On the divergence of time-dependent perturbation theory applied to laser-induced molecular transitions

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Received 25 June 2009, in final form 30 July 2009
Published 22 September 2009
Online at stacks.iop.org/JPhysB/42/195402

Abstract
Population transfer between electronic molecular states can be effectively induced via the interaction with shaped laser pulses. Regarding a numerical example, it is demonstrated that perturbation theory, as is often applied in numerical simulations of field-matter interactions, might lead to divergences. The occurring error accumulating in the norm of the wavefunction can be decomposed into two contributions. The first one is a small numerical error, which is controllable by minimization of the time-propagation step, whereas the second one is related to the order of the perturbative expansion. These two contributions behave differently upon variations of the potential energy surface of the system and also the laser pulse parameters. An improved scheme is proposed in which the first part carrying the numerical error disappears.

1. Introduction
Time-dependent perturbation theory is a powerful tool to examine the interaction of atoms [1] and molecules [2] with electromagnetic fields. Although perturbative methods, in general, are not norm-conserving and non-perturbative norm-conserving algorithms are available to solve the time-dependent Schrödinger equation, a perturbative ansatz is interesting because of the following reason: due to the systematic expansion in the field-system interaction, it is possible to clearly decompose a multi-photon process into contributions which stem from different orders. As an example, we mention time-resolved four-wave-mixing spectroscopy, where a theoretical description needs the evaluation of the induced third-order polarization associated with a certain direction of the emitted field [3]. Although there exist methods for extracting these desired contributions to the total polarization [4–6], perturbation theory provides a most straightforward approach [7–9].

Regarding a process where, e.g., a high-intensity laser pulse interacts with a molecule, it is then important to investigate how the results of perturbation theory converge to the exact results. This convergence behaviour depends on numerical parameters and will also change for different molecules and laser interactions. In particular, it is of interest to analyse if occurring numerical errors are due only to the approximate numerical method or the fact that the number of included orders of perturbation is not sufficient.

In this work, we address the question in how far perturbation theory implemented via a numerical algorithm is applicable to ultra-short laser pulse-molecule interactions. The physical situation we regard is the temporal evolution of molecular wavefunctions in pump/shaped-dump experiments as have recently been realized [10–12]. The excitation scheme is sketched in figure 1. There, diabatic potential curves along a reaction coordinate are displayed. The inclusion of non-adiabatic couplings will modify these potentials in the region they cross each other and an avoided crossing (or in the more general case a conical intersection [13]) occurs. The laser excitation scheme is as follows: a pump-pulse transfers population from the ground (|0⟩) to an excited electronic state (|1⟩). There, the prepared wave packet evolves in time and, due to the gradient of the excited state potential surface, moves towards larger distances. A time-delayed interaction with a shaped second pulse (dump), then couples the two electronic states in a region well separated from the curve-crossing, giving rise to multi-photon transitions between them.

Extensive recent calculations investigated which pulse-shaping leads to an efficient population transfer to the ground state [11, 14]. Here, we use the same model of a molecular...
system with two electronic states and a single nuclear degree of freedom. The convergence of perturbation theory is analysed with respect to parameters of the involved potential energy curves and a parameter introducing a spectral chirp for a Gaussian ultrashort laser pulse. Moreover, the influence of the time discretization-step is discussed.

This paper is organized as follows. In section 2, we summarize the basics of perturbation theory and show how a simple (S) and an improved (I) algorithm for the calculation of wavefunctions can be derived. This section contains an analysis which reveals that, for the simple algorithm, there exist two different kinds of contributions of errors which are related to numerical approximations and the order of the perturbative expansion, respectively. The analytical results are illustrated by a numerical example in section 3, and the paper is concluded with a summary in section 4.

2. Theory

2.1. Hamiltonian

We regard the interaction of an ultrashort laser pulse (in our case: a shaped-dump pulse) with a molecule where, for the latter, two electronic states (1) and (0) are included. For the nuclear degrees of freedom, we restrict our treatment to a single coordinate \( R \). The time-dependent Schrödinger equation for the two-component nuclear wavefunction \( \Psi(R, t) \) then reads (in atomic units)

\[
\frac{\partial}{\partial t} \begin{pmatrix} \Psi_0(R, t) \\ \Psi_1(R, t) \end{pmatrix} = \hat{H}(R, t) \begin{pmatrix} \Psi_0(R, t) \\ \Psi_1(R, t) \end{pmatrix}.
\]

(1)

The Hamiltonian consists of the system Hamiltonian \( \hat{H}_0(R) \) and the field-matter interaction term \( \hat{W}(t) \):

\[
\hat{H}(R) = \hat{H}_0(R) + \hat{W}(t) = \begin{pmatrix} \hat{T} + V_j(R) & 0 \\ 0 & \hat{T} + V_0(R) \end{pmatrix} + \begin{pmatrix} 0 & -\mu E(t) \\ -\mu E(t) & 0 \end{pmatrix}.
\]

(2)

Here, \( \hat{T} \) is the kinetic energy operator and \( V_j(R), j \in \{0, 1\} \) are the potential energy curves in the two electronic states. The perturbation term contains the electric dipole interaction with the electric field \( E(t) \) of the laser pulse and the projection \( \mu \) of the transition dipole moment on the laser polarization vector. We assume the Condon approximation where the dependence of the transition dipole-moment on the nuclear coordinates is neglected. Furthermore, we do not include a dipole-coupling within a single electronic state.

In our numerical examples, we employ linear approximations to the potential curves in the two electronic states as

\[
V_0(R) = m_0 (R - R_d)
\]

(3)

\[
V_1(R) = m_1 (R - R_d) + \Delta \varepsilon.
\]

(4)

The \( m_i, i \in \{0, 1\} \) are the potential gradients which we set to \( m_1 = -m_0 \). The energy gap \( \Delta \varepsilon \) is the potential difference \( V_1(R) - V_0(R) \) at distance \( R = R_d \).

Figure 1. Pump/shaped-dump scheme applied to molecules: after excitation (pump) from the electronic ground state \( |0\rangle \) to the electronically excited state \( |1\rangle \), a wave-packet dynamics in the excited state takes place. The time-delayed interaction with a shaped-dump pulse couples the two electronic states so that multi-photon processes take place. Shown are diabatic potential energy curves which in this work are approximated by lines with gradients of an opposite sign.

Table 1. Parameters employed in the numerical calculation. All values are given in the system of atomic units.

| Parameter | Value |
|-----------|-------|
| \( \varepsilon_0 \) | \( 2 \times 10^{-2} \) |
| \( m_0 \) | \( 10^{-3}; 2 \times 10^{-3}; 3 \times 10^{-3} \) |
| \( R_d \) | \( 7.56 \times 10^1 \) |
| \( m \) | \( 35 \times 10^3 \) |
| \( \Delta \varepsilon = \omega_0 \) | \( 5.69 \times 10^{-2} \) |
| \( E_0 \) | \( 1.19 \times 10^{-2} \) |
| \( \tau_{E,0} \) | \( 4.13 \times 10^2 \) |
| \( b_2 \) | \(-1.71 \times 10^6; -6.84 \times 10^6; 0; 6.84 \times 10^6 \) |
| \( l_t \) | \( 2.59 \times 10^4 \) |
| \( \mu \) | \( 1 \) |
| \( \Delta t \) | \( 1.83; 3.31 \) |
| \( k \) | \( 6; 14 \) |

As an initial wavefunction we use a Gaussian in the upper electronic state \( |1\rangle \):

\[
\tilde{\Psi}(R, t = 0) = \sqrt{\pi} e^{-\varepsilon_0 (R - R_d)^2}. \]

(5)

Thus, we do not implicitly treat the pump process as sketched in figure 1 but populate only the excited state initially. The value of the mass, the parameters for the potentials and also the initial function are collected in table 1.

2.2. Perturbation theory

In what follows, we suppress the dependence of all quantities on the vibrational coordinate \( R \), for clarity. Time-dependent perturbation theory starts from the integral equation for the wavefunction [15]

\[
\tilde{\Psi}(t) = e^{-i\hat{H}_0 t} \tilde{\Psi}(0) - i \int_0^t dt' e^{-i\hat{W}(t')} \tilde{\Psi}(t') \tilde{\Psi}(t'),
\]

(6)

where we assumed that the interaction starts at time \( t_0 = 0 \). The wavefunction in first order \( \tilde{\Psi}(t, 1) \) is obtained by
substituting the exact wavefunction $\tilde{\Psi}(t')$ appearing under the integral by the initial function (zeroth-order wavefunction) evolving in time with the system propagator ($\tilde{\Psi}(t, 0) = e^{-i\hat{H}_d t} \tilde{\Psi}(0)$) to obtain

$$\tilde{\Psi}(t, 1) = e^{-i\hat{H} t} \tilde{\Psi}(0) - i \int_0^t dt' e^{-i\hat{H}_d(t-t')} W(t') \tilde{\Psi}(t', 0).$$

(7)

Higher order corrections are then obtained by iteration as

$$\tilde{\Psi}(t, k) = e^{-i\hat{H} t} \tilde{\Psi}(0) - i \int_0^t dt' e^{-i\hat{H}_d(t-t')} W(t') \tilde{\Psi}(t', k-1),$$

(8)

where $k$ denotes the order of perturbation theory. The latter equation can be used as a basis to construct numerical algorithms to calculated perturbative wavefunctions [16]. Therefore, time $t$ is discretized into time steps $\Delta t$ yielding a time grid given at times $t_n = n\Delta t$. Let us regard the wavefunction of order $k$ at time $t_{n+1} = t_n + \Delta t$ which we denote as $\tilde{\Psi}(n+1, k)$. Dividing the integral in equation (8) into a first integral reaching from $t' = 0$ to $t' = t_n$ and a second contribution with limits $t' = t_n$ and $t' = t_n + \Delta t$, it is straightforward to see that

$$\tilde{\Psi}(n + 1, k) = e^{-i\hat{H} t_n} \tilde{\Psi}(n, k) - i \int_{t_n}^{t_n + \Delta t} dt' e^{-i\hat{H}_d(t_n + \Delta t-t')} W(t') \tilde{\Psi}(n, k-1).$$

(9)

Here, we have used the approximation that the wavefunction under the integral evolves with the unperturbed Hamiltonian in the small time interval $[t_n, t']$, i.e. $\tilde{\Psi}(t', k - 1) \approx e^{-i\hat{H}_d(t'-t_n)} \tilde{\Psi}(n, k - 1)$.

This expression for the wavefunction has the simple interpretation that the first term describes an unperturbed time evolution of the system (during the time interval $[t_n, t_n + \Delta t]$), whereas the second term accounts for the possibility that during this interval an interaction takes place.

We now specify a first numerical scheme for the evaluation of the wavefunctions which, in what follows, is referred to as the simple algorithm (S). It consists in representing the integral in equation (9) by a single term at time $t' = t_{n+1}$ as

$$\tilde{\Psi}_S(n + 1, k) = e^{-i\hat{H} t_{n+1}} \tilde{\Psi}_S(n, k) - i\Delta t W(n + 1) \tilde{\Psi}_S(n + 1, k - 1),$$

(10)

with the initial conditions $\tilde{\Psi}_S(0, 0) = \tilde{\Psi}(0)$ and the notation $W(t_{n+1}) = W(n + 1)$. In the second term of equation (10), the appearing functions are taken at time $t_{n+1}$. Equally well, values at any time $t'$ between $t_n$ and $t_{n+1}$ can be used without affecting the following discussions.

Another algorithm, henceforth referred to as the improved algorithm (I), is obtained from equation (9) by approximating the integral by two terms at times $t' = t_{n+1}$ and $t' = t_n$. The formula for the improved algorithm is then given by

$$\tilde{\Psi}_I(n + 1, k) = e^{-i\hat{H} t_{n+1}} \tilde{\Psi}_I(n, k) - \frac{i\Delta t}{2} \left( e^{-i\hat{H}_d t_{n+1}} W(n + 1) \tilde{\Psi}_I(n, k - 1) + W(n + 1) \tilde{\Psi}_I(n + 1, k - 1) \right),$$

(11)

where, as for the simple algorithm, $\tilde{\Psi}_I(0, 0) = \tilde{\Psi}(0)$. The wavefunctions $\tilde{\Psi}_S(n, k)$ calculated with the simple algorithm are correct in first order in $\Delta t$ only, while the wavefunctions $\tilde{\Psi}_I(n, k)$ calculated with the improved algorithm are correct in first order in $\Delta t$ for $k = 1$, but in second order for all $k > 1$. The analytical calculations, where it is analysed which are the highest orders in $\Delta t$ in which the simple and the improved algorithm are correct, are presented in [17, 18].

One might wonder why we do not use in equation (11) the more intuitive value $\hat{W}(n)$ for the interaction appearing in the first term in the brackets. The reason is that this yields wavefunctions (in all orders $k$) being correct in first order in $\Delta t$ only. This is straightforward to show for a single time propagation step. The general proof is given in [18].

The short-time propagator $e^{-i\hat{H}_d \Delta t}$ which moves the wavefunction $\tilde{\Psi}_G(n, k)$, ($G = S, I$) over a time step $\Delta t$ appears in both algorithms. The numerical evaluation of this term is done by the method of Feit and Fleck [19] using a grid for the spatial coordinate $R$. This method is correct in second order in the time step $\Delta t$, so that the application of this method in our algorithms does not diminish the orders in $\Delta t$ in which both algorithms are correct.

Because of the way the wavefunctions $\tilde{\Psi}_G(n, k)$ are computed, it is obvious that they differ for all perturbation orders $k > 2$ from the wavefunctions $\tilde{\Psi}_G(n, 2)$ only in higher orders in the time step $\Delta t$ than $O(\Delta t^2)$. Hence at first sight, it seems to be doubtful that a calculation of wavefunctions $\tilde{\Psi}_G(n, k)$ for a perturbation order $k > 2$ leads to better numerical results compared with the results gained with the wavefunctions $\tilde{\Psi}_G(n, 2)$. However, numerical results (see section 3) show that one can indeed improve the numerical results for both algorithms by using a higher order in the perturbation order $k$ than 2. This can be understood by an analysis of the deviations from unity of the norm $N_{k,G}^k$ of the wavefunction $\tilde{\Psi}_G(n, k)$, which will be performed in the following subsection.

2.3. Error analysis

Within perturbation theory, in general, the norm of the wavefunction is not conserved. In what follows, we discuss the numerical deviation from unity of the norm $N_{k,G}^k$ of the wavefunction $\tilde{\Psi}_G(n, k)$ which occurs in the application of perturbation theory to our population transfer problem. A detailed mathematical treatment is given in [17, 18], and we here only summarize the central points of the analysis. This enables us to interpret all results obtained in our numerical example given in section 3.
We start the analysis of the norm by writing it in the following expansion:

$$N_{n,G}^{k} = (\tilde{\mathcal{W}}_{G}(n,k)|\tilde{\mathcal{W}}_{G}(n,k)) = 1 + \sum_{m=1}^{k} N_{n,2m,G}^{k},$$

(12)

where the terms $N_{n,2m,G}^{k}$ are norm deviations from unity containing the electric field in $(2m)$th order. Note that odd terms do not appear in the sum, because due to the choice of the initial wavefunction $\Psi(0)$, where only the electronic state $|1\rangle$ is populated, these terms involve the scalar product of wavefunctions in the different electronic states $|0\rangle, |1\rangle$, which are orthogonal. We will now examine the structure of the expansion in orders of $\Delta t$ for the different terms $N_{n,2m,G}^{k}$.

For $k \geq 2m > 0$ the terms $N_{n,2m,G}^{k}$, which, in what follows, will be referred to as stationary orders, can be expanded in orders of the time step $\Delta t$ as

$$N_{T,2m,G}^{k} = \begin{cases} (-1)^{m} \frac{T^{m}}{m!} \Delta t^{m} \mathcal{W}^{2m} & (G = S) \\ 0 & (G = I) \end{cases}.$$  

(13)

In the latter equation, we have replaced the index $(n)$ corresponding to the propagation time $T = n \Delta t$ by referring explicitly to this time. Furthermore, the complicated time structure of the interaction $\mathcal{W}(n)$ is substituted by an averaged strength of perturbation $\mathcal{W}$, which, most simply, can be identified with the Rabi-frequency $\omega_{R} = \mu E_{0}$.

In analogy with (13) the terms $N_{n,2m,G}^{k}$ with $k < 2m < 2k$ can be expanded yielding

$$N_{T,2m,G}^{k} = \frac{(-1)^{k-m} T^{m} \Delta t^{m}}{m!(2m-1-k)!} \mathcal{W}^{2m} + \mathcal{O}(\Delta t^{m+1})$$

$$+ \mathcal{O}(\Delta t^{2k_{2m}+\delta_{G,S}}), (G = S, I).$$

(14)

These latter terms will from now on be called the oscillatory orders. Equations (13) and (14) provide the basis of our discussion of the errors introduced by our approximations.

Let us first discuss the above expressions for the simple algorithm. There, the stationary orders depend on the $m$th power of the time step $\Delta t$. For not too long propagation time $T$ and a small time step, the leading term in equation (13) is the one with $m = 1$ being

$$N_{T,2.5}^{k} = -T \Delta t \mathcal{W}^{2} + \mathcal{O}(\Delta t^{2}).$$

(15)

Thus, the norm deviations caused by the stationary orders are negative, are approximately independent of the order $k$, and depend linearly on the time step $\Delta t$. Also, in the limit $\Delta t \rightarrow 0$, the norm deviations caused by the stationary orders vanish. Thus, these errors are numerical deviations which arise from the approximation of the integral in (9) by only one summand.

For longer propagation times $T$, equation (15) does not hold. However, in taking the ratio between the stationary and oscillatory orders one finds that this number scales with $(\Delta t/T)^{m}$ which means that, for large $T$, the stationary terms are negligible. Then, because in the improved algorithm the stationary orders are not present, the oscillatory orders dominate the norm deviations for longer propagation times for both algorithms. In what follows, we discuss these terms in more detail.

As a first interesting fact we note that the oscillatory terms, in leading order, do not depend on the time step $\Delta t$. In particular, and opposite to the stationary orders, they do not vanish in the limit $\Delta t \rightarrow 0$. For early times $T$ the oscillatory order with the lowest value of $m$ (being equal to $(k + 2)/2$ for even order $k$ and $(k + 1)/2$ for odd order) gives the largest contribution to the norm deviation of all oscillatory orders, because all other oscillatory orders are suppressed by the factor $m![2m - 1 - k]!$ appearing in the denominator of the ratio in equation (14). Depending on the order of perturbation theory, this contribution to the total norm deviation is negative or positive. With increasing propagation time $T$, the factor $T^{2m}$ increases and thus the contributions with larger values of $m$ gain influence on the norm deviations. The sign of the terms alternates as a function of $m$, so that with increasing propagation time $T$, the sign of the contribution of the oscillatory orders to the norm deviation changes. This justifies our convention to name these terms oscillatory orders.

Finally, for large propagation times $T$, the influence of the highest oscillatory order,

$$N_{T,2k,G}^{k} = \frac{T^{2k}}{(k!)^{2}} \mathcal{W}^{2k} + \mathcal{O}(\Delta t^{2k_{2m}+\delta_{G,S}}),$$

(16)

dominates the norm deviation because the exponent $(2m)$ in equation (14) reaches its largest value for $m = k$. The contribution of the highest oscillatory order $N_{T,2k,G}^{k}$ is positive for arbitrary values of $k$ and due to this reason this leads to a divergence towards $+\infty$. However, it is noteworthy that an increase of the order $k$ can retard or even suppress the point in time when the total norm deviation becomes essential. This can clearly be interpreted on physical grounds: the order $k$ determines the number of photons interacting with the molecule in the numerical simulation. Because the norm deviations related to the oscillatory terms are, in leading order, independent of the time step $\Delta t$ but dependent on the order $k$ (see (14)), we can interpret norm deviations form unity as being due to truncating the order of the multi-photon processes.

In this context, we mention that the interpretation of the numerical results for the deviations from unity is much simpler for the improved than for the simple algorithm. Using the former numerical scheme, one has to distinguish between the deviations from unity related to the stationary orders, which are due to purely numerical errors, and the deviations related to the oscillatory orders, which are related to the chosen perturbation order $k$. Moreover, the latter deviations can have opposite signs. For the improved algorithm, this kind of distinction is unnecessary due to the vanishing of the stationary orders. Having outlined the general behaviour of the norm deviations occurring in the simple and improved algorithms, we are now in a position to interpret the numerical results presented in section 3.

2.4. Shaped-dump pulses

We perform numerical calculations for various electric fields $E(t)$ of the shaped-dump laser pulse. The numerical parameters are collected in table 1. Starting from the (Fourier
limited) unchirped pulse with carrier frequency \( \omega_0 \) the electric field is of the form

\[
E(t) = \Re \left( E'_0 e^{-\beta(t - t_d)^2} e^{-i[\omega_0(t - t_d)]} \right).
\]

The introduction of a linear chirp with parameter \( b_2 \) in the frequency domain leads to a time-dependent field as

\[
E(t) = \Re \left( E_0 e^{-\beta(t - t_d)^2} e^{-i[\omega_0(t - t_d) + \beta(t - t_d)^2]} \right).
\]

In the last equations, the field strengths are denoted as \( E'_0 \) and \( E_0 \) for the unchirped and chirped fields, respectively. We assume a Gaussian envelope function having a full width at half maximum (FWHM) of \( \tau = \sqrt{(4 \ln 2) / \beta} \) and a maximum at time \( t = t_d \). The various parameters appearing in the equations for the shaped and unshaped electric fields are related as follows [20]:

\[
E_0 = \sqrt{\frac{1}{1 + 2i\beta b_2}} E'_0, \quad |E_0| = (1 + 4\beta^2 b_2^2)^{-1/4} |E'_0| \quad \beta = \frac{1}{\tau^2 + 4\beta^2 b_2^2} \quad a_2 = \frac{b_2}{\tau^2 + b_2^2}.
\]

In our calculations, we regard the case that the maximum of the wave-packet evolving in the excited state is located at distance \( R_d \) at time \( t_d \) when the envelope of the laser pulse assumes its maximum. This is the time, when the time-dependent frequency equals \( \omega_0 \) which corresponds to the energy gap \( V_1(R_d) - V_0(R_d) = \Delta \mathcal{E} \). Thus, the start position \( R_s \) of the excited state wave packet is not independent of the other parameters of our model. It is determined by the classical equation of motion as

\[
R_s = R_d + \frac{m_1}{2m} \left( \frac{\tau}{t_d} \right)^2,
\]

where \( m \) denotes the mass.

3. Results

3.1. General norm deviations

As a first issue, we document that, under certain circumstances, divergences for the norm of the two-component wavefunction occur. Here, and in what follows, a linear time grid is used. This is sufficient to follow the electric field even in the case of a large chirp. The shortest oscillation period appearing in our numerical calculations is about 2.11 fs which is much larger than the maximal time step of 0.08 fs.

Numerical results obtained from calculations performed within the improved algorithm are shown in figure 2. Here, a time step of \( \Delta t = 8 \times 10^{-2} \) fs and a potential gradient of \( m_0 = 10^{-3} \) au are used, and two orders of perturbation, \( k = 6 \) and \( k = 14 \), are compared. Panels (a) and (b) of the figure depict the cases of a chirped pulse (panel (a), \( b_2 = -400 \text{ fs}^2 \)) and an unchirped pulse interaction (panel (b), \( b_2 = 0 \)). The envelopes of the two electric fields, denoted as \( |E_n(t)| \) (chirped) and \( |E_n(t)| \) (unchirped) are also shown in the figure (panel (b)) on a relative scale. The maxima of the pulses correspond to intensity values of \( |E'_0|^2 = 5.0 \times 10^{12} \text{ W cm}^{-2} \) and \( |E_0|^2 = 2.3 \times 10^{11} \text{ W cm}^{-2} \), respectively. Note that although all quantities of our model are given in the system of atomic units, we prefer to convert time into the more convenient unit of femtoseconds.

For the unchirped pulse, the norm remains almost conserved in the case of \( k = 6 \) and is conserved for \( k = 14 \). It is then striking that although the pulse energy remains the same if a chirp is introduced into the Fourier-limited pulse, for the chirped pulse tremendous deviations of the norm from unity are found (reaching values of about \( 6 \times 10^4 \) (\( k = 6 \)) and \( 1 \times 10^5 \) (\( k = 14 \))). This extremely different behaviour for shaped versus unshaped-dump pulse interactions can be rationalized as follows. Regarding longer propagation times \( T \) it was argued in section 2.3 that the positive norm deviations are due to the contribution of the highest order term, see equation (16) (in the oscillatory terms, which are the only ones present in the improved algorithm). Let us regard this case for a square pulse such that \( \mathcal{W} = -\mu E'_0 \), and this unchirped pulse acts resonantly, e.g., for a time \( T/2 \). After this time, the norm remains constant and we find, from equation (16),

\[
N_{n,k,G}^{2k} = T^{2k}/(2k)!^2 (\mu E'_0)^{2k} + O(\Delta t^{2k+4k_G}),
\]

The introduction of a chirp has the effect that the pulse is lengthened which is accompanied by a reduction of the peak intensity. For a chirp which doubles the pulse length, so that the effective interaction time is \( T/2 \), the field amplitude has to be divided by \( \sqrt{2} \) because the pulse energies of the chirped and unchirped pulses are identical. Then, the norm deviation is

\[
N_{n,k,G}^{k} = T^{2k}/(2k)!^2 (\mu E_0)^{2k} + O(\Delta t^{2k+4k_G}).
\]
In section 2.3 it was presented that within the simple numerical scheme, there are stationary and also oscillatory terms contributing to the norm deviation of the calculated wavefunctions. In Figure 3, we show the time-dependent norm obtained by application of the simple algorithm for perturbation orders of $k = 6$ and $k = 14$. Here, a potential gradient of $m_0 = 10^{-3}$ au, a spectral chirp parameter of $b_2 = -400$ fs$^2$, and two different time steps $\Delta t = 8 \times 10^{-2}$ fs and $\Delta t = 4 \times 10^{-2}$ fs are employed.

Initially, all curves exhibit a negative norm deviation. This is the case mentioned in section 2.3 where, for smaller times (here: before $t \approx 510$ fs), the norm is dominated by the contribution of the stationary terms. Then, equation (15) applies which predicts that the negative deviations scale linearly with the time step $\Delta t$, and also, approximately, are independent of the order $k$. This trend is obvious if the various curves in Figure 3 are compared. At later times, the oscillatory orders gain influence which leads to a $k$-dependent time evolution of the norm deviations and the divergence discussed in the last subsection. Note the oscillatory behaviour of the $(k = 6)$ curves which is characteristic for the importance of the oscillatory orders; see the discussion in section 2.3. The time when the divergence occurs depends on the order of perturbation theory. For $k = 6$ this happens about a time of $t = 580$ fs while the divergence for $k = 14$ occurs later at about $t = 630$ fs, independent of the chosen time step $\Delta t$. Thus, the divergences are exclusively related to the fact that the maximal included number of molecule–photon interactions is too small. In the present example the different evolution of the norm deviations for different values of $k$ at times $t > 510$ fs means that transitions involving more than six photons become relevant to describe the dump process. The same applies if the improved algorithm is employed: there, the negative norm deviations at shorter times vanish because the stationary orders are not present. Nevertheless, the divergence of the norm occurs at the same times as seen in Figure 3.

Here, we note another interesting feature of the stationary terms which are present only in the simple algorithm. Regarding equation (15), one sees that, to leading order, the terms which are present only in the simple algorithm. Here, we note another interesting feature of the stationary terms which are present only in the simple algorithm. Regarding equation (15), one sees that, to leading order, the terms which are present only in the simple algorithm.

3.2. Simple algorithm: stationary versus oscillatory orders

In section 2.3 it was presented that within the simple numerical scheme, there are stationary and also oscillatory terms contributing to the norm deviation of the calculated wavefunctions. In Figure 3, we show the time-dependent norm obtained by application of the simple algorithm for perturbation orders of $k = 6$ and $k = 14$. Here, a potential
These findings document again that the norm deviations related to the stationary orders are only numerical errors. In particular, it is well known that pulses with an up or a down chirp cause very different population transfer between molecular electronic states [21] whereas the norm deviations discussed here (for $b_2 = \pm 400$ fs$^2$) are identical.

3.3. Dependence on the potential energy curves

In this subsection, we regard the influence of the potential energy curves on the norm deviations, i.e., we present results for different gradients $m_0$ of the potentials. Therefore, we use numerical values of $m_0 = \lambda \times 10^{-3}$ au, where the parameter $\lambda$ assumes values of $\lambda_1 = 3$, $\lambda_2 = 2$ and $\lambda_3 = 1$, respectively. The spectral chirp parameter is set to $b_2 = -400$ fs$^2$, a time step of $\Delta t = 8 \times 10^{-2}$ fs is used, and we regard a perturbation order of $k = 14$.

In figure 5 we compare results obtained from the simple ($S$, upper panel) and the improved ($I$, lower panel) algorithm. In the former case, the (negative) norm deviations for times $t < 450$ fs show the same behaviour for all values $m_0$ of the potential gradient. On the other hand, for the improved scheme, the norm deviations approximately vanish for $t < 450$ fs. This means that the error originates from the contributions of the stationary orders and, to be more specific, it is due to the influence of the lowest stationary order. This, in turn, means that these norm deviations are exclusively due to numerical inaccuracies which stem from the approximation of the integral term in equation (9) for the simple algorithm, and that these deviations do not depend on the shape of the potential surfaces of the molecular system. For times $t \gtrsim 500$ fs and a gradient of $m_0 = 10^{-3}$ au the norm rises and then diverges for both algorithms which documents the influence of the oscillatory orders and implies that here a limitation of the description to processes involving maximal $k = 14$ photons is not sufficient. With increasing steepness of the potentials, the improved scheme works better. In particular, for $m_0 = 3 \times 10^{-3}$ au the norm is conserved (whereas the simple scheme still shows the numerical error introduced by the lowest stationary order $N_{2,3}$). In this case the perturbation order is sufficient to describe the induced multi-photon processes.

The dependence of the norm deviation on the potential gradient can be analysed in detail [17, 18]. Here we note that, with increasing gradient, the excited state wave-packet moves faster down the slope of the potential which shortens the interaction time. This diminishes the probability of high-order multi-photon processes to take place.

4. Summary

We investigate the numerical application of perturbation theory to describe shaped laser-pulse interactions with molecules. In regarding the norm of the wavefunction it is shown that the necessary discretization of the appearing time integrals can lead to substantial divergences. Two numerical algorithms are compared. In a simple algorithm, two terms of different character contribute to the norm deviation. The first ones are of purely numerical nature and can be suppressed in the limit of small time steps. An improved algorithm is introduced where these terms disappear. The second kind of contributions are present in both schemes and may cause oscillations in the norm of the total wavefunction. For longer propagation times, these terms are responsible for a divergence of the norm towards $+\infty$. The oscillatory terms directly correlate with the order of the multi-photon transitions to be described and, in increasing the order of the perturbation theory, the norm deviations can be reduced.

Numerical results on a model system incorporating a single nuclear degree of freedom, where shaped laser pulses
induce electronic transitions, document that an application of perturbation theory can yield severe numerical errors. This is most drastically seen in a case where the population transfer induced by a Fourier-transform limited pulse can be handled within perturbation theory. The introduction of a chirp, leading to a lengthened pulse with equal energy, then has the consequence that dramatic numerical errors appear.

The numerical 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 with the help of expressions which are presented here without proof. A detailed mathematical analysis can partly be found in [17], and will be published soon [18].

For future investigations, we are able to employ the here obtained results to gain insight into the nature of multi-photon processes. In particular, it will be possible to disentangle processes of various orders contributing to measured signals by comparison of results obtained from converged perturbation theory and numerically exact results.

5. Acknowledgment

Financial support by the DFG within the Graduiertenkolleg 1221 is gratefully acknowledged.

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