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Research Article

On the Divergence of Time-Dependent Perturbation Theory Applied to Laser-Induced Molecular Transitions: Analytical Calculations for the Simple Algorithm

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Abstract Time-dependent perturbation theory is a suitable tool for the description of population transfer induced by weak shaped laser pulses, however its application can lead to norm divergences. We presented in a recently published work by numerical evidence but without analytical proofs in which way the norm deviations from unity can be split into numerical errors caused by the discretization of time and errors which are related to the perturbative expansion order. These proofs are elucidated in this publication for what we have called in our recent work "simple algorithm". Moreover, we present new results for the "simple algorithm".

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1 Introduction

In a recently published work [17], we discussed how far numerical algorithms for the implementation of perturbation theory are applicable to ultra-short laser pulse molecule interactions. This is an important issue because time-dependent perturbation theory is most commonly employed for the investigation of the interaction of atoms [5] and molecules [14] with electromagnetic fields. However, the disadvantage of the application of time-dependent perturbation theory is that it is generally not norm-conserving. Although non-perturbative and norm-conserving algorithms can be used to solve the time-dependent Schrödinger equation, the advantage of perturbative methods is that they allow for a clear decomposition of multi-photon processes into contributions which stem from different orders. As an interesting example, we mention time-resolved four-wave mixing spectroscopy, where one determines the third-order polarization associated with the signal emitted into a given direction [2]. It is possible to analyze four-wave mixing experiments with non-perturbative methods [7, 12, 19]. Nevertheless, within perturbation theory it is possible to differentiate contributions form higher-order interactions [4, 10, 20].

In the analysis presented in [17], we used a model of two molecular electronic states (ground state ($|0\rangle$) and excited state ($|1\rangle$)). In this model, initially only one of these two states is populated. Such conditions are realized, for example, in pump/shaped-dump experiments which have recently been reported [1, 9, 22]. In such processes where high intensity laser pulses interact with molecules, it is important to understand how the results of perturbation theory converge to the exact results. Although this convergence behavior, depending in detail on the chosen numerical parameters, on the molecular system, and on the electric fields, cannot easily be described quantitatively, it is still possible to analyze qualitatively the general trends of how the deviations of the norm from unity depend on the chosen parameters and the physical situation. In our former analysis, we used a simple and an improved algorithm, and we stated that the norm deviations can be decomposed into two parts, which we named the *stationary orders* and the *oscillatory orders*. These different parts differ in their behavior when the following parameters are changed: the time step for the discretization of time in the numerical algorithm, the order of perturbation in which the wave functions are calculated, the shape of the potentials of the two electronic states $|0\rangle$ and $|1\rangle$, and the electric field. In short, the stationary orders occur only for the simple algorithm; they depend on the electric field and the time step; they converge to zero for the limit that the time step goes to zero, but they do not depend on the shape of the potentials. Thus, we concluded that norm deviations caused by the stationary orders are purely numerical and they are not related to norm deviations that are caused by the discarding of higher-order interactions. In contrast to the norm deviations caused by the stationary orders, the norm deviations caused by the oscillatory orders occur for both algorithms, they do not depend in leading order on the time step, and thus they do not vanish in the limit of a vanishing time step. Moreover, they depend strongly on the chosen perturbation order for the wave function, the

shape of the potentials of the two electronic states $|0\rangle$ and $|1\rangle$, and on the electric field. This clearly indicates that the errors are related to the perturbative expansion of the wave function. The numerical results presented in [17] were interpreted with the help of analytical expressions which, however, were given without proofs. It is the purpose of the present paper to fill this gap for those analytical expressions, which are related to the simple algorithm. Due to reasons to conciseness, we explain here the main ideas of the mentioned proofs; the analytical details can be found in an extended version of this article published in arXiv [16]. The according calculations for the improved algorithm will be presented in an additional paper, which is in preparation. Besides mathematical proofs for results which were presented but not proven in [17], we show in this publication new numerical results and explanations for the behavior of the simple algorithm.

The paper is organized as follows: we describe in Section 2 the structure of the discussed Hamiltonian, summarize the basis of perturbation theory, and show how the simple algorithm introduced in [17] using perturbation theory for the calculation of the wave function can be derived. Section 3 contains an analytical analysis of the wave function calculated with the simple algorithm, and in Section 4, an analytical analysis of the norm of this wave function is given (in this section we derive the expressions which were given in [17] without proofs). Then, in Section 5 we summarize shortly an interpretation of the analytical results of Section 4, which was published in [17], and we show how, based on this interpretation, new conclusions and explanations for the behavior of the simple algorithm can be drawn. Finally, the paper is finished by a summary in Section 6.

2 Theory

2.1 Hamiltonian

As mentioned in the introduction, we investigate the interaction of an ultrashort laser pulse with a molecule in a model where we consider two electronic states $|1\rangle$ and $|0\rangle$. The nuclear degrees of freedom are represented by a single coordinate R. The total Hamiltonian $\hat{H}(R,t)$ consists of the system Hamiltonian $\hat{H}_0(R)$, and the field-matter interaction term $\hat{W}(t)$,

$$\hat{H}(R,t) = \hat{H}_0(R) + \hat{W}(t) = \begin{pmatrix} \hat{T}+V_1(R) & 0 \\ 0 & \hat{T}+V_0(R) \end{pmatrix} + \begin{pmatrix} 0 & -\mu E(t) \\ -\mu E(t) & 0 \end{pmatrix}, \tag{2.1}$$

where $\hat{T}$ is the kinetic energy operator, and where $V_j(R)$, $j \in \{0,1\}$, are the potentials in the electronic states. The term for the operator $\hat{W}(t)$ appearing in (2.1) results from the dipole interaction with the electric field $E(t)$ of the laser pulse and the projection μ of the transition dipole moment on the laser polarization vector. We take into account the Condon approximation and neglect the dependence of the transition dipole-moment on the nuclear coordinates. Moreover, dipole-coupling within a single electronic state is not regarded. As we analyze a system with two electronic states, we have to work with a two-component nuclear wave function $\vec{\Psi}(R,t)$ and the time-dependent Schrödinger equation reads (in atomic units):

$$i\frac{\partial}{\partial t}\begin{pmatrix} \Psi_1(R,t) \\ \Psi_0(R,t) \end{pmatrix} = \hat{H}(R,t)\begin{pmatrix} \Psi_1(R,t) \\ \Psi_0(R,t) \end{pmatrix}. \tag{2.2}$$

Due to the structure of the perturbation operator $\hat{W}(t)$ for even powers of $\hat{W}(t)$ with $\eta \in \mathbb{N}$, the following equation holds:

$$W(t)^{2\eta} = \mu^{2\eta}E(t)^{2\eta}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mu^{2\eta}E(t)^{2\eta}\mathbf{1}. \tag{2.3}$$

In order to emphasize this point, we will denote even powers of the perturbation operator $\hat{W}(t)$ without an operator head as $W(t)^{2\eta}$ in the following. According to (2.3) for odd powers of the perturbation operator $\hat{W}(t)$ we have

$$\hat{W}(t)^{2\eta-1} = W(t)^{2(\eta-1)}\hat{W}(t) \Longrightarrow \big[\hat{W}(t)^{2\eta-1}, \hat{H}_0(R)\big] = W(t)^{2(\eta-1)}\big[\hat{W}(t), \hat{H}_0(R)\big].$$

Thus odd powers written in the form $\hat{W}^{2\eta-1}$ are proportional to the perturbation *operator* $\hat{W}(t)$. As initial condition we fix [15, 17]

$$\vec{\Psi}\big(R, t=t_0\big) = \begin{pmatrix} \Psi_1\big(R, t=t_0\big) \\ 0 \end{pmatrix}. \tag{2.4}$$

In the following calculations, for clarity, we suppress in the notation dependencies on the vibrational coordinate R for all quantities.

2.2 Perturbation theory

The starting point of time-dependent perturbation theory is the integral equation for the wave function [11],

$$\vec{\Psi}(t) = e^{-i\hat{H}_0 t}\vec{\Psi}(0) - i\int_0^t dt' e^{-i\hat{H}_0(t-t')}\hat{W}(t')\vec{\Psi}(t'), \tag{2.5}$$

where we assumed that the interaction starts at time $t_0 = 0$. In perturbation theory, the wave function $\vec{\Psi}(t)$ is expanded in orders of the interaction-operator, and an approximative wave function $\vec{\Psi}(t,k)$ is obtained which contains all terms up to order k.

The wave function in first-order $\vec{\Psi}(t,1)$ is obtained by substituting the exact wave function $\vec{\Psi}(t')$ appearing under the integral by the initial function (0th-order wave function) evolving in time with the system propagator ($\vec{\Psi}(t,0) = e^{-i\hat{H}_0 t}\vec{\Psi}(0)$):

$$\vec{\Psi}(t,1) = e^{-i\hat{H}_0 t}\,\vec{\Psi}(0) - i\int_0^t dt'\, e^{-i\hat{H}_0(t-t')}\,\hat{W}(t')\,\vec{\Psi}(t',0). \tag{2.6}$$

By iterating (2.6), we obtain higher-order corrections as

$$\vec{\Psi}(t,k) = e^{-i\hat{H}_0 t}\,\vec{\Psi}(0) - i\int_0^t dt'\, e^{-i\hat{H}_0(t-t')}\,\hat{W}(t')\,\vec{\Psi}(t',k-1). \tag{2.7}$$

We can use (2.7) as a basis to devise a numerical algorithm for the calculation of perturbative wave functions [3]. For this aim we discretize the time t into time steps Δt yielding a time-grid where the times t_n are defined as $t_n = n\,\Delta t$ with whole-number values for n. As a next step, we set up an iteration scheme, where $\vec{\Psi}(t_{n+1},k)$ is calculated from $\vec{\Psi}(t_n,k)$.

Therefore the integral in (2.7) is divided into a first integral in the limits from $t' = 0$ to $t' = t_n$, and a second one reaching from $t' = t_n$ and $t' = t_n + \Delta t$, yielding

$$\vec{\Psi}\big(t_{n+1},k\big) = e^{-i\hat{H}_0\Delta t}\,\vec{\Psi}\big(t_n,k\big) - i\int_{t_n}^{t_n+\Delta t} dt'\, e^{-i\hat{H}_0(t_n+\Delta t-t')}\,\hat{W}(t')\,\vec{\Psi}(t',k-1). \tag{2.8}$$

This expression (2.8) for the wave function can be interpreted easily: the first term represents an unperturbed time-evolution of the system (during the time-interval $[t_n, t_n + \Delta t]$), whereas the second term stands for the possibility that during this interval at least one interaction takes place.[1] With these considerations a numerical scheme for the evaluation of the wave functions can be developed, which we call the *simple algorithm* (S). This algorithm is constructed by a replacement of the integral in (2.8) by a single term at the time $t' = t_{n+1}$, what leads to wave functions $\vec{\Psi}_S(t_n,\Delta t;k)$ depending on t_n, Δt, and k. Introducing the abbreviating notations $\vec{\Psi}(n,k) := \Psi_S(t_n,\Delta t;k)$ and $\hat{W}(n) := \hat{W}(t_n)$, we get the following equation for the simple algorithm [17]:

$$\vec{\Psi}_S(n+1,k) = e^{-i\hat{H}_0\Delta t}\,\vec{\Psi}_S(n,k) - i\Delta t\,\hat{W}(n+1)\,\vec{\Psi}_S(n+1,k-1) \tag{2.9}$$

with the start conditions $\vec{\Psi}_S(0,k) = \vec{\Psi}(0)$.

As a last purpose in this section, we explicate how the short-time propagator $e^{-i\hat{H}_0\Delta t}$, which appears in (2.9) and moves the wave function $\vec{\Psi}_S(n,k)$ over a time step Δt, can be executed numerically: this is customarily done by the split operator method of Feit and Fleck [6], where a grid for the spatial coordinate R is used. Being a one-step method correct in second order in the time step Δt, the application of the split-operator method in the simple algorithm S does not diminish the order in the time-step Δt, in which the simple algorithm is correct. The reason for this is as we will see in the following section that the simple algorithm is a one-step method which applies perturbation theory correctly only in first order in Δt.

[1] Here we note that equation (9) of [17], which corresponds to (2.8) in this paper, is misleading, because there interactions taking place in the small time interval $[t_n, t']$ were discarted.

3 Error analysis of the wave functions $\vec{\Psi}_S(n,k)$

In this analysis of the wave functions $\vec{\Psi}_S(n,k)$, first we state a closed form for them, and then we show that the simple algorithm is a one-step method correct in first order in Δt.

Before we start our analytic analysis of the wave functions $\vec{\Psi}_S(n,k)$, we have to introduce notations that are important for the following.

First, we define the sequence of non-commuting operators $\hat{A}_j$ when we use the product symbol $\prod$:

$$\prod_{j=0}^{n} \hat{A}_j := \hat{A}_0 \hat{A}_1 \cdots \hat{A}_n. \tag{3.1}$$

In the subsequent calculations combinatorial arguments are important. In particular, we will analyze combinatorial problems, where we have to calculate sums over all possible combinations with repetition. In these combinations m elements are taken out of a set that contains n elements, and the sequence in which the elements are chosen has no relevance. We specify a particular combination with repetition by a vector $\vec{\nu}^{(n,m)}$ that has n components, which are natural numbers or zero. The jth component $\nu_j^{(n,m)}$ of such a vector equals the number of cases how often the jth element is chosen in this particular combination. By definition this implies

$$\sum_{j=1}^{n} \nu_j^{(n,m)} = m.$$

Moreover, we introduce the combinatorial sum symbol $\Sigma_{\mathcal{P}_{\vec{\nu}^{(n,m)}}}$,

$$\sum_{\mathcal{P}_{\vec{\nu}^{(n,m)}}} f\big(\nu_1^{(n,m)}, \nu_2^{(n,m)}, \ldots, \nu_n^{(n,m)}\big),$$

where f is a function in the components of the vector $\vec{\nu}^{(n,m)}$, and where the sum contains all possible combinations with repetition for the situation that m elements are taken out of a set with n elements. For example, it is obvious that for $n = 2$, $m = 3$ the equation

$$\sum_{\mathcal{P}_{\vec{\nu}^{(2,3)}}} f\big(\nu_1^{(2,3)}, \nu_2^{(2,3)}\big) = f(3,0) + f(2,1) + f(1,2) + f(0,3)$$

is valid. Now the preparation for the virtual analysis is complete, so we can introduce the announced closed form of the wave functions $\vec{\Psi}_S(n,k)$

$$\vec{\Psi}_S(n,k) = \left[\sum_{m=0}^{k} (-i\,\Delta t)^m \sum_{\mathcal{P}_{\vec{\nu}^{(n,m)}}} \prod_{j=0}^{n-1} \left(\hat{W}(n-j)^{\nu_{n-j}^{(n,m)}} e^{-i\hat{H}_0 \Delta t} \right) \right] \vec{\Psi}(0). \tag{3.2}$$

This is proved in [16, Appendix A]. The expression (3.2) allows an analysis of the norm given in Section 4.

Now we show that the simple algorithm is a one-step method that applies perturbation theory correctly in first order in Δt for all $k \in \mathbb{N}$. Therefore, we expand the perturbation wave function $\vec{\Psi}(\Delta t, k)$ for all $k \in \mathbb{N}$ in second order in the time step Δt, where we regard as a starting point the equation (2.7) for $t = \Delta t$:

$$\begin{aligned} \vec{\Psi}(\Delta t, k) &= e^{-i\hat{H}_0 \Delta t} \vec{\Psi}(0) - i \int_0^{\Delta t} dt'\, e^{-i\hat{H}_0(\Delta t - t')} \hat{W}(t') \vec{\Psi}(t', k-1) \\ &= \left[1 - i\Delta t \big(\hat{H}_0 + \hat{W}(0)\big) - \frac{\Delta t^2}{2} \left(\hat{H}_0^2 + \hat{W}(0)\hat{H}_0 + \hat{H}_0 \hat{W}(0) + \big(1 - \delta_{k1}\big) W(0)^2 + i \frac{\partial W(t')}{\partial t'} \Big|_{t'=0} \right) \right] \vec{\Psi}(0) \\ &\quad + \mathcal{O}\big(\Delta t^3\big). \end{aligned} \tag{3.3}$$

Then we calculate with (2.9) the wave function $\vec{\Psi}_S(1,k)$ for all $k \in \mathbb{N}$ by propagation of the start wave function $\vec{\Psi}(0)$ over one-time step with the simple algorithm and expand the result in second order in Δt. For this calculation

it is practicable to write $\hat{W}(\Delta t)$ instead of $\hat{W}(1)$:

$$\begin{aligned}\vec{\Psi}_S(1,k) &= e^{-i\hat{H}_0\Delta t}\vec{\Psi}(0) - i\Delta t\hat{W}(\Delta t)\vec{\Psi}_S(1,k-1)\\ &= e^{-i\hat{H}_0\Delta t}\vec{\Psi}(0) - i\Delta t\hat{W}(\Delta t)\left[e^{-i\hat{H}_0\Delta t}\vec{\Psi}(0) - i\Delta t\big(1-\delta_{k1}\big)\hat{W}(\Delta t)\vec{\Psi}_S(1,k-2)\right]\\ &= \left[e^{-i\hat{H}_0\Delta t} - i\Delta t\hat{W}(\Delta t)e^{-i\hat{H}_0\Delta t} - \Delta t^2\big(1-\delta_{k1}\big)W(\Delta t)^2 e^{-i\hat{H}_0\Delta t}\right]\vec{\Psi}(0) + \mathcal{O}\big(\Delta t^3\big)\\ &= \left[1 - i\Delta t\big(\hat{H}_0+\hat{W}(0)\big) - \frac{\Delta t^2}{2}\left(\hat{H}_0^2 + 2\hat{W}(0)\hat{H}_0 + 2\big(1-\delta_{k1}\big)W(0)^2 + 2i\frac{\partial W(t')}{\partial t'}\Big|_{t'=0}\right)\right]\vec{\Psi}(0)\\ &\quad + \mathcal{O}\big(\Delta t^3\big).\end{aligned} \tag{3.4}$$

By comparison of (3.3) and (3.4), it can be recognized that

$$\vec{\Psi}(\Delta t,k) - \vec{\Psi}_S(1,k) = \frac{\Delta t^2}{2}\left(\hat{W}(0)\hat{H}_0 - \hat{H}_0\hat{W}(0) + \big(1-\delta_{k1}\big)W(0)^2 + i\frac{\partial W(t')}{\partial t'}\Big|_{t'=0}\right)\vec{\Psi}(0) + \mathcal{O}\big(\Delta t^3\big), \tag{3.5}$$

so the simple algorithm is a one-step method which applies perturbation theory correctly in first order in Δt for all $k \in \mathbb{N}$. Due to standard numerical textbook analysis of the asymptotic development for the global discretization error of one-step methods [21], the difference between the perturbation wave function $\vec{\Psi}(t,k)$, which is independent of the time step Δt, and the wave function $\vec{\Psi}_S(n,k)$ propagated over the time t with the simple algorithm, with $n = t/\Delta t$, is given by[2]

$$\vec{\Psi}(t,k) - \vec{\Psi}_S(n,k) = \Delta t\vec{\chi}(t,k) + \mathcal{O}\big(\Delta t^2\big). \tag{3.6}$$

For the function $\vec{\chi}(t,k)$ appearing in the above equation it holds that it is independent of the time step Δt and it fulfils $\vec{\chi}(0,k) = 0$.

For the evaluation of the accuracy of the simple algorithm, it has to be taken into account that the perturbation wave function $\vec{\Psi}(t,k)$ is itself an approximative solution of the Schrödinger equation (2.2), which deviates from the exact solution $\vec{\Psi}(t)$. This deviation can be noted as $\vec{\Psi}(t) - \vec{\Psi}(t,k) = \vec{\phi}(t,k)$. Therefore for the difference between $\vec{\Psi}_S(n,k)$ and the exact solution $\vec{\Psi}(t)$ the following holds:

$$\vec{\Psi}(t) - \vec{\Psi}_S(n,k) = \vec{\phi}(t,k) + \Delta t\,\vec{\chi}(t,k) + \mathcal{O}\big(\Delta t^2\big). \tag{3.7}$$

As the main conclusion of this section, the simple algorithm is a one-step method that applies perturbation theory correctly for all $k \in \mathbb{N}$ only in first order in Δt, so one might think that it is not useful to calculate wave functions $\vec{\Psi}_S(n,k)$ with $k > 1$. However, this reasoning is not correct because the use of a higher perturbation order k takes according to (3.7) influence on the difference $\vec{\Psi}(t) - \vec{\Psi}_S(n,k)$ and stabilizes so the simple algorithm against divergences of the norm; see the appendant discussions in Section 5.

4 Error analysis of the norms for the wave functions $\vec{\Psi}_S(n,k)$

4.1 Preliminary remarks

From the closed form expression (3.2) for the wave functions $\vec{\Psi}_S(n,k)$, it emerges that the wave functions can be decomposed into terms of $\vec{\Psi}_{m,S}(n)$ for different orders of perturbation:

$$\vec{\Psi}_S(n,k) = \sum_{m=0}^{k}\vec{\Psi}_{m,S}(n) \tag{4.1}$$

with

$$\vec{\Psi}_{m,S}(n) = (-i\,\Delta t)^m \sum_{\mathcal{P}_{\vec{\nu}(n,m)}}\prod_{j=0}^{n-1}\left(\hat{W}(n-j)^{\nu_{n-j}^{(n,m)}}e^{-i\hat{H}_0\Delta t}\right)\vec{\Psi}(0), \tag{4.2}$$

[2] The associated proposition in [21] to the equation (3.6) was discussed there for real functions instead of a complex wave function but it is straightforward to see that this is no limitation for an application of this proposition here. Furthermore, we suppose that the electric field $E(t)$ and therefore the wave function $\vec{\Psi}(t)$, too, depend in practical applications of the simple algorithm smoothly on time so that the proposition requirements given in [21] are not violated.

where the parameter m denotes the order of perturbation. The wave functions $\vec{\Psi}_{m,S}(n)$ have a clear interpretation as they are related to an interaction between the laser pulse and the molecular system, where m photons are exchanged, and therefore the electronic state changes m times during the time interval $[0, n\,\Delta t]$. Employing the decomposition (4.1), the norm yields

$$N_{n,S}^{k} = \left\langle \vec{\Psi}_S(n,k) | \vec{\Psi}_S(n,k) \right\rangle = \sum_{j=0}^{k} \sum_{h=0}^{k} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{h,S}(n) \right\rangle. \tag{4.3}$$

Using the substitution $p = j + h$, we can transform (4.3) regarding that the norm of the initial wave function $\vec{\Psi}(0)$ is defined as $\langle \vec{\Psi}(0) | \vec{\Psi}(0) \rangle = 1$ as follows:

$$\begin{aligned} N_{n,S}^{k} &= \sum_{j=0}^{k} \sum_{p=j}^{j+k} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{p-j,S}(n) \right\rangle = \sum_{p=0}^{2k} \sum_{j=\max(0,p-k)}^{\min(p,k)} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{p-j,S}(n) \right\rangle \\ &= 1 + \sum_{p=1}^{2k} \sum_{j=\max(0,p-k)}^{\min(p,k)} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{p-j,S}(n) \right\rangle. \end{aligned} \tag{4.4}$$

We note that terms for odd p in (4.4) are zero, which results from the choice of the initial conditions, where only the electronic state $|1\rangle$ is populated (see (2.4)). These terms involve the scalar product of wave functions in the different electronic states $|0\rangle, |1\rangle$, which are orthogonal. Due to this connection we substitute $p = 2m$ in (4.4), which yields

$$N_{n,S}^{k} = 1 + \sum_{m=1}^{k} \sum_{j=\max(0,2m-k)}^{\min(2m,k)} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{2m-j,S}(n) \right\rangle := 1 + \sum_{m=1}^{k} N_{n,2m,S}^{k}, \tag{4.5}$$

where the terms $N_{n,2m,S}^{k}$, given by

$$N_{n,2m,S}^{k} = \sum_{j=\max(0,2m-k)}^{\min(2m,k)} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{2m-j,S}(n) \right\rangle, \tag{4.6}$$

characterize norm deviations from unity. As was already discussed in [15, 17], these orders $N_{n,2m,S}^{k}$ can be decomposed into two different types: for $2k \geq 2m > k$ we call these orders *oscillatory orders*:

$$N_{n,2m,S}^{k} = \sum_{j=2m-k}^{k} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{2m-j,S}(n) \right\rangle \tag{4.7}$$

and for $k \geq 2m > 0$ they are called *stationary*:

$$N_{n,2m,S}^{k} = \sum_{j=0}^{2m} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{2m-j,S}(n) \right\rangle. \tag{4.8}$$

Note that the stationary orders contain no explicit dependence on k any more.

In [17], it has been shown that these two kinds of orders behave differently when parameters in the numerical simulation are changed and thus they have different physical interpretations. The former presented discussion was based on equations, which were presented without proof. In what follows the missing derivation will be given for the simple algorithm.

4.2 Norm analysis for the simple algorithm S

In the norm analysis for the simple algorithm in this section, we state first that the stationary orders can be written in a closed form. Secondly, we discuss that for the oscillatory norm orders we can introduce an approximation that allows to analyze how these norm orders scale in the time step Δt, and in this context we explain an evidence called annihilation thesis, which is a pre-condition for the approximation. Thirdly, we show that we can easily apply this approximation method, implemented foremost for the oscillatory orders, and for the stationary orders too.

In the calculations given here we are focussing on the considerations referring to the mentioned approximation because the most important point for the understanding of the mathematical background of the results presented in [17] is to get the idea how this approximation is introduced. In addition, all further calculations for the norm analysis for the simple algorithm are given in [16].

Thus, for the stationary norm orders $N^k_{n,2m,S}$ of the perturbative wave functions calculated via the simple algorithm we first note that

$$N^k_{n,2m,S} = (-1)^m \Delta t^{2m} \sum_{\mathcal{P}_{\vec{\nu}(n,m)}} \prod_{j=1}^{n} W(j)^{2\nu_j^{(n,m)}}. \tag{4.9}$$

The proof of this equation is given in [16, Appendix B]. We emphasize that in (4.9) only even orders of $\hat{W}(n)$ appear, for which (2.3) is valid.

After having presented the closed form (4.9) for the stationary orders of the simple algorithm $N^k_{n,2m,S}, k \geq 2m > 0$, we will investigate now the announced properties of the oscillatory orders $N^k_{n,2m,S}, k < 2m \leq 2k$. To do so, we employ (4.7) to calculate that for the orders $N^k_{n,2m,S}$, $k < 2m \leq 2k$ the following equation holds:

$$\begin{aligned} N^k_{n,2m,S} &= \sum_{j=2m-k}^{k} \left\langle \vec{\Psi}_{j,S}(n) | \vec{\Psi}_{2m-j,S}(n) \right\rangle \\ &= \Delta t^{2m} \sum_{j=2m-k}^{k} \sum_{\mathcal{P}_{\vec{\nu}(n,j)}} \sum_{\mathcal{P}_{\vec{\rho}(n,2m-j)}} (-1)^{m-j} \\ &\quad \times \left\langle \vec{\Psi}(0) \left| \prod_{q=1}^{n} \left(e^{i\hat{H}_0 \Delta t} \hat{W}(q)^{\nu_q^{(n,j)}} \right) \prod_{p=0}^{n-1} \left(\hat{W}(n-p)^{\rho_{n-p}^{(n,2m-j)}} e^{-i\hat{H}_0 \Delta t} \right) \right| \vec{\Psi}(0) \right\rangle. \end{aligned} \tag{4.10}$$

Each summand of the sums in (4.10) over $j, \mathcal{P}_{\vec{\nu}(n,j)}$ and $\mathcal{P}_{\vec{\rho}(n,2m-j)}$ is a product of the sign factor $(-1)^{m-j}$ and a bracket term $\langle \vec{\Psi}(0) | \cdots | \vec{\Psi}(0) \rangle$. The same bracket terms $\langle \vec{\Psi}(0) | \cdots | \vec{\Psi}(0) \rangle$ appear multiple in different summands of these sums, but the j-value of these summands differs, and thus they have different sign factors $(-1)^{m-j}$. Due to these different sign factors, these summands must cancel (at least) partly each other. Thus, all remaining summands for a *certain* type of bracket term survive with the *same* sign factor. But this leaves the question open if the surviving summands related to *different* types of bracket terms can have *different* signs. It can be shown that the surviving summands for all types of bracket terms appearing in (4.10) do *not* have *different* signs but the *same* sign, namely $(-1)^{k-m}$. This coherence is from now on called the *annihilation thesis* and the proof of it is presented in [16, Appendix C].

Our aim is to count the total number $\#^k_{n,2m,S}$ of all the surviving summands in (4.10) because the scaling of the number of these terms in the time step Δt helps to draw conclusions how the oscillatory order $N^k_{n,2m,S}$ scales in the time step Δt. Employing the annihilation thesis allows to count the total number of all the surviving summands, and it can be concluded that

$$\#^k_{n,2m,S} = \left| \sum_{j=2m-k}^{k} \left[(-1)^j \left(\sum_{\mathcal{P}_{\vec{\nu}(n,j)}} 1 \right) \left(\sum_{\mathcal{P}_{\vec{\rho}(n,2m-j)}} 1 \right) \right] \right|. \tag{4.11}$$

Now we introduce an approximation for the calculation of the norm orders $N^k_{n,2m,S}$ by approximating each of the surviving summands in (4.10) with a constant factor $\overline{W}^{2m}$ and we take into account the fact that all the surviving terms have the sign prefactor $(-1)^{k-m}$ by a global sign prefactor $(-1)^{k-m}$ for the calculation of the norm orders $N^k_{n,2m,S}$:

$$\begin{aligned} N^k_{n,2m,S} &= (-1)^{k-m} \Delta t^{2m} \overline{W}^{2m} \#^k_{n,2m,S} \\ &= (-1)^{k-m} \Delta t^{2m} \overline{W}^{2m} \left| \sum_{j=2m-k}^{k} \left[(-1)^j \left(\sum_{\mathcal{P}_{\vec{\nu}(n,j)}} 1 \right) \left(\sum_{\mathcal{P}_{\vec{\rho}(n,2m-j)}} 1 \right) \right] \right|. \end{aligned} \tag{4.12}$$

Since the sum $\sum_{\mathcal{P}_{\vec{\nu}(n,j)}}$ is executed over all combinations with repetition for a choice of j elements out of a set with n elements, elementary statistics yield [8]

$$\begin{aligned}\sum_{\mathcal{P}_{\vec{\nu}(n,j)}} 1 &= \binom{n+j-1}{j} = \frac{(n+j-1)(n+j-2)\cdots(n+1)n}{j!} \\ &= \frac{n^j}{j!} + \left(\sum_{q=1}^{j-1} q\right)\frac{n^{j-1}}{j!} + \mathcal{O}\left[\left(\frac{1}{n}\right)^{2-j}\right] = \frac{n^j}{j!}\left\{1+\frac{1}{2}\frac{j(j-1)}{n} + \mathcal{O}\left[\left(\frac{1}{n}\right)^2\right]\right\}.\end{aligned} \tag{4.13}$$

Inserting (4.13) in (4.12) and shifting the sum index j by m, we find

$$\begin{aligned}N^k_{n,2m,S} &= (-1)^{k-m}\Delta t^{2m}\overline{W}^{2m}n^{2m}\left|\sum_{j=-(k-m)}^{k-m}\frac{(-1)^j}{(m+j)!(m-j)!}\right|\left[1+\mathcal{O}\left(\frac{1}{n}\right)\right] \\ &:= (-1)^{k-m}\Delta t^{2m}\overline{W}^{2m}n^{2m}\,|\xi(m,k)|\left[1+\mathcal{O}\left(\frac{1}{n}\right)\right],\end{aligned} \tag{4.14}$$

where we introduced the help function $\xi(m,k)$:

$$\xi(m,k) = \sum_{j=-(k-m)}^{k-m}\frac{(-1)^j}{(m+j)!(m-j)!}. \tag{4.15}$$

With an induction proof over k one can show that if the oscillatory condition $k < 2m \leq 2k$ is valid, $\xi(m,k)$ can be written in the form (for proof see [16])

$$\xi(m,k) = \frac{(-1)^{k-m}}{m}\frac{1}{k!(2m-1-k)!}. \tag{4.16}$$

For a re-writing of (4.14), we first substitute the expression (4.16) for $\xi(m,k)$ in (4.14), and second, introducing the propagation time $t = n\,\Delta t$, we substitute furthermore $\frac{t}{\Delta t}$ for n in (4.14). So as a final result we get a central equation of [17] presented there without proof:

$$N^k_{t,2m,S} = \frac{(-1)^{k-m}}{m}\frac{t^{2m}}{k!(2m-1-k)!}\overline{W}^{2m} + \mathcal{O}(\Delta t). \tag{4.17}$$

In the latter equation, we have replaced the index n on the left side by t referring explicitly to time.

As the third task in this section, the above approximation can be applied not only for the oscillatory orders $N^k_{n,2m,S}, k < 2m \leq 2k$, but as well for the stationary orders $N^k_{n,2m,S}$, $k \geq 2m > 0$, because in (4.9) it can be seen that all terms appearing in the sum over $\mathcal{P}_{\vec{\nu}(n,m)}$ have the same global sign $(-1)^m$. Therefore, we approximate all factors $W(j)^2$ by $\overline{W}^2$ in (4.9). Regarding (4.13), this leads to

$$\begin{aligned}N^k_{n,2m,S} &= (-1)^m\Delta t^{2m}\sum_{\mathcal{P}_{\vec{\nu}(n,m)}}\prod_{j=1}^{n}W(j)^{2\nu_j^{(n,m)}} = (-1)^m\Delta t^{2m}\overline{W}^{2m}\sum_{\mathcal{P}_{\vec{\nu}(n,m)}}1 \\ &= (-1)^m\Delta t^{2m}\overline{W}^{2m}\frac{n^m}{m!}\left[1+\mathcal{O}\left(\frac{1}{n}\right)\right].\end{aligned}$$

Substituting $n = \frac{t}{\Delta t}$, we receive the final result

$$N^k_{t,2m,S} = (-1)^m\frac{t^m}{m!}\Delta t^m\overline{W}^{2m} + \mathcal{O}\left(\Delta t^{m+1}\right) \tag{4.18}$$

which was presented in [17] without proof, too.

In Section 5, we will discuss further consequences of the results derived in this section.

5 New conclusions

In this section, we will pick up the areas of interest established in [17, Sections 2.3 and 3]. Therefore, we summarize how the equations (4.17) and (4.18), which we discussed analytically in Section 4.2, were interpreted in [17]. Moreover, we will show how, based on the calculations done in Section 4, new conclusions and explanations for the behavior of the simple algorithm can be drawn, which complement the above-mentioned interpretation.

As a starting point we will focus on the interpretation of the stationary orders $N^k_{n,2m,S}$, $k \geq 2m > 0$. The norm deviations caused by the stationary orders depend according to (2.3) and (4.9) only on the time step Δt, the projection μ of the transition dipole moment on the laser polarization vector, and the electric field $E(t)$, but neither on the shape of the potential surfaces $V_j(R)$, $j \in \{0,1\}$ of the two electronic states $|1\rangle$ and $|0\rangle$, nor on the propagation of the wave function components $\Psi_1(R,n)$ and $\Psi_0(R,n)$ (here we explicitly wrote out the R-dependence) onto these surfaces. Due to (4.18) the stationary orders disappear in the limit $\Delta t \to 0$. So the stationary orders are only purely numerical errors which arise using the simple algorithm because of the approximation of the integral in (2.8) by only one summand and they are related to the Δt-dependent part in the difference of the approximative wave functions $\vec{\Psi}_S(n,k)$ to the exact wave function $\vec{\Psi}(t)$ (see (3.7)).

For a not too large propagation time t and a small time step Δt, the stationary order for $m = 1$, $N^k_{t,2,S}$, gives the dominant contribution to the norm deviation. In [17], we derived a result for $N^k_{t,2,S}$ by choosing $m = 1$ in (4.18),

$$N^k_{t,2,S} = -t\,\Delta t\,\overline{W}^2 + \mathcal{O}\big(\Delta t^2\big) \tag{5.1}$$

which can be used for a qualitative discussion of the behavior of $N^k_{t,2,S}$. However, we show here that a quantitative calculation of $N^k_{t,2,S}$ is possible, too.

Therefore, we compute the norm deviation caused by the stationary orders $N^k_{n,2m,S}, k \geq 2m > 0$, for an electric field given by

$$E(t) = A(t)\cos\big(\Phi(t)\big), \tag{5.2}$$

where $A(t)$ is the envelope of the electric field and $\Phi(t)$ is a fast oscillating phase function. We consider that permutation vectors of the form $\vec{\nu}^{(n,1)}$ have n components at which one component is 1 and all other components are 0. So we can simplify (4.9) for $m = 1$:

$$N^k_{n,2,S} = -\Delta t^2 \sum_{\mathcal{P}_{\vec{\nu}^{(n,1)}}} \prod_{j=1}^{n} W(j)^{2\nu_j^{(n,1)}} = -\Delta t \sum_{j=1}^{n} W(j)^2 \Delta t. \tag{5.3}$$

Inserting (2.3) and (5.2) into (5.3) and approximating the sum by an integral leads to the result

$$N^k_{t,2,S} = -\mu^2\,\Delta t \int_0^t dt'\, A(t')^2 \cos^2\big(\Phi(t')\big). \tag{5.4}$$

Here, we denoted the time dependency again by t. Since this integral in the limits 0 and t is proportional to the stored energy in the laser pulse in this time interval, the norm deviations caused by the stationary orders at a certain point in time t are approximately a proportion for this quantity. Therefore for the limit $t \to \infty$, the stationary order $N^k_{t,2,S}$ is proportional to the total energy of the laser pulse. Within the "slow-varying envelope approximation" [13,18] we can approximate (5.4) by substituting the factor $\cos^2(\Phi(t'))$ under the integral by $\frac{1}{2}$ and get as a result

$$N^k_{t,2,S} = -\frac{\mu^2\,\Delta t}{2} \int_0^t dt'\, A(t')^2. \tag{5.5}$$

This result reveals that if the "slow-varying envelope approximation" is valid, the norm deviations caused by the stationary orders do not depend approximately on the phase $\Phi(t)$ but on the time integral over the squared envelope of the electric field. Furthermore, it can be recognized from (5.5) that $N^k_{t,2,S}$ depends linearly on the time step Δt. This result is related to the fact that according to (3.7) the leading order of the Δt-dependent part of the deviations of the wave functions $\vec{\Psi}_S(n,k)$ to the exact solution $\vec{\Psi}(t)$ is the first order.

In particular, we regard as an example for the use of (5.5) the Gaussian laser pulse modified by a linear spectral chirp b_2 we employed for our numerical application of the simple algorithm in [17] and compare the results we got there numerically with the norm deviations we are now able to calculate analytically with (5.5).

The unchirped pulse is given by

$$E(t) = E_0' e^{-\beta'(t-t_d)^2} \cos\big[\omega_0\big(t - t_d\big)\big] \tag{5.6}$$

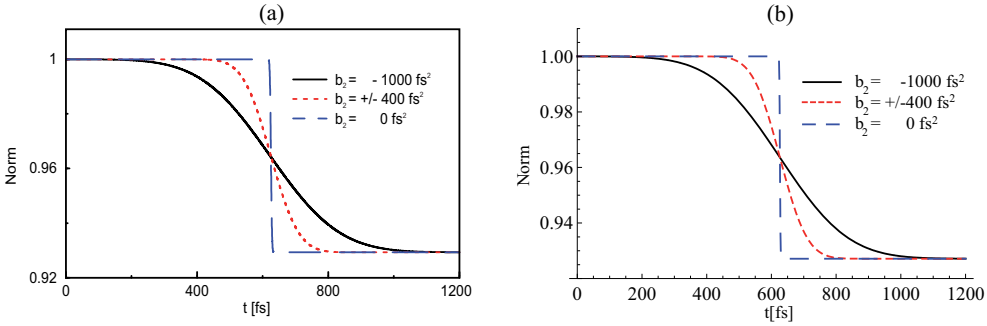

Figure 1: The norm deviations arising from a numerical simulation employing the simple algorithm (panel (a)), and the norm deviations calculated analytically with (5.9) (panel (b)). The analytically calculated deviations in panel (b) accurately match the numerical results in panel (a).

with an envelope having a full width at half maximum of $\tau' = \sqrt{4\ln 2/\beta'}$, and the chirped laser pulse is given by

$$E(t) = E_0 e^{-\beta(t-t_d)^2} \cos\left[\omega_0(t-t_d) + \frac{a_2}{2}(t-t_d)^2\right]. \tag{5.7}$$

In the last equations, the field strengths are denoted as E_0' and E_0 for the unchirped and for the chirped fields, respectively, and t_d denotes the point in time when the envelope of the field is maximal. The various parameters appearing in the equations for the shaped and for the unshaped electric fields are related as follows [23]:

$$\begin{aligned} E_0 &= \sqrt{\frac{1}{1+2i\beta' b_2}}\,E_0', \quad |E_0| = \left(1+4\beta'^2 b_2^2\right)^{-\frac{1}{4}} |E_0'| \\ \beta &= \frac{1}{\frac{1}{\beta'}+4\beta' b_2^2}, \quad a_2 = \frac{b_2}{\frac{1}{4\beta'^2}+b_2^2}. \end{aligned} \tag{5.8}$$

For the electric field given by (5.7), we can calculate with (5.5) and (5.8) that the norm deviations caused by the stationary orders are given by

$$N^k_{t,2,S} = -\mu^2 \Delta t\, E_0'^2 \tau' \sqrt{\frac{\pi}{128\ln 2}} \left\{1 + \operatorname{erf}\left[\sqrt{\frac{32\ln 2\,\tau'^2}{\tau'^4 + (16\ln 2\, b_2)^2}}\,(t-t_d)\right]\right\}. \tag{5.9}$$

Norm deviations calculated with (5.9) match excellently with the numerical results which are presented in [17, Figure 4]. This relation is presented in Figure 1, where the norm deviations from unity caused in the numerical simulation with the simple algorithm are shown again in panel (a), and the norm deviations from unity calculated analytically are shown in panel (b). For the analytical calculation, we used the parameter values which lead to the numerical results presented in [17, Figure 4], namely $\mu = 1$ a.u., $\Delta t = 3.31$ a.u., $\tau' = 4.13 * 10^2$ a.u. and $E_0' = 1.19 * 10^{-2}$ a.u., and different values for the spectral chirp parameter b_2, which are given in Figure 1.

Furthermore, in the limit $t \to \infty$, one obtains from (5.9)

$$\lim_{t\to\infty} N^k_{t,2,S} = -\mu^2 \Delta t\, E_0'^2 \tau' \sqrt{\frac{\pi}{32\ln 2}}. \tag{5.10}$$

This result is independent of the spectral chirp parameter b_2 because the total energy of the laser pulse does not depend on the spectral chirp parameter b_2. For the parameters of our numerical example, (5.10) leads to a value of 0.927, which is in excellent agreement to our numerical results.

Next, we summarize the analysis of the norm deviations caused by the oscillatory orders $N^k_{n,2m,S}, k < 2m \leq 2k$, we gave in [17]. For longer propagation times t these orders make up the dominant contribution to the norm deviations for the simple algorithm because in taking the ratio between the stationary and oscillatory orders (see (4.18) and (4.17)), this number scales with $(\Delta t/t)^m$. Thus for large t the stationary terms are negligible. As can be deduced from (4.17), the oscillatory terms in contrast to the stationary terms, in leading order, do not depend on the time step Δt and they lead to oscillations in time for the norm deviation. Therefore, we can conclude that the oscillatory orders $N^k_{n,2m,S}, k < 2m \leq 2k$, in contrast to the stationary orders $N^k_{n,2m,S}, k \geq 2m > 0$, do depend on

the Δt-independent part of the difference of the approximative wave functions $\vec{\Psi}_S(n,k)$ to the exact wave function $\vec{\Psi}(t)$, which is given in (3.7) by $\vec{\phi}(t,k)$. For large enough t, the highest oscillatory order for $m=k$, $N^k_{n,2m,S}$, leads to a divergence of the norm deviations towards infinity. However, it is possible to retard or even to suppress this divergence if the perturbation order k is chosen high enough. Since a choice of a perturbation order k for the calculation of the wave functions $\vec{\Psi}_S(n,k)$ is equivalent to exclude all interactions which involve more than k photons, these kinds of norm divergences can be interpreted in such a way that system-field interaction pathways which involve more than k photons have to be taken into account to describe the system-field interaction correctly.

We discussed in [17] that the oscillatory orders $N^k_{n,2m,S}$, $2k \geq 2m > k$, (in contrast to the stationary orders) depend on the shape of the potentials $V_1(R)$ and $V_0(R)$. However, we presented there only a numerical example without an analytical explanation for this dependency. This gap is filled with the following discussion.

Therefore, we calculate explicitly with (4.2) and (4.7) the oscillatory orders for the simple algorithm:

$$\begin{aligned} N^k_{n,2m,S} = & \sum_{j=2m-k}^{k} (-1)^{m-j} \Delta t^{2m} \\ & \times \sum_{\mathcal{P}_{\vec{\nu}^{(n,j)}}} \sum_{\mathcal{P}_{\vec{\rho}^{(n,2m-j)}}} \left\langle \vec{\Psi}(0) \middle| \prod_{q=1}^{n} \left(e^{i\hat{H}_0 \Delta t} \hat{W}(q)^{\nu_q^{(n,j)}} \right) \prod_{p=0}^{n-1} \left(\hat{W}(n-p)^{\rho_{n-p}^{(n,2m-j)}} e^{-i\hat{H}_0 \Delta t} \right) \middle| \vec{\Psi}(0) \right\rangle . \end{aligned} \tag{5.11}$$

The bracket terms $\langle \Psi(0)| \cdots |\Psi(0)\rangle$ in (5.11) describe the overlap between a bra-state that is influenced by interaction operators $\hat{W}(q)$ at certain points in time ($\nu_q^{(n,j)} \neq 0$) with a ket-state that is influenced by interaction operators $\hat{W}(n-q)$ at other points in time ($\rho_{n-q}^{(n,2m-j)} \neq 0$). Through the impact of the interaction operators at different points in time the bra-state and the ket-state propagate over the time interval $[t_0, t_n]$ in a different way.

That means for points in time $t_{n'}$ with $t_0 < t_{n'} < t_n$ the bra-state and the ket-state can be localized in different electronic states. But at t_n, when the overlap is calculated, the bra-state and the ket-state must be in the same electronic state, otherwise the overlap is zero. If the absolute value of the difference between the potential gradients in the two electronic states $\Delta V'(R) := |\frac{dV_1(R)}{dR} - \frac{dV_0(R)}{dR}|$ is large in the spatial region, where the wave function is positioned during the interaction of the molecular system with the laser pulse, the differences in the temporal propagation in these two electronic states $|1\rangle$ and $|0\rangle$ lead to a small overlap of the bra-state and the ket-state. This leads to the effect that the oscillatory orders are suppressed for large potential gradient differences $\Delta V'(R)$.

This effect can interpreted in that way that for a large potential gradient difference $\Delta V'(R)$ the interaction time, where the laser pulse induces transitions between the two electronic states $|1\rangle$ and $|0\rangle$ effectively, is small and then a smaller amount of photon is enough to describe the interaction between the pulse and the system properly. As a result, in contrast to the stationary orders not only the electric field $E(t)$ but as well the full dynamics of the molecular system are relevant for the values of the oscillatory orders $N^k_{n,2m,S}$, $2k \geq 2m > k$.

6 Summary

In [17], we presented methods for the numerical application of perturbation theory with the aim to characterize the interaction of shaped laser-pulses with molecules. In order to control the quality of the calculations, we analyzed norm deviations caused by the necessary discretization of the appearing time-integrals and also the truncation of the perturbation expansion; both causes can lead to substantial deviations. Moreover, in [17] numerical results on a model system incorporating a single nuclear degree of freedom were presented, where a chirped-shaped laser pulse induces electronic transitions. These results, in particular the dependence of the different contributions to the norm deviation on parameters like the propagation time step, the steepness of the potential curves, and the chirp parameter are explained in [17] for brevity by some equations and interrelationships without proofs. The latter are provided in the present paper for what we called simple algorithm in [17], where the time-integral over one time step occurring in perturbation theory is approximated by one term.

In our analysis of norm deviations from unity calculated with the simple algorithm in [17], we stated that two classes of terms of different character contribute to the norm deviation: the first ones are called the *stationary orders* and are of purely numerical nature. They can be suppressed in the limit of small time steps. The second kind of contributions, called the *oscillatory orders*, are related to the property of time-dependent perturbation theory, which is not norm conserving. These orders can cause oscillations in the norm of the total wave function, and moreover, for long enough propagation times, these terms can lead to divergences of the norm towards infinity. In this publication, we prove equations and interrelations which explain this behavior of the stationary and the oscillatory orders for the simple algorithm that was documented for numerical calculated results in [17]. Moreover, here we present a method to calculate the norm deviations caused by the stationary orders quantitatively analytically. The accuracy of this

method is demonstrated for a numerical example. In addition, we show an analytical explanation why the oscillatory orders are suppressed for large potential gradient differences between the electronic states which are coupled by the laser pulse.

In the future, we will publish how the calculation done in this paper can be devolved from the simple algorithm to what in [17] we called improved algorithm. Moreover, our research goals are to implement the results depicted in [17] and in this publication in order to get a better understanding of multi-photon processes. With the help of the derived results we are now in the position to analyze which processes of different orders are relevant for the correct description of a chemical reaction. Therefore, we will compare the results calculated with converged perturbation theory and numerically exact results, which contain all perturbation orders.

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