions is set to four for all the phonon DOFs, and each site basis function is expressed by a linear combination of eight eigenfunctions of the harmonic oscillator from the lowest quantum number.

![FIG. 1. Time evolution of the exciton population with various methods for the 1-D and 2-D systems. The populations at the opposite end of the initially populated site are shown.](image-url)
The MCTDH and MPS-MCTDH methods described in this letter were implemented in Python3.

Figure 1 shows the population dynamics of an exciton in a molecular aggregate consisting of eight molecules 1-D aligned and sixteen molecules 2-D aligned. The population of the electronic-state $|\alpha\rangle$ in which the exciton is localized on the $i$-th molecule from the end is calculated as $\rho_i(t) = \langle \Psi | i \rangle | \Psi \rangle = \langle \Psi | i \rangle | \Psi \rangle$. At time $t = 0$, only the monomer at one end of the 1-D aggregate is electronically excited, and time evolution of the population of the exciton on the opposite end monomer are shown. The values for the parameters are $\omega^\alpha_v = 1255$ cm$^{-1}$ and $\kappa^\alpha_v = 1.072 \times \omega^\alpha_v$, typical values for intramolecular modes of organic semiconductors. The electronic states in which the excitons are located at the nearest neighbor to each other interact with each other by the diabatic coupling $J$ in 1-D and 2-D systems.

A multiset time-dependent Hartree (TDH) method, in which each vibrational wavefunction $\Psi^\alpha$ associated with an electronic-state is expressed by a Hartree product, hence the vibrational DOFs are non-entangled, are also performed for comparison. In all cases, the deviations between the TDH and MCTDH methods are found to be significant, which can be regarded as a measure of the strength of the entanglement between the vibrational DOFs in the system. The earliest maximum of the population in the plots corresponds to the first arrival of the exciton from the initial location, i.e. reflects the mobility of excitons, and the waves should go back and forth causing interference with each other. For the 1-D system with the $J=800$ cm$^{-1}$ (top panel), the MPS well reproduces the results of the MCTDH method, even with the smallest bond dimensions, $m=4$. For the same 1-D system with $J=2200$ cm$^{-1}$ (middle panel), the MPS($m=4$) plots deviates from the MCTDH plots after 70 fs for. The MPS($m=8$) is more robust and can trace the MCTDH plot and slightly deviate after 200 fs. The MPS with the largest bond dimensions $m=16$ reproduces the MCTDH result. It suggests that the required size of the bond dimension $m$ to maintain the same accuracy depends on the strength of the coupling. For the 2-D system with $J=800$ cm$^{-1}$ (bottom panel), the convergence of population dynamics to the result with large $m$ is slower than that for the 1-D system with the same coupling strength. Due to the nature of the MPS, which is a sequential product of tensors, the required size of $m$ is increased for 2-D and higher dimensional systems.

Table I shows the elapsed CPU time for computing the mean-field operators and propagation of the MCTDH coefficients $A_J$ or the MPS site functions $a_{i,j}^{\alpha}$, $a_{j}^{\alpha} \alpha_{i,j}^{\alpha}$, $\ldots$, $a_{i,j}^{\alpha \cdots \alpha}$, by the short-time Lanczos algorithm, per one step of the CMF integration algorithm, in which the mean-filed operators are evaluated two times and the coefficient are propagated three times including the backward propagation for the error estimation [23]. Due to the linear parametrization of the Hilbert space, the elapsed time for the MCTDH grows exponentially with the number of the molecules. The formal computational scaling of the MPS is $O(nm^3 k^2 f)$, where $k$ is the number of electronic states, for the evaluation of the mean-field operators and the time propagation of the site functions. In this excitonic systems, the number of vibrational DOFs $f$ and electronic states $k$ grows linearly with the number of molecules $N$, thus the formal computational scaling with respect to $N$ is cubic when $n$ and $m$ are constant, and that with $m$ is also cubic. The actual scaling with $m$ between $m=8$ and $m=16$ is linear, and that between $m=16$ and $m=32$ is quadratic, i.e. smaller than the formal scaling. This is because the most time consuming steps are relatively small matrix-matrix multiplication; typically the tensor contraction in Eq. 13, in which the matrix size for the matrix-matrix multiplication is $m \times m$, and high throughput cannot be achieved by the current implementation for small $m$.

To summarize, a matrix product state formulation of the multiconfiguration time-dependent Hartree is presented. The MPS can efficiently encode the Hilbert space of the phonon DOFs, which grows exponentially with the number of modes. Due to the nature of the MPS form, it is particularly effective for extended systems and modes that are strongly correlated as is often the case with molecular systems. The efficiency of the method was demonstrated on the quantum dynamics of the extended excitonic systems.

The author thanks Yoshitaka Tanimura for many valuable discussions.

[1] S. R. White, Phys. Rev. Lett. 69, 2863 (1992).
