

Instabilities and inaccuracies of multi-configuration time-dependent Hartree-Fock

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Abstract. We demonstrate that the widely used multi-configuration time-dependent Hartree-Fock method is restricted to a certain class of applications and fails for scenarios where periods of low entanglement occur during the propagation. By using illustrative and physically relevant examples, based on the Hubbard model of solid state physics, we show the existence of serious instabilities in the method itself and demonstrate that the method does not converge with respect to electron correlations. Possible cures of the approach are discussed.

1. Introduction

In recent years, time-dependent processes in many-particle systems have seen increased attention since their more complex structure leads to the emergence of previously unobserved effects. While it is theoretically possible to describe these systems exactly with methods like time-dependent full configuration interaction (FCI) [1], it is not viable in practice for most of them due to the exponential growth of the configuration space with respect to the particle number, the so called exponential wall.

To mitigate the influence of the exponential wall, it is necessary to employ approximations which is usually possible due to the fact that not all parts of the entire Hilbert space are accessed during the time propagation. This is, for example, exploited by the multi-configuration time-dependent Hartree-Fock (MCTDHF) method [2–5], which is a reformulation of the multi-configuration time-dependent Hartree (MCTDH) method [6, 7] for systems with exchange correlation. This family of methods is particularly suited for systems which require a large number of basis functions.

However, it turns out that MCTDHF suffers from serious instabilities if it is applied to a certain class of systems. This issue is especially severe if the simulation needs to be very accurate or encompasses a long timescale. This makes the validity of applying MCTDHF to such a system uncertain. These difficulties are known in the mathematical literature [8, 9] and recently mentioned in the quantum chemistry literature [10] but are not considered seriously in the physics community.

In this contribution, we will demonstrate the problem on the basis of a physically relevant example. Finally, we will discuss several possible approaches to cure this problem.



2. Theory

Prior to discussing the actual problem, we will give a short overview about the principles of MCTDHF. A more elaborate review can be found in Ref. [1]. Throughout this contribution, we will assume an N-particle Hamiltonian of the form

$$\hat{H}(t) := \sum_{pq} h_{pq}(t) \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} w_{pqrs} \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \quad (1)$$

with a (time-dependent) single-particle Hamiltonian $\hat{h}(t)$ and an interaction \hat{w} , respectively their matrix elements h_{pq} and w_{pqrs} in a given basis set.

In the MCTDHF framework, the wave function is expressed as a superposition of time-dependent Slater determinants (or configurations),

$$|\Psi\rangle = \sum_I C_I(t) |I, t\rangle, \quad (2)$$

which are written in occupation number representation with respect to the time-dependent orbitals $\{|\phi_i(t)\rangle\}$. The equations of motion for the expansion coefficients $C_I(t)$ and the orbitals $|\phi_i(t)\rangle$ can be obtained by using the Lagrange formulation of the time-dependent variational principle which involves the minimization of the action functional,

$$S[\{C_I\}, \{|\phi_i\rangle\}] = \int dt \left\{ \langle \Psi | \hat{H} - i \frac{\partial}{\partial t} | \Psi \rangle - \sum_{kl} \mu_{kl}(t) (\langle \phi_k | \phi_l \rangle - \delta_{kl}) \right\}, \quad (3)$$

with respect to the expansion coefficients, the orbitals and the Lagrange multiplier $\mu_{kl}(t)$. For example, the resulting conditions for the orbitals would read

$$0 \equiv \frac{\delta}{\delta \langle \phi_i |} S[\{C_I\}, \{|\phi_i\rangle\}]. \quad (4)$$

After taking the functional derivatives and simplifying the results, one obtains the wave function equation,

$$i\dot{C}_I(t) = \sum_J \langle I | \hat{H}(t) | J \rangle C_J(t), \quad (5)$$

and the orbital equation,

$$i|\dot{\phi}_n\rangle = \hat{P} \left\{ \hat{h}(t) |\phi_n\rangle + \sum_{pqrs} (\mathbf{D}^{-1})_{np} d_{pqrs} \langle \phi_r | \hat{w} | \phi_s \rangle |\phi_q\rangle \right\}, \quad (6)$$

with the single-particle density matrix $D_{pq} := \langle \Psi | \hat{a}_p^\dagger \hat{a}_q | \Psi \rangle$ and the two-particle density matrix $d_{pqrs} := \langle \Psi | \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q | \Psi \rangle$. $\hat{P} := \hat{1} - \sum_m |\phi_m\rangle \langle \phi_m|$ is the projection operator onto the orthogonal complement of the subspace spanned by the orbitals. An additional equation—ensuring the orthogonality of the orbitals—can be obtained via the Lagrange multipliers. However, this condition is already implicitly fulfilled by the orbital equation and is usually omitted.

As pointed out in the introduction, it is usually not necessary to consider the entire FCI Hilbert space at each point of time. The MCTDHF approximation exploits this by only trying to describe this subspace at each point of time, making it possible to use a relatively small number of orbitals M . At the same time, the *time dependence* of the orbitals allows to continuously adapt the spanned subspace to hopefully imitate the evolution of the exact subspace as closely

as possible. As the number of orbitals restricts the possible entanglement contained in the N-particle state, the MCTDHF approximation is only applicable for systems with small to medium entanglement. Conversely, one can significantly reduce the computational complexity, especially if it is necessary to use a large single-particle basis to describe the system. As the number of orbitals is increased, the result should converge to the exact FCI result.

From a numerical point of view, the restriction to a smaller subspace can be interpreted as performing a low-rank approximation with respect to the density matrix. While the scheme provides the ability to specify the *highest possible* rank for any calculation, nothing prohibits it to actually use a smaller rank. This results in two problems: First, the scheme does not need to be improved by the addition of an orbital as the algorithm might simply exclude it from the calculation. This might result in a difficult convergence which is actually observed in practice. The second issue is even more severe and is the focus of this contribution. It turns out that the MCTDHF equations (5) and (6) do not uniquely describe the evolution of the N-particle state for a large class of systems. Moreover, the resulting numerical instability actually leads to larger errors for an increasing number of orbitals instead of a convergence.

This flaw is not a problem of the numerical implementation but a fundamental one since it stems directly from the definition of the action functional (3). Since unoccupied (or virtual) orbitals do not give a contribution to the N-particle state $|\Psi\rangle$ the action as per definition (3) stays invariant under rotation of these orbitals. A direct consequence of this is that the functional derivatives (4) with respect to these orbitals vanish as those are postulated to be orthonormal. Hence, the evolution of these orbitals is not uniquely described by equation (6). As the cause is an inherent property of its derivation, it is in general not possible to rectify this flaw within the MCTDHF framework.

One might argue that this additional freedom should not change the result of the calculation, since the N-particle state does not depend on the virtual orbitals. However, any orbital might be (re-)occupied during the calculation. At this point of time, the state of the orbital might influence not only the physical state of the system—which is described by the N-particle state—but also all orbitals including the virtual ones. Therefore, an important insight is that the entire mathematical state of the simulation—described by the wave function coefficients and all orbitals—is very important for the behavior of the MCTDHF equations. Even the validity of a certain MCTDHF approximation could be changed by the choice of virtual orbitals. Another crucial point is that the MCTDHF equations are non-linear equations, hence even slight modifications of the virtual orbitals may lead to substantial errors. It should be noted however that all of this is irrelevant if the virtual orbitals are never occupied. This property mitigates the problem at least in the case of time-dependent Hartree-Fock (TDHF).

While it is so far not clear if the virtual orbitals actually influence the simulation in practice or if the MCTDHF equations are able to correctly adjust the virtual orbitals upon occupation, we will demonstrate in this contribution that the former is the case. Even from a purely theoretical point of view, this leads to some serious problems. One consequence is that MCTDHF calculations are not easily reproducible. For example, it is not sufficient to specify that the initial state is the ground state of the system as the set of obtained virtual orbitals may vary between different methods to calculate it. Furthermore, even the existence of several valid solutions makes this method, strictly speaking, mathematically ill-posed which might affect the applicability of certain numerical methods to solve the equations of motion.

In the case of a numerical implementation, all the above problems become even more critical. Due to the finite accuracy of floating point calculations, implementation varieties may lead to small differences in the virtual orbitals and as a result to divergent behavior between these implementations. If an implementation is parallelized, even different runs of the same simulation could show this behavior due to changes in the order of execution. Furthermore, orbitals with very low occupation need to be counted as unoccupied since the difference is not distinguishable

within the accuracy of the implementation. Hence, one might see the same problems even for a wider class of problems.

Numerically, the most crucial calculation is the inversion of the single-particle density matrix \mathbf{D} in the orbital equation (6), respectively, the solution of the corresponding system of linear equations. One way to quantify the numerical stability of this operation is the calculation of the singular value decomposition (SVD),

$$\mathbf{D} = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^\dagger, \quad (7)$$

and subsequent analysis of the singular values,

$$\sigma_i := \Sigma_{ii}. \quad (8)$$

From a physical point of view, the singular values are nothing more than the occupations of the natural orbitals and the matrices \mathbf{U} and \mathbf{V} specify the transformation between the time-dependent orbitals and the natural orbitals. Using the singular values, one can now calculate the condition number of the single-particle density matrix,

$$\kappa(\mathbf{D}) := \|\mathbf{D}\| \|\mathbf{D}^{-1}\|, \quad (9)$$

which can be expressed via the singular values as,

$$\kappa(\mathbf{D}) = \frac{\sigma_{\max}}{\sigma_{\min}}, \quad (10)$$

if one chooses the spectral norm $\|\cdot\|_2$ in equation (9). σ_{\max} and σ_{\min} are the largest respectively the smallest singular value. If one solves the linear system

$$\mathbf{D}x = b, \quad (11)$$

the relative error in the solution $\frac{\|\Delta x\|}{\|x\|}$ due to a change Δb in the right-hand side is bounded by

$$\frac{\|\Delta x\|}{\|x\|} \leq \kappa(\mathbf{D}) \frac{\|\Delta b\|}{\|b\|}. \quad (12)$$

Such a change might be introduced by a modification of the virtual orbitals or a general numerical inaccuracy during the calculation of the right-hand side. A similar bound can be found for the error with respect to a change in the matrix \mathbf{D} , though we will not discuss this here as the effect is quite similar.

Due to its occurrence as a factor on the right-hand side of the inequality (12), the condition number $\kappa(\mathbf{D})$ can be interpreted as an 'error amplification factor'. Hence, for a large condition number even small implementation variances may lead to significantly different results. This condition is fulfilled if at least one of the natural orbitals is significantly less occupied than the other ones. The worst case is, by construction, a Hartree-Fock-like state, as some orbitals are exactly unoccupied. On the contrary, if all natural orbitals are equally occupied—which corresponds to a state of maximal entanglement—this stability problem never manifests itself. From this observation, we can deduce another consequence. Since the added orbitals will be used to approximate ever smaller portions of the exact state, their occupation will inevitably decrease. The only imaginable system where this might not occur at some point would be a system with extremely large entanglement. But since the MCTDHF approximation only works for moderately entangled systems anyway without degenerating into a full CI calculation this point is rather moot. This leaves two choices: (1) Either one tries to reach convergence which will eventually be prevented by the invariably increasing instability, or (2) one stays at a low

number of orbitals and accepts the approximation error. Ultimately this means, that MCTDHF can not converge in most cases. While there is an optimal parameter for the number of orbitals w.r.t. to the introduced error, it is debatable if this suffices for most applications, especially if one has high accuracy requirements.

In practice, this numerical problem is usually suppressed by regularizing the single-particle density matrix. A possible workaround has recently been formulated by using a different integration scheme [11], which however introduces other shortcomings [10]. In our implementation we use the regularization

$$\mathbf{D} \rightarrow \mathbf{D} + \epsilon e^{-\frac{\mathbf{D}}{\epsilon}} \quad (13)$$

proposed in [7] with a regularization parameter ϵ . All possible choices have in common that they will inevitably introduce a systematic error. To avoid this, the parameter is set to a sufficiently small value, a typical choice is $\epsilon = 10^{-10}$. While small enough to be neglectable as a source of error, it turns out that this amount of regularization is insufficient in practice. Hence, it is arguable if regularization is a suitable solution for most applications of MCTDHF.

3. Numerical Results

To illustrate the problem in practice, we focus on a simple, but physically relevant system. Let us consider a small Hubbard cluster with strongly confined initial state. For a demonstration of the breakdown in atomic and molecular systems, we refer to a forthcoming publication [12].

We use a small Hubbard cluster with nearest-neighbor hopping and on-site interaction which is described by the Hamiltonian

$$\hat{H} = - \sum_{\langle ss' \rangle} \sum_{\sigma=\uparrow,\downarrow} a_{s\sigma}^\dagger a_{s'\sigma} + U \sum_s a_{s\uparrow}^\dagger a_{s\uparrow} a_{s\downarrow}^\dagger a_{s\downarrow}. \quad (14)$$

The first summation in equation (14) goes over all combinations of neighboring sites. A more comprehensive discussion of Hubbard clusters can be found in Ref. [13]. For this benchmark, we use two electrons, either one spin up and spin down, in eight sites. The effective interaction strength U is set to 1.

For times $t < 0$ the electrons are confined to the left-most (first) site by applying an infinitely large potential to all other sites. Conveniently, this implies that the initial state of the simulation can be analytically specified. Since only the occupation of first site leads to a finite energy contribution, all configurations except

$$|\Psi_0\rangle := |\phi_{0\uparrow}\phi_{0\downarrow}\rangle \quad (15)$$

must vanish. Therefore, the initial state $|\Psi_0\rangle$ is a Hartree-Fock state.

This fact has far reaching consequences for the time-dependent propagation. Since all time-dependent orbitals except for the first one are initially not occupied and as a result do not take part in the determination of the physical state, the choice of these virtual orbitals is arbitrary. The only restriction is that they must form a basis together with the first orbital.

One way of exploiting these additional degrees of freedom is to apply a unitary transformation to all orbitals which leaves the occupied ones invariant. In general, such a transformation takes the form of a block diagonal matrix,

$$\mathbf{U}_{\text{virt}} := \begin{pmatrix} \mathbb{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{U} \end{pmatrix}, \quad (16)$$

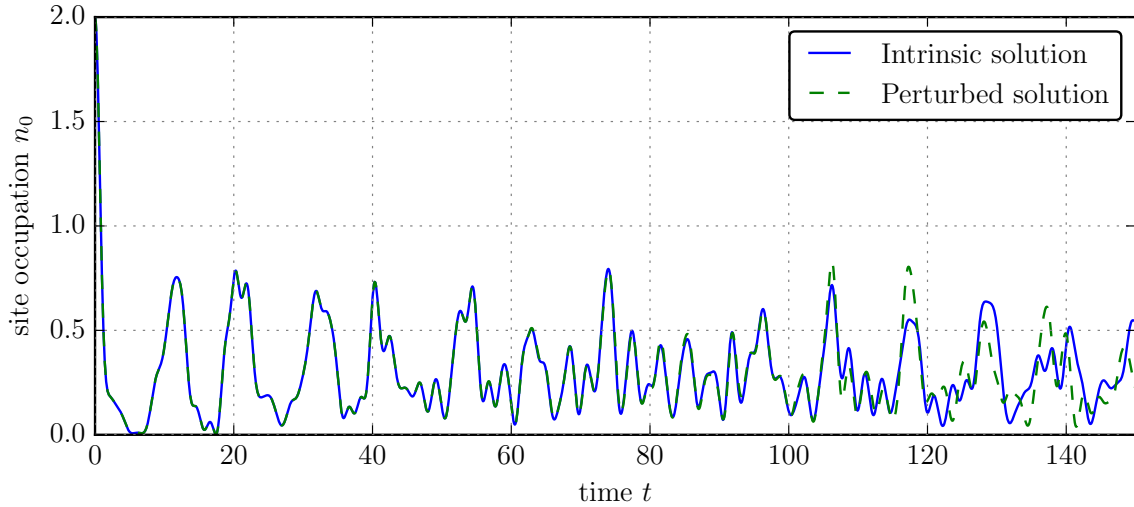


Figure 1. (color online) Occupation of the left-most Hubbard site for the intrinsic solution (blue, solid) and the perturbed solution (green, dashed). The Hubbard cluster consists of two particles in eight sites.

where the first block is the identity matrix and the second block is an arbitrary unitary matrix. In equation (16), we assume that the orbitals are sorted in descending order with respect to their occupation and that \mathbf{U} only acts on the virtual orbitals. For his calculation, we have chosen

$$\mathbf{U} = e^{i\mathbf{K}} \quad (17)$$

as the unitary transformation which is applied to the virtual orbitals. The matrix \mathbf{K} in equation (17) is an arbitrary Hermitian matrix which we define as

$$\mathbf{K} = \mathbf{J} + \mathbf{J}^\dagger \quad (18)$$

with a random complex matrix \mathbf{J} . Figure 1 depicts what happens if one applies the matrix \mathbf{U}_{virt} to the orbitals prior to the time-dependent propagation. The perturbed solution (dashed line) deviates significantly from the intrinsic solution even though the initial physical states are equivalent. Since all other parts of the simulation remained unchanged between the two runs, one has to conclude that the choice of virtual orbitals may have a substantial effect on the solution.

It should be noted that this problem occurs although the implementation was regularizing the single-particle density matrix with a parameter $\epsilon = 10^{-10}$. Hence, regularization is unable to solve the stability problem in general. While it might be possible to improve the stability using a larger regularization parameter, this has its own issues as one introduces another source of errors. Since it is practically impossible to predict or even measure the impact of these additional errors due to the non-linear nature of the MCTDHF equations, we have to assume that it will change the result significantly. As we will see below, even a small error might be amplified to a relevant deviation. However, the simulation would not be possible without some sort of regularization due to an arbitrarily large condition number during the initial phase of the simulation. If the resulting error grows large enough, the density matrices loose their defining properties, for example they cease to be positive semidefinite and self-adjoint, violating the fundamentals of quantum mechanics.

During the second benchmark, we will investigate the influence of implementation variations on the simulation results for a Hubbard cluster. To emulate the differing behavior of distinct

implementations, we introduce small artificial errors into our simulation in each time step. Using equation (12), one can define a set of possible deviations for a given relative error in the right-hand side of the linear system $\frac{b}{\|b\|}$ and a given exact solution x . All of these deviations are contained in a sphere of radius

$$\Delta := \frac{b}{\|b\|} \|x\|. \quad (19)$$

For this demonstration, we have chosen to use deviations which are uniformly distributed over the surface of this sphere. Such deviations can be calculated via the formula

$$D_r := \Delta \sqrt[3]{U} \frac{d_r}{\|d_r\|_2}. \quad (20)$$

U is chosen to be one while d_r is a vector of random numbers with a standard normal distribution. Another possible way to obtain a deviation would be to sample the variable U in definition (20) from a uniform real distribution in the range $[0, 1]$ which results in a uniform distribution within the sphere. However we have not pursued this here as we wanted to analyze the worst possible case.

To calculate the exact solution, we have solved the system with 256-bit precision which should give us a sufficiently good approximation. In the case of the right-hand side of Eq. (11), this is unfortunately not possible since the computational costs would be too high. Instead, we assume that the double precision solution is accurate enough and choose an relative error in units of the machine epsilon for double precision $\epsilon_M = 1.1 \cdot 10^{-16}$. Given that the computation of the right-hand side consist of several million floating point operations even a relatively high error is feasible. Even if the double precision solution differs significantly from the analytical one, our results still hold since in this case the error would be larger resulting in an even less stable propagation. After determining the deviation, it is simply added to the exact solution.

To investigate the effect of these artificial variances, we consider a Hubbard cluster with two particles in ten sites. To decrease the entanglement for the demonstration, the particles are initially confined by a harmonic oscillator potential $\frac{1}{2}\Omega^2\hat{x}^2$ with a trap frequency $\Omega = 0.75$. As the relative error of the right-hand side, we choose $\frac{b}{\|b\|} = 2 \cdot 10^9 \epsilon_M$. This large error was chosen to bypass the problem that for Hubbard-like systems MCTDHF becomes extremely instable with increasing number of orbitals. Even small changes in the parameters lead to a totally different behavior including program termination due to violated assumptions in the algorithm. To avoid this erratic behavior and provide reproducible results, we have chosen to use only four orbitals and increase the error of the right-hand side accordingly to obtain roughly the same error in the solution as for 6 orbitals. This avoids the failure while still allowing us to investigate the issue in a reasonable setup. Besides, a relative error in the order of magnitude of 10^{-8} is quite realistic for most numerical calculations.

As depicted in Fig. 2, the deviations between solutions corresponding to two different seeds can be much larger than the introduced error due to error amplification. Moreover, not only do the solutions differ quantitatively but also qualitatively at certain times of the simulation. It should be also noted that the occupation of the natural orbitals increases quickly which lessens the effect for later times. Thus, it is even more surprising that the effect is fairly pronounced.

While this effect is a problem for lowly entangled systems, Hubbard-like systems are strongly entangled in many important setups, thus avoiding this issue. However, as we will show below, the MCTDHF approximation even fails in those cases. To demonstrate this, we examine a Hubbard cluster with 8 particles in 8 basis functions. Similar to the first benchmarking system, the particles are confined to the four left-most sites for times $t < 0$. The effective interaction strength U is set to 0.1. The parameters were taken from Ref. [14] which discusses the system in the context of several other methods.

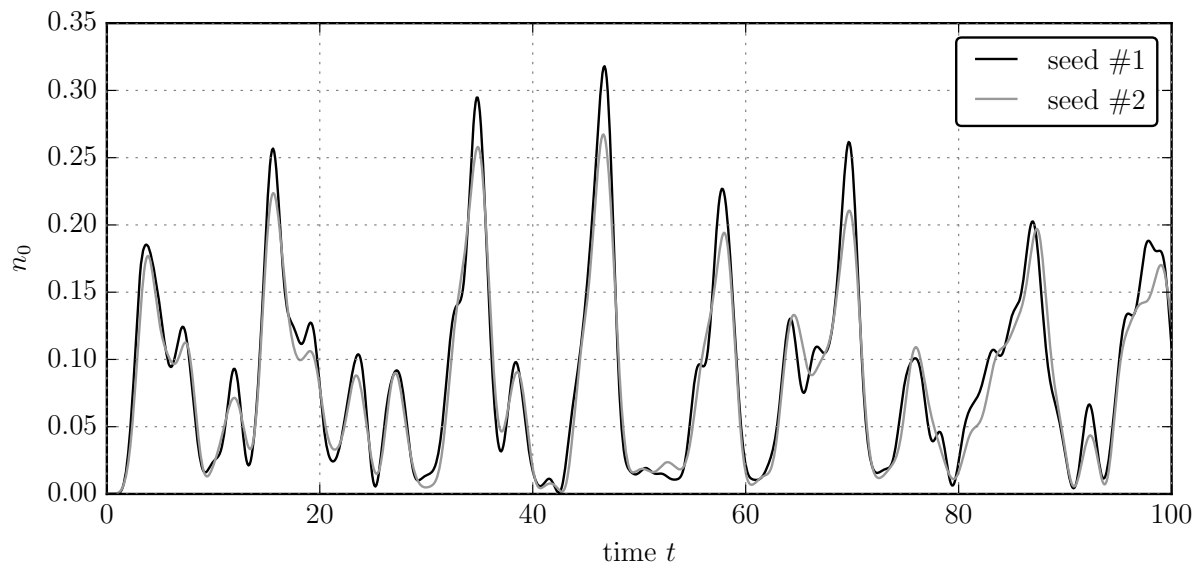


Figure 2. Occupation of the left-most Hubbard site for a cluster consisting of two electrons and ten sites for two different seeds. The electrons are initially confined by a harmonic oscillator potential with an angular frequency $\omega = 0.75$.

While the system starts in a Hartree-Fock-like state, and thus produces a comparably large deviation during the first few time steps, the strong excitation rapidly produces a strongly entangled state and as a result averts the stability problem for later times. Therefore, the system has not enough time to accumulate a significant error. Though, care must be taken to avoid that the error within the first few time steps is small enough. To avoid this pitfall, we have applied a regularization of $\epsilon = 10^{-10}$ to the single-particle density matrix.

It is obvious from Fig. 3 that MCTDHF is unsuitable even in this favorable case. For times prior to $t = 20$, the Hartree-Fock result almost matches the exact solution and the application of MCTDHF does not lead to definite improvements. Depending on one's accuracy requirements the much simpler TDHF might already suffice. At the same time, both TDHF and the best MCTDHF approximation ($M = 7$) fail to describe the behavior of the system for later times. Not only do they fail to describe the properties of the system quantitatively but also qualitatively. Again, the obtained improvement of MCTDHF beyond Hartree-Fock is uncertain as both methods show quite similar deviations at times. In conclusion, it is obvious that MCTDHF is not suitable to describe neither lowly nor strongly entangled systems.

4. Discussion

In this contribution, we have demonstrated that the practicalness of the MCTDHF method is severely restricted by an inherent instability caused by unoccupied orbitals. Due to error amplification, even small errors in the initial state or any intermediate step can cause significant changes in the obtained results. In the end, the convergence of MCTDHF against the exact FCI result is defeated by the increasing error with respect to the number of orbitals.

These problems are only avoided if the system exhibits strong entanglement throughout the entire simulation. However, as shown in Section 3, this would imply necessity of a full CI calculation making the usage of MCTDHF disputable. Apart from that, MCTDHF is only applicable to problems with low accuracy requirements, since one can stay at a lower number of orbitals, or very short calculations. Even in this case, one should carefully monitor the stability of the calculations—for example via the condition number—and reduce the number of time-dependent

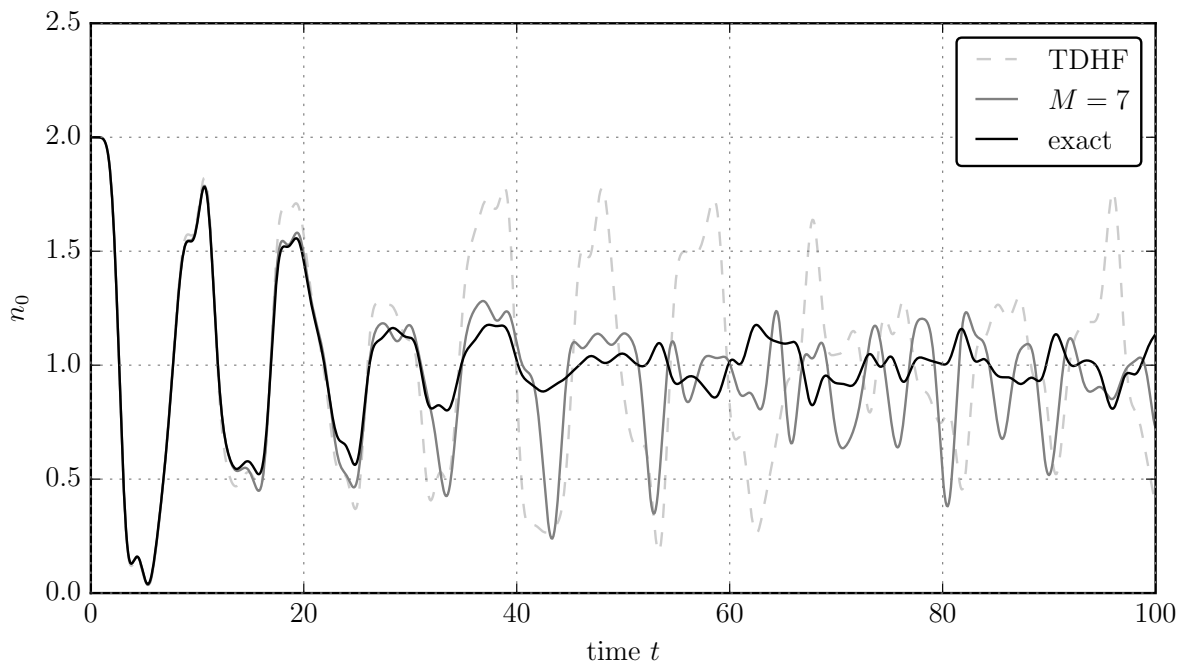


Figure 3. Occupation of the left-most Hubbard site for TDHF (light-gray, dashed), MCTDHF with $M = 7$ (medium-gray, solid) and FCI (black, solid). The system consists of 8 particles in 8 sites.

orbitals accordingly.

One possible solution would be to solve the orbital equation with sufficiently high accuracy to suppress any error amplification. Apart from the issue of consuming vastly more computational resources in itself, this has another severe limitation. From our experience, the condition number, and, therefore, the instability, tends to increase exponentially with respect to the number of orbitals making this practically intractable as one would need to expend an also exponentially increasing amount of resources. In the end, this would just create another exponential wall making the method ineffectual. Another solution which one might think of is an adaptive scheme which adds or removes orbitals as their occupation changes. Unfortunately, this idea is flawed since without a governing principle one would need to guess new orbitals and the inherently arbitrary choice would change the result of the calculation. One way to circumvent this is to specify another set of equations which determine the evolution of the virtual orbitals. A possible choice for such a system of equations was recently proposed by U. Manthe [10]. As of now, it is not obvious if this method can remove the instability or just hides it. Since the equations and their implementation will be reflected in the results, the effects of the intrinsic instability of the orbital equation can only be avoided if it is possible to solve these equations with sufficiently high accuracy.

Another way to avoid this instability would be the choice of an entirely different method. Unfortunately, the variety of candidates is quite restricted as it is most likely that other MCTDH-like methods, for example, time-dependent complete-active-space self-consistent-field [15, 16], time-dependent restricted-active-space self-consistent-field [17] and ultimately MCTDH itself, will exhibit the same instability. Moreover, we suspect that other methods using time-dependent orbitals, like the time-dependent renormalized natural orbital theory [18] and orbital-adaptive time-dependent coupled-cluster [19], might show similar problems as all of these methods involve an inversion of the single-particle density matrix or equivalent operations. One contender for

a replacement are CI-based methods with time-independent orbitals, like the time-dependent generalized-active-space configuration interaction (TD-GAS-CI) method [1, 20–22], due to their static Hilbert space. Another class of methods which have proven to be especially suited for Hubbard-like systems are based on the non-equilibrium Green function (NEGF) approach [14, 23–25]. However, the associated increase in the computational complexity necessitates the development of more powerful computational facilities.

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