JCTC Journal of Chemical Theory and Computation

Article

pubs.acs.org/JCTC

Accelerating Real-Time Time-Dependent Density Functional Theory with a Nonrecursive Chebyshev Expansion of the Quantum Propagator

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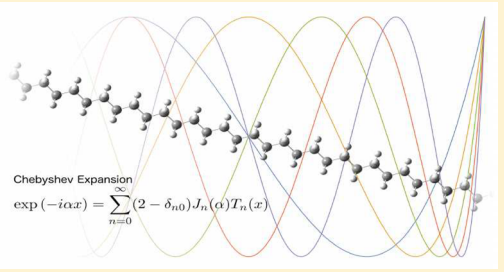
Supporting Information

ABSTRACT: Solutions of the real-time time-dependent density functional theory (RT-TDDFT) equations provide an affordable route to understanding the electronic dynamics that underpins many spectroscopic techniques. From the solutions of the RT-TDDFT equations, it is possible to extract optical absorption and circular dichroism spectra, as well as descriptions of charge transfer and charge transport dynamics. In order to apply RT-TDDFT to increasingly large systems, it is necessary to develop methods to overcome computational bottlenecks. One current bottleneck is the $O(N^3)$ cost required to form the time propagator for the RT-TDDFT equations, because of the full matrix diagonalization that is required at each time step. Here, we present a (semi)diagonalization-free formation of the propagator based on a nonrecursive Chebyshev polynomial expansion. The Chebyshev expansion relies only on matrix multiply operations which have lower computational cost and are furthermore extremely parallelizable. We demonstrate the accuracy and stability of the Chebyshev approach, and then discuss the favorable scaling of the method, compared to traditional approaches based on matrix diagonalization. The Chebyshev expansion method should enable the application of RT-TDDFT methods to large systems such as nanocrystals and biomolecules.



1. INTRODUCTION

Electronic motion is fundamental to our understanding of chemical and physical phenomena. From electronic reorganization upon photoinduced charge transfer in the chromophores of solar cells to the ultrafast excitonic dynamics in nanocrystalline materials, electron dynamics lies at the heart of chemistry. As such, to properly model these phenomena theoretically, we must often venture into the time domain to capture the physics necessary to completely understand the problem at hand. In the nonrelativistic treatment of quantum systems, quantum dynamics is governed by the many body time-dependent Schrödinger equation, given in atomic units (a.u.) by

$$i\partial_t|\Psi(t)\rangle = \mathcal{H}(t)|\Psi(t)\rangle \tag{1}$$

where $|\Psi(t)\rangle$ is the time-dependent many-body wave function and $\mathcal{H}(t)$ is the time-dependent Hamiltonian. One may, in principle, solve eq 1 simultaneously for all of the electronic degrees of freedom to obtain the electronic dynamics within the frozen nuclei extension of the Born−Oppenheimer approximation exactly. However, this approach is intractable for quantum systems exceeding more than a few particles. Within the mean-field description of the many-body wave function of Hartree−Fock (HF) or Kohn−Sham (KS) density functional theory, one may describe the electronic dynamics of a quantum system via (real-time) time-dependent Hartree−Fock (RT-TDHF)[1−4] or time-dependent Kohn−Sham density functional theory (RT-TDKS),[5−12] respectively. In this treatment, electronic dynamics is governed by the Liouville−von Neumann equation,

$$i\partial_t\mathbf{D}(t) = [\mathbf{F}(t), \mathbf{D}(t)] \tag{2}$$

where $\mathbf{D}(t)$ is the time-dependent single particle density matrix (1PDM) and $\mathbf{F}(t)$ is the time-dependent Fock (Kohn−Sham) matrix of HF (KS) theory. Both $\mathbf{D}(t)$ and $\mathbf{F}(t)$ are taken to be expressed in an orthonormal basis.

Integration of eq 2 formally scales as $O(N^4)$, where N is the number of basis functions used to describe the quantum system. This steep scaling is due to the high computational cost of the formation of the Fock/Kohn−Sham matrix, which must be performed for each time point,

$$\mathbf{F}(t) = \mathbf{h}(t) + \mathbf{J}[\mathbf{D}(t)] + (1-\eta)\mathbf{K}[\mathbf{D}(t)] + \eta\mathbf{V}_{xc}[\mathbf{D}(t)] \tag{3}$$

where $\mathbf{h}(t)$ is the core Hamiltonian, $\mathbf{J}[D(t)]$ and $\mathbf{K}[\mathbf{D}(t)]$ are the density-dependent Coulomb and exchange operators, and $\mathbf{V}_{xc}[\mathbf{D}(t)]$ is the KS exchange-correlation contribution to the Kohn−Sham matrix. $\eta \in [0, 1] \subset \mathbb{R}$ is a continuous and free parameter that spans HF ($\eta = 0$) and pure-KS ($\eta = 1$) with $\eta \in (0,1)$ denoting hybrid KS theories. Much work has gone into reducing the scaling of the Fock/Kohn−Sham matrix formation, achieving near linear-scaling with system size.[13−22] Even with an asymptotically linear-scaling Fock formation,

Received: July 12, 2016
Published: October 17, 2016

DOI: 10.1021/acs.jctc.6b00693
J. Chem. Theory Comput. 2016, 12, 5333−5338

however, traditional approaches to the integration of eq 2 still carry a relatively steep scaling of $O(N^3)$, because of the presence of a matrix diagonalization step at each time point.

All techniques to integrate eq 2 require the formation of a time propagator, $\mathbf{U}(t; \Delta t)$, that is, in some way, related to the matrix exponential of the Fock/Kohn−Sham matrix,

$$\mathbf{U}(t; \Delta t) = \mathrm{e}^{-i\beta(\Delta t)\mathbf{F}(t)} \tag{4}$$

where Δt is a time step, and $\beta(\Delta t)$ is some function of Δt that is dependent on the integration method. $\beta(\Delta t)$ is a simple function that is often Δt itself for many integration techniques, such as forward-Euler, but is, at times, a scalar multiple of Δt, such as $2\Delta t$ in the modified-midpoint unitary transformation (MMUT)[4,13,23,24] technique that is the focus of this article. The steep $O(N^3)$ scaling of dense matrix diagonalization greatly hinders the application of RT-TDHF and RT-TDKS to many large systems, such as nanocrystals or biomolecules. In addition, while the Fock/Kohn−Sham formation is easily parallelized, parallelization of matrix diagonalization is nontrivial.

It is known that matrix diagonalization can be avoided in the evaluation of matrix exponentials,[25−27] for example, the Padé approximation or various polynomial expansions, such as the Taylor and Chebyshev expansions. Polynomial expansions offer an attractive alternative to other methods as they only involve general matrix multiply (GEMM) operations. GEMM operations offer multiple advantages over matrix diagonalizations, namely, in scaling and parallelization. GEMM operations offer an improved scaling[28,29] of $O(N^{2.807})$, which leads to a sizable improvement over the diagonalization performance for large N. Crucially, while diagonalization suffers in the age of high-performance computing, GEMM operations thrive as they are an highly parallelizable task.[30,31] In this article, we explore the rapidly converging Chebyshev expansion[25−27,32−34] as an alternative to matrix diagonalization in the evaluation of eq 4. While the introduction of the Chebyshev expansion (or variants) is not completely new to the realm of quantum simulations,[27,34−36] its practical implementation and use in the field of *ab initio* real-time simulations has been limited. In this work, we demonstrate the general effectiveness of the Chebyshev expansion for RT-TDDFT and RT-TDHF.

2. METHODOLOGY

2.1. RT-TDDFT Using Chebyshev Expansion. We examine the propagation of the electronic degrees of freedom via a modified midpoint unitary transformation (MMUT) method.[4,13,23] In an orthonormal basis, the time evolution of the one particle density matrix may be obtained via a unitary transformation evaluated at the midpoint of the time interval,

$$\mathbf{D}(t_{k+1}) = \mathbf{U}(t_k; \Delta t)\mathbf{D}(t_{k-1})\mathbf{U}^{\dagger}(t_k; \Delta t) \tag{5}$$

where Δt is the time step of the MMUT integrator and t_k is the midpoint of t_{k+1} and t_{k-1}. Given that $\mathbf{U}$ is unitary, eq 5 maintains the idempotency of the density matrix. In the MMUT, the propagator is given in terms of the Fock/Kohn−Sham matrix via the exponential

$$\mathbf{U}(t_k, \Delta t) = \mathrm{e}^{-2i\Delta t\cdot\mathbf{F}(t_k)} \tag{6}$$

Once the density matrix has time-evolved to some time-point t_{k+1} via eq 5, the Fock/Kohn−Sham matrix may be updated (eq 3) to form a new propagator (eq 6). This new propagator may then be used to again propagate the density matrix in time.

The propagator of eq 6 can be constructed via diagonalization of the Fock/Kohn−Sham matrix,

$$\mathbf{F}(t) = \mathbf{C}(t)\boldsymbol{\varepsilon}(t)\mathbf{C}^{\dagger}(t) \tag{7}$$

$$\mathbf{U}(t; \Delta t) = \mathbf{C}(t)(\mathrm{e}^{-2i\Delta t\boldsymbol{\varepsilon}(t)})\mathbf{C}^{\dagger}(t) \tag{8}$$

where $\mathbf{C}(t)$ and $\boldsymbol{\varepsilon}(t)$ are the time-dependent orthonormal molecular orbitals (MOs) and diagonal matrix of canonical MO energies, respectively. This approach is, subject to the numerical precision, exact, but carries an $O(N^3)$ computational scaling and is inefficiently parallelized. An alternative approach is to expand the unitary propagator eq 6 in a polynomial series and utilize the highly efficient matrix product operations. However, such a polynomial expansion is often associated with a large computational prefactor, especially when high-accuracy solutions or higher-order terms in the expansion are needed. In the following section, we present an efficient Chebyshev expansion to construct the unitary propagator matrix.

2.2. Efficient Chebyshev Expansion of the Matrix Exponential. The Chebyshev expansion of the exponential of some complex $N \times N$ matrix, $\mathbf{X}$, may be written in terms of the Chebyshev polynomials of the first type:

$$\mathrm{e}^{-i\alpha\mathbf{X}} = \mathcal{N}\sum_{n=0}^{\infty}(-i)^n a_n(\tilde{\alpha})T_n(\tilde{X}) \quad \alpha \in \mathbb{R}^+ \tag{9}$$

Here, $T_n(\boldsymbol{\omega})$ is the set of Chebyshev polynomials of the first type, subject to the condition that the eigenvalues of $\boldsymbol{\omega}$ are bounded by the unit disk. For a complex general linear matrix, $\mathbf{X} \in \mathrm{GL}(N, \mathbb{C})$, this condition can be achieved through a *general linear* to *unit linear* transformation of $\mathbf{X}$, i.e., $\tilde{\mathbf{X}} = f(\mathbf{X})$, where f: $\mathrm{GL}(N, \mathbb{C}) \rightarrow \mathrm{UnL}(N, \mathbb{C})$. Here, we have taken $\mathrm{UnL}(N, \mathbb{C})$ encapsulate the properties given for $\boldsymbol{\omega}$ above. $\mathcal{N}$ and $\tilde{\alpha}$ are, respectively, a normalization constant and scaled prefactor that correspond to f. The choice of f and, consequently, $\mathcal{N}$ and α, are free, given certain criteria, and will be explored later in this article.

a_n represents the set of expansion coefficients corresponding to the Chebyshev polynomials at each order, given by[25−27,32,33]

$$a_n(x) = (2 - \delta_{n0})J_n(x) \tag{10}$$

where J_n is the set of Bessel functions of the first type,

$$J_n(x) = \sum_{m=0}^{\infty}\frac{(-1)^m}{m!(m+n)!}\left(\frac{x}{2}\right)^{2m+n} \tag{11}$$

In practice, one must truncate the Chebyshev expansion at some finite order K, in the evaluation of the complex matrix exponential. Herein lies the power of the Chebyshev expansion over other polynomial expansions, as it represents a near-optimal polynomial expansion for functions with rapidly converging power series.[32,37] The required Chebyshev polynomials may be evaluated recursively using the generating equations

$$\begin{aligned} T_0(\boldsymbol{\omega}) &= \mathbf{I} \\ T_1(\boldsymbol{\omega}) &= \boldsymbol{\omega} \\ T_n(\boldsymbol{\omega}) &= 2\boldsymbol{\omega}T_{n-1}(\boldsymbol{\omega}) - T_{n-2}(\boldsymbol{\omega}) \end{aligned} \tag{12}$$

where $\mathbf{I}$ is the identity matrix. The implementation of this recursion up to order K may be efficiently implemented with K dense matrix multiply operations. Efficient implementations of

DOI: 10.1021/acs.jctc.6b00693
J. Chem. Theory Comput. 2016, 12, 5333−5338

recursive Chebyshev have been applied to real-time TDDFT electronic dynamics.[34−36]

In this work, we propose a more efficient nonrecursive approach via a general unraveling of the Chebyshev polynomial recursion to obtain coefficients for the matrix powers directly. Equation 9 can be rewritten in terms of a matrix power series,

$$e^{-i\alpha \mathbf{X}} = \mathcal{N} \sum_{k=0}^{K} c_k(\tilde{\alpha})(-i\tilde{X})^k \tag{13}$$

where c_k represents a set of coefficients, specific to the Chebyshev polynomials, that expand the matrix powers of $-i\tilde{\mathbf{X}}$. Given the expressions in eqs 9−11, c_k can be computed as[38,39]

$$c_k(x) = \sum_{n=k}^{K} (2 - \delta_{n0})\zeta(n, k) J_n(x) \tag{14}$$

$$\zeta(n, k) = \begin{cases} 0 & (k + n) = \text{odd or } n < k \\ 1 & k = 0 \text{ and } n = \text{even} \\ \dfrac{2^{k-1} n}{k} \begin{pmatrix} \dfrac{n+k}{2} - 1 \\ k - 1 \end{pmatrix} & \text{else} \end{cases} \tag{15}$$

For an even truncation order, the range of matrix powers may be bisected to obtain

$$e^{-i\alpha \mathbf{X}} = \mathcal{N} \sum_{k=0}^{K/2} c_k(\tilde{\alpha})(-i\tilde{X})^k + \mathcal{N}(-i\tilde{X})^{K/2} \sum_{k=1}^{K/2} c_{k+K/2}(\tilde{\alpha})(-i\tilde{X})^k \quad (K = \text{even}) \tag{16}$$

This result is trivially extended to odd truncation orders. Implementation of eq 16 requires the same amount of storage as eq 12, only it requires half of the dense matrix multiply operations, compared to the recursive formation of the Chebyshev polynomial. This reduction effectively cuts the prefactor of the evaluation of the complex matrix exponential in half.

Note that the expression in eq 16 is completely general to any polynomial expansion, including that of the Taylor expansion, given some explicit form of the expansion coefficients. Equation 16 may be considered to be a variant on scaling and squaring, which is standard practice in the polynomial expansion of matrix functions to reduce error propagation.[40] In essence, the purposed algorithm in this work has made it possible to seamlessly interface any implementation of a polynomial expansion of the quantum propagator (given the form of eq 13) with the Chebyshev expansion with only a redefinition of the expansion coefficients.

2.3. Practical Numerical Implementation. By choosing $\alpha = 2\Delta t$ and $\mathbf{X} = \mathbf{F}$ in eq 16, the unitary propagator (eq 6) can be constructed using the Chebyshev expansion. In order to ensure that the spectral range, $\tilde{\boldsymbol{\varepsilon}}$, of the Chebyshev root matrix $\tilde{\mathbf{X}}$ satisfies the $-1 \leq \tilde{\boldsymbol{\varepsilon}} \leq 1$ condition, a *general linear* to *unit linear* transformation of the Fock/Kohn−Sham matrix must be carried out, $\tilde{\mathbf{X}} = f(\mathbf{F})$. The scaling function f may take any form that maps the spectral range of $\mathbf{F}$ to some subset of the unit disk. Out of simplicity, we have chosen the form[27]

$$\tilde{X} = f(\mathbf{F}) = \frac{1}{\gamma}(\mathbf{F} - (\gamma - \varepsilon_{\min}\mathbf{I})$$
$$\tilde{\alpha} = \gamma \Delta t$$
$$\mathcal{N} = e^{-2i(\gamma + \varepsilon_{\min})\Delta t} \tag{17}$$

where γ is a scaling factor that is chosen to be greater than the magnitude of the spectral range of $\mathbf{F}$, i.e., $\gamma > (\varepsilon_{\max} - \varepsilon_{\min})$, where $\varepsilon_{\max}$ and $\varepsilon_{\min}$ are the upper and lower bounds of the eigenspectrum of $\mathbf{F}$. In our experience and extensive testing, we have found the following definitions for the scaling parameters that properly suit the needs of the majority of MMUT calculations:

$$\gamma = \frac{3}{2}(\varepsilon_{\max} - \varepsilon_{\min}) \tag{18}$$

where $\varepsilon_{\max}$ and $\varepsilon_{\min}$ are the maximum and minimum MO energies of $\mathbf{F}$.

The transformation function defined in eqs 17 and 18, in principle, requires the *on-the-fly* evaluation of the upper and lower bounds of the Fock/Kohn−Sham matrix. This can be achieved using a Davidson-like iterative algorithm,[41−44] or direct diagonalization of the matrix. The latter seems counterintuitive as the purpose of using polynomial expansion is to avoid the direct diagonalization of the Fock/Kohn−Sham matrix. However, for cases with weak or no external perturbation time-dependent perturbations, where eq 18 is able to ensure the existence of *general linear* to *unit linear* transformation of the Fock/Kohn−Sham matrix throughout the simulation, one only needs a single diagonalization step to obtain the eigenspectrum of the perturbation-free Fock/Kohn−Sham matrix.

In cases where an external perturbation (e.g., intense laser field) can lead to large fluctuations in the eigenspectrum of the Fock/Kohn−Sham matrix, such a simple algorithm may not be sufficient. In such cases, the eigenspectrum of the Fock/Kohn−Sham matrix can be evaluated at some regular interval throughout the simulation, e.g., performing a full diagonalization of the time-dependent Fock/Kohn−Sham matrix to update the scaling parameters in eq 18. As shown later, a performance gain is still obtained over full-diagonalization-based methods, even for relatively frequent updates of the scaling parameters.

3. BENCHMARK AND DISCUSSION

The Chebyshev expansion of the MMUT time propagator has been implemented in a locally modified version of the Gaussian Development Version[45] suite of programs. In this section, we demonstrate the performance increase of the Chebyshev expansion over the eigen-decomposition approaches. All calculations performed in this benchmark study were carried out on a dual Intel(R) Xeon(R) (2 × 8 NUMA cores, 2.6 GHz) CPUs with 64 GB of RAM. Level-3 BLAS parallelism was achieved through ATLAS. The truncation order of the Chebyshev expansion was adjusted until agreement, with respect to the eigen-decomposition reference, was achieved up to a tolerance. For the systems studied, the Chebyshev expansion was found to truncate to desired (10^{-10}) accuracy within 16 terms (9 GEMM dense matrix multiply operations) with $\tilde{\alpha} \approx 1.2$, as the power series expansion coefficients decrease monotonically for a given eigenspectrum. Throughout this section, all quantities will be given in their respective

DOI: 10.1021/acs.jctc.6b00693
J. Chem. Theory Comput. 2016, 12, 5333−5338

atomic units: energy (E_h), electric field ($E_h/(ea_0)$), time ($\hbar/E_h$), and frequency ($E_h/\hbar$).

3.1. Performance Benchmark. To illustrate the performance of the Chebyshev expansion, RT-TDKS calculations were performed on alkane chains of increasing length using an MMUT integrator. All calculations were performed using the RT-TDB3LYP/6-31G(d) level of theory,[46−50] in the presence of a far off-resonant (ω = 0.2 a.u.) oscillatory electric field of amplitude 0.05 a.u., using a reasonably modest time step of 0.05 a.u. for 1000 time steps. Although excellent energy conservation was achieved with these benchmark systems, even with a single diagonalization step to recalculate the parameters in eq 17 throughout the MMUT integration, calculations were also performed with the parameters being recalculated to indicate the effect of intermittent eigen-decomposition on the performance of the Chebyshev expansion.

A summary of the computational acceleration may be seen in Figure 1. In these benchmark simulations, T^N_{Cheb} denotes the total wall-clock time of the simulation using Chebyshev expansion with a total of N number of eigen-decomposition operations in the simulation to recompute the parameters in eq 17. Performance enhancement over the full diagonalization/eigen-decomposition based method can be seen for all of the performed simulations at all degrees of parallelism, indicating that the Chebyshev expansion is a suitable alternative, even for computationally serial simulations. Figure 1a shows that, for the largest simulations performed, a computational acceleration of >100% is regularly observed, with the most marked improvement peaking just under 500%.

Figure 1b shows that, while the introduction of intermittent diagonalization throughout the propagation does introduce additional computational cost, the slowdown is small, compared to the complete eigen-decomposition method with N_{CPU} = 16. In the worst possible scenario in the given set of simulations (diagonalization every five time steps, T^{200}_{Cheb}), the slowdown is just shy of 2× over the T^1_{Cheb} Chebyshev simulation. Comparing this with the near 6× slowdown over the eigen-decomposition, even frequent restart of the Chebyshev time propagation is a marked improvement over traditional methods, as might be needed by simulations that involve intense or frequently oscillating perturbations.

3.2. Stability Case Study: H_2^+ Rabi Oscillation. A classic indication of time-propagation stability is that of correct prediction of the coherent Rabi oscillation (i.e., complete population inversion) of a two-state model problem.[4,51−57] As has been examined in previous work,[4] we have chosen to perform RT-TDHF on the single electron H_2^+ model system with a STO-3G basis, as it constitutes an ideal two-state problem with an analytic solution with which to compare. With STO-3G at the equilibrium geometry ($R_{\text{H−H}}$ = 1.0603 Å), the resonant excitation frequency is ω = 0.4746 a.u. We apply a sinusoidal electric field with frequency ω and a constant envelope amplitude of 0.05 a.u. to H_2^+ at a constant MMUT time step of 0.05 a.u. for a total duration of 200 a.u. To follow the Rabi oscillation dynamics, we analyze the time evolutions of the molecular orbital occupations, which are calculated by the projection of the time-dependent density matrix onto the initial ground-state field-free orbital space:[4]

$$n_i(t_k) = \mathbf{C}_i^{\dagger}(t_0)\mathbf{D}(t_k)\mathbf{C}_i(t_0) \tag{19}$$

where n_i is the occupation of the ith molecular orbital. The MMUT results for this time simulation are shown in Figure 2.

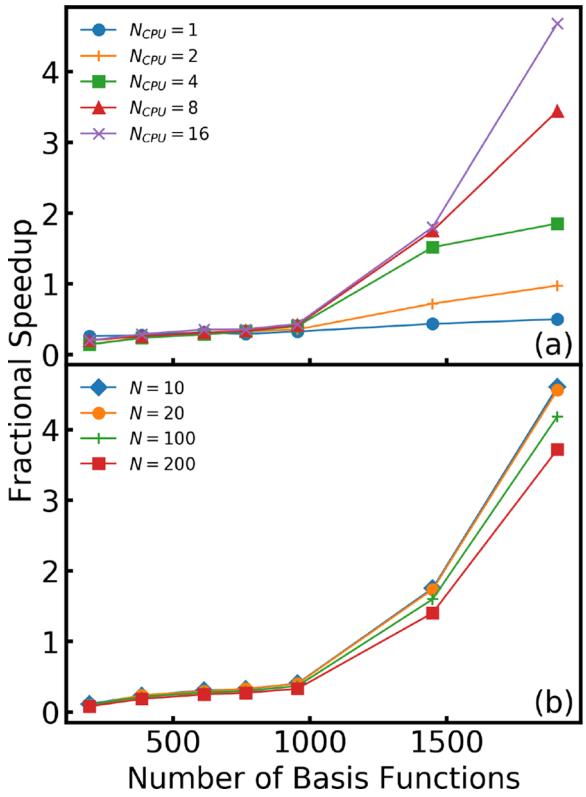


Figure 1. Comparison of the computational cost of the eigen-decomposition and the Chebyshev expansion methods for linear alkane chains, C_nH_{2n+2}. All calculations were performed with RT-TDB3LYP/6-31G(d) level of theory with Δt = 0.05 a.u. for 1000 steps. For all of the species in this test, $\tilde{\alpha} \approx 1.2$. Fractional computational acceleration over the full eigen-decomposition-based method is plotted as a function of the number of basis functions. All results are given in terms of the ratio $(T_{\text{Diag}} - T^N_{\text{Cheb}})/T^1_{\text{Cheb}}$, where T_{Diag} denotes the wall-clock computational time for the eigen-decomposition method and T^N_{Cheb} denotes the computational time for the Chebyshev expansion with N numbers of eigen-decomposition operations of the Fock/Kohn−Sham matrix during the simulation. Larger positive values means greater computational acceleration. (a) Parallel performance of MMUT with Chebyshev expansion T^1_{Cheb} compared to a full eigen-decomposition-based method T_{Diag} (N_{CPU} is the number of CPU cores). (b) Performance of MMUT with Chebyshev expansion with different number of intermediate eigen-decomposition operations T^N_{Cheb} during the simulation, compared to a full eigen-decomposition-based method T_{Diag} with N_{CPU} = 16.

The Rabi oscillation of H_2^+ represents a very challenging case for the Chebyshev expansion, as the eigenspectrum of the Fock matrix has a large oscillation amplitude. The scaling function, as proposed in eq 18, seems to be able to handle such a challenging situation quite well. The results for the Chebyshev expansion method are almost identical to that the eigen-decomposition method. In Figure 2b, even with only a single eigen-decomposition, the Chebyshev expansion only gives rise to a very small deviation from the exact result. This indicates that the Chebyshev expansion is a suitably stable alternative for eigen-decomposition.

4. CONCLUSION

In this study, we presented a nonrecursive Chebyshev expansion of the complex matrix exponential as an alternative of eigen-decomposition-based methods. Specifically, we have examined the application of this expansion to the evaluation of

DOI: 10.1021/acs.jctc.6b00693
J. Chem. Theory Comput. 2016, 12, 5333−5338

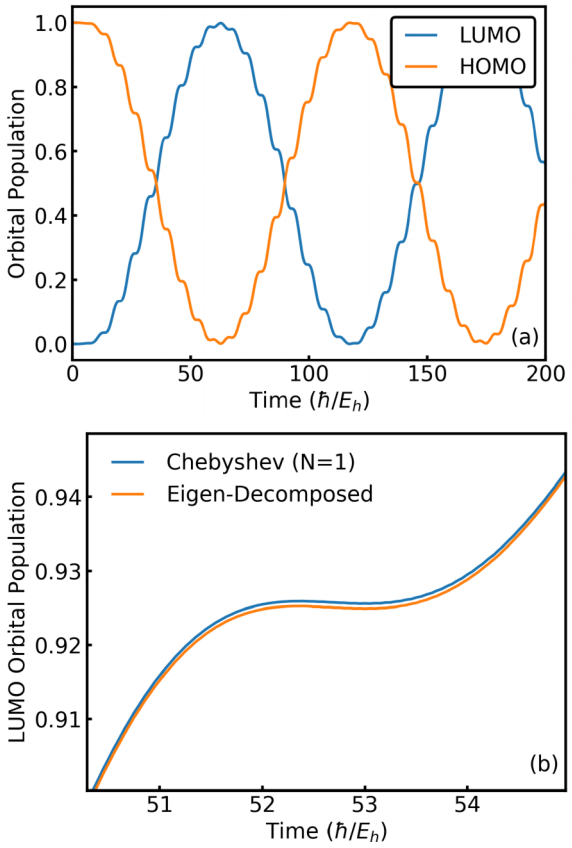


Figure 2. (a) RT-TDHF MMUT simulation of Rabi oscillation of H_2^+ in a minimal basis (STO-3G). Full population inversion is observed at a Rabi frequency of 0.0567 a.u., in excellent agreement with previous work[4] and the analytical result. The eigen-decomposition method and the Chebyshev expansion method are superimposable. (b) Zoom-in snapshot that shows a small deviation in orbital populations from simulations using the Chebyshev expansion with only one eigen-decomposition and the full eigen-decomposition-based method. The deviations are on the order of 10^{-3} electrons and have no bearing on the calculation of the Rabi oscillation frequency.

the time propagator for MMUT-RT-TDHF/TDKS simulations and its performance and stability, relative to eigen-decomposition. We have shown in our results that the Chebyshev expansion provides a suitably stable alternative to the eigen-decomposition method for evaluating the complex matrix exponential with the potential for implementation on high-performance computing platforms.

Although the nonrecursive Chebyshev expansion is, in the current formulation, dependent explicitly on some metric dependent on the eigenspectrum of the Fock/Kohn−Sham matrix, we have shown that with intermittent updates of the Chebyshev scaling parameters, excellent agreement with the eigen-decomposition can be achieved. Even for cases that involve large oscillations of the Fock/Kohn−Sham matrix, such at the Rabi oscillation for minimal basis H_2^+, very good agreement can be achieved, even for large time gaps between updates of the Chebyshev scaling parameters. This indicates that the Chebyshev expansion is suitably stable for the purpose of MMUT-RT-TDHF/TDKS.

In the performance benchmark, we have shown that the nonrecursive Chebyshev expansion outperforms the eigen-decomposition method for evaluation of the time propagator for reasonably sized molecules at all levels of parallelism. This performance gain scales very well with system size, peaking at an acceleration of ∼6× for the largest molecular system tested. The performance gain achieved with the nonrecursive Chebyshev expansion holds the potential of allowing routine treatment of systems which eigen-decomposition renders impractical, such as large biomolecules or nanocrystals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.6b00693.

Error accumulation of the Chebyshev and Taylor series expansions of the quantum propagator for the decane molecule (Figure S1) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The method development is supported by the U.S. National Science Foundation (Grant No. CHE-1565520). The University of Washington Student Technology Fund is gratefully acknowledged. This work was facilitated though the use of advanced computational, storage, and networking infrastructure provided by the Hyak supercomputer system at the University of Washington. This work is further supported by the U.S. National Science Foundation Graduate Research Fellowship No. DGE-1256082 to J.J.G.

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DOI: 10.1021/acs.jctc.6b00693
J. Chem. Theory Comput. 2016, 12, 5333−5338

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