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Quantum molecular dynamics driven by short and intense light pulses: Towards the limits of the Floquet picture

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Abstract

Photoinduced quantum molecular dynamics is numerically investigated using two different Schrödinger formulations based on adiabatic (“bare”) and Floquet (“dressed”) molecular state representations. Computer simulations for the two approaches are compared in terms of numerical accuracy and efficiency where special emphasis is laid on the limit of very short and intense laser pulses. The optical excitation of the HCl^+ ion from the $X^2\Pi$ to the $A^2\Sigma^+$ state near resonance frequency is investigated as a model system. For a variety of pulse intensities and durations the final population transfer is reproduced accurately by a model based on seven Floquet states only. Elimination of the highly oscillatory terms from the resulting equations allows for the use of much longer time steps in the numerical integration. Even for extremely short pulses with durations down to a single optical cycle, dressed states are still found to be useful. Thus, the Floquet approach provides an efficient tool for the simulation of molecules interacting with short and intense pulses beyond the perturbative regime.

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Keywords: Quantum molecular dynamics; Floquet states; Numerical propagation scheme; Ultrashort laser pulses; Intense fields; Electronic excitation; HCl cation

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1. Introduction

In recent years the investigation of molecular dynamics in real time has benefited enormously from experimental progress in generating ever shorter and more intense laser pulses which has lead to novel possibilities to observe and to control molecular dynamics on a picosecond to femtosecond timescale [1–3]. At the same time, this has created a great challenge to theoretical work which is indispensable for understanding the results of ultrafast molecular dynamics. In particular, the requirements for theoretical models of molecular dynamics interacting with ultrashort and intense external fields are threefold: First of all, the dynamics of the molecular system under investigation has to be modelled quantum-mechanically in order to simulate wave-mechanical phenomena typically occurring in photo-induced processes. Second, the interaction of

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the molecule with the external field has to be modelled beyond the level of perturbation theory in order to account for very intense fields and non-linear effects. Finally, the description should allow for extremely short pulses which are far from the limit of strictly periodic fields. In order to comply with those requirements, (coupled) time-dependent Schrödinger equations have to be solved for a Hamiltonian including the coupling to the external field, in most cases within the semi-classical dipole approximation [4]. In particular for the practical treatment of multidimensional problems, the numerical efficiency and accuracy can become a key point of the possible approach.

Based on the Floquet theorem for differential equations with periodically oscillating terms [5], photo-induced effects on quantum systems can be described in an extended Hilbert space spanned by “photon dressed” states which are constructed as a direct product of system and field states. For strictly time-periodic fields it allows to transform the original time dependent problem into a time-independent formulation yielding quasi-stationary eigenstates which can be expressed in harmonics of the carrier frequency of the field [6–10]. In order to be more generally applicable, the original concept has undergone several modification and extensions. Apart from the frequent use for atomic systems [11], such techniques are also applied to electronic transitions of molecular systems [12]. Multi-mode Floquet theories have been developed which are instrumental in modelling multi-photon processes in polychromatic fields [8,13]. Complex coordinate techniques have been added to deal with non-Hermitian Hamiltonian operators used to describe ionization and dissociation processes and higher harmonic generation [14–18]. In other work, a generalized Floquet formulation for time-dependent density function theory has been developed allowing for a non-perturbative treatment of a multi-electron system subjected to intense fields [19,20]. Finally, the concept of “dressed” states plays an important role in the field of light-induced control of quantum molecular dynamics. In particular, it represents the theoretical framework for the concept of stimulated rapid adiabatic passage [21–25] where the assumption of molecular dynamics adiabatically following Floquet “dressed states” allows for intuitive schemes to control molecular dynamics. These ideas can be extended towards the control of non-adiabatic transitions where the intersections of dressed states are manipulated by shaped laser pulses [26–30].

In order to describe interaction of quantum systems with pulsed light sources, Floquet theory must be applied to fields with varying amplitude and/or frequency [27,31–35]. In the limit of infinitely slow variation of the field parameters, the dynamics of the system adiabatically follows instantaneous Floquet states. For more rapid variations of the field, the quantum dynamics is subject to non-adiabatic effects which can be treated at various levels of approximation [18,27–30, 36,37]. In addition to providing a physically intuitive interpretation of photoinduced dynamics, the main advantage of a Floquet-based description stems from the separation of time scales. The only time-dependence of the Floquet–Hamiltonian results from the (usually) slow time scale of the pulse modulation while the fast time scale connected with the carrier frequency is eliminated from the resulting equations of motion.

In the present work the performance of numerical simulations of photoinduced molecular dynamics driven by short laser pulses is investigated. We aim at a systematic comparison of the Floquet (dressed) state representation versus molecular (bare) state representation both in terms of accuracy and efficiency. In particular, the question shall be addressed whether or not a Floquet based formulation offers numerical advantages over the bare state approach to solve the time-dependent Schrödinger equation: On the one hand, it is expected that elimination of the fast time scale in the Floquet approach allows for larger time steps which directly reduces the numerical effort. On the other hand, the increased dimensionality of the extended Hilbert space creates additional computational load. The latter aspect is directly related to the question of a suitable truncation scheme for the Floquet space where again a compromise between accuracy and efficiency has to be found.

Finally, with the availability of increasingly shorter and more intense laser pulses, the question of the limit of Floquet-based models arises. When going to extremely short pulses comprising of only a few optical cycles, it is generally believed that—apart from becoming physically less transparent—dressed states lose their computational advantage. Instead, quantum dynamics is often expressed in terms of instantaneous field-modified states that follow the oscillations of the field [38–43]. However, there is evidence from a study using super-adiabatic states that Floquet approaches can be usefully applied to pulses as short as ten optical cycles [27]. In the present work the limit of Floquet-based descriptions of quantum molecular dynamics driven by extremely short pulses of a few optical cycles down to a half-cycle pulse is critically investigated.

The remainder of this paper is organized in the following way. Section 2 presents the formulation of quantum molecular dynamics in terms of "bare" molecular and "dressed" Floquet states. In Section 3 we will introduce a diatomic model system for which the use of Floquet picture is investigated by means of various numerical simulations for a large variety of pulse durations and intensities. Our conclusions are discussed in Section 4.

2. Quantum dynamical method

Considerable effort has been devoted to the use of Floquet states for molecular systems subject to strong fields [12]. The principle difference from the treatment of atomic systems results from the coexistence of electronic and rovibrational degrees of freedom and the corresponding discrepancy of time and energy scales. In the following we shall shortly review two approaches to light-induced molecular dynamics driven by electronic transitions where the use of the Floquet picture is restricted to field-dressed electronic, rather than vibronic, states. Hence, this approach is tailored to the theoretical description of electronic excitation processes. Despite of many similarities with the "dressed state" treatment of electronic excitation of atoms, the nuclear degrees of freedom add to the complexity of the problem.

2.1. Hamiltonian operator

The quantum dynamics of a molecular systems consisting of nuclei of mass M and electrons of mass m can be described by two sets of position and momentum operators $\widehat{R}$, $\widehat{P}$ and $\hat{r}$, $\hat{p}$, respectively. Usually, the molecular Hamiltonian can be split into potential and kinetic energy of the heavy particles

$$\widehat{H}(\hat{r},\hat{p},\widehat{R},\widehat{P},t)=\widehat{V}(\hat{r},\hat{p},\widehat{R},t)+\frac{\widehat{P}^2}{2M}. \tag{2.1}$$

In the absence of an external field, the former one can be written as

$$\widehat{V}_0(\hat{r},\hat{p},\widehat{R})=\frac{\hat{p}^2}{2m}+\widehat{U}(\hat{r},\widehat{R}). \tag{2.2}$$

Within the framework of the semi-classical dipole approximation [44], the light-matter interaction can be included

$$\begin{aligned}\widehat{V}(\hat{r},\hat{p},\widehat{R},t)&=\widehat{V}_0(\hat{r},\hat{p},\widehat{R})\\&\quad+\frac{1}{4\pi\epsilon_0}\hat{\mu}(\hat{r},\widehat{R})\cdot F(t),\end{aligned} \tag{2.3}$$

where the electric dipole moment $\hat{\mu}$ of the molecular system interacts with the external electric field (using SI units). Note that the dot product accounts for the vectorial nature of the two quantities and allows for the description of polarization effects.

2.2. Molecular eigenstate representation

The standard approach of quantum molecular dynamics rests on the extreme mass ratio of electrons vs. nuclei, m/M. In the absence of an external field, adiabatic eigenstates of the electronic system are defined as

$$\widehat{V}_0(R)\big|n(R)\big\rangle_r=E_n(R)\big|n(R)\big\rangle_r,\quad |n\rangle_r\in\mathcal{H}_r, \tag{2.4}$$

where E_n are adiabatic eigenenergies of $\widehat{V}_0$ and where $\mathcal{H}_r$ is the Hilbert space spanned by the electronic degrees of freedom. This representation allows us to write the total Hamiltonian of the total system in matrix form using a coordinate representation of the heavy particle operators $\widehat{R}$, $\widehat{P}$

$$\begin{aligned}H(R,t)&=E(R)-\frac{\hbar^2}{2M}\big(\Delta_R+2C(R)\cdot\nabla_R+T(R)\big)\\&\quad+\frac{1}{4\pi\epsilon_0}\mu(R)\cdot F(t)\end{aligned} \tag{2.5}$$

where $E(R)$ is a diagonal matrix containing the adiabatic potential energy functions. Due to the parametric R-dependence of the adiabatic eigenstates (2.4), there are first and second order non-adiabaticity operators with matrix elements

$$\begin{aligned}C_{n'n}(R)&=\big\langle n'(R)\big|\nabla_R\big|n(R)\big\rangle_r,\\T_{n'n}(R)&=\big\langle n'(R)\big|\Delta_R\big|n(R)\big\rangle_r\end{aligned} \tag{2.6}$$

while the matrix elements of the dipole moment operator are defined as

$$\mu_{n'n}(R) = \big\langle n'(R)\big|\hat{\mu}(\hat{r}, R)\big|n(R)\big\rangle_r. \tag{2.7}$$

The diagonal or off-diagonal elements are referred to as permanent or transition dipole moment functions, respectively. For symmetric molecules some elements of the matrices C, T, μ may vanish if the corresponding states $|n\rangle$, $|n'\rangle$ transform according to certain irreducible representations of the molecular point group [45].

2.3. Dressed state representation

While the approach described above works for an arbitrary time-dependence of the electric field, $F(t)$, we shall now discuss an approach that is specifically tailored to rapidly oscillating fields with a constant carrier frequency ω and with a slowly modulated amplitude

$$F(t) = F_0(t/\tau)\cos(\omega t). \tag{2.8}$$

Normally, the optical period $T = 2\pi/\omega$ is much shorter than the typical timescale τ imposed by the variation of the shape function. In these cases it is of advantage to construct "photon dressed" states, or Floquet states. Mathematically, this technique is equivalent to a Fourier expansion of the time-dependence of the Hamiltonian. As a first step we derive states of the field in the limit of an infinitely large number of photons as eigenstates of the (relative) photon number operator [10]

$$\widehat{N}\big|m(\omega)\big\rangle_t = m\omega\big|m(\omega)\big\rangle_t, \quad |m\rangle_t \in \mathcal{H}_t. \tag{2.9}$$

Using a coordinate representation in time, the operator $\widehat{N}$ maps to $-i\hbar\,\mathrm{d}/\mathrm{d}t$ and the corresponding Hilbert space $\mathcal{H}_t$ is the space of the T-periodic functions [7]. "Dressed" states are then constructed as tensor products of molecular states (2.4) and field states (2.9)

$$\begin{aligned}&\big|n, m(R,\omega)\big\rangle\!\big\rangle \equiv \big|n(R)\big\rangle_r \otimes \big|m(\omega)\big\rangle_t,\\ &\quad |n,m\rangle\!\rangle \in \mathcal{H}_{rt} \equiv \mathcal{H}_r \otimes \mathcal{H}_t\end{aligned} \tag{2.10}$$

where $\mathcal{H}_{rt}$ is the extended Hilbert space, or Floquet space, with the orthonormality of the extended space basis given by the respective scalar product

$$\begin{aligned}&\big\langle\!\big\langle n', m'(R,\omega)\big|n, m(R,\omega)\big\rangle\!\big\rangle\\ &\quad = \big\langle n'(R)\big|n(R)\big\rangle_r \big\langle m'(\omega)\big|m(\omega)\big\rangle_t = \delta_{n'n}\delta_{m'm}.\end{aligned} \tag{2.11}$$

The quasi-energy operator, $\widehat{\mathcal{V}}$, or Floquet Hamiltonian, is defined as the sum of the Hamiltonian, $\widehat{V}$, for the electronic subsystem interacting with the field (2.3), and the photon number operator, $\widehat{N}$. Using the "dressed state" basis defined in Eq. (2.10), the potential matrix is obtained as an expansion of the r-dependence in adiabatic molecular states combined with a Fourier expansion of the t-dependence in harmonics of the carrier frequency ω

$$\begin{aligned}&\mathcal{V}_{n'm',nm}(R,\omega,t)\\ &\quad = \big\langle\!\big\langle n', m'(R,\omega)\big|\widehat{V}(R,t) + \hbar\widehat{N}(\omega)\big|n, m(R,\omega)\big\rangle\!\big\rangle\\ &\quad = \big(E_n(R) + m\hbar\omega\big)\delta_{n'n}\delta_{m'm}\\ &\qquad + \mu_{n'n}(R)\cdot\frac{F_0(t)}{8\pi\epsilon_0}(\delta_{m',m-1} + \delta_{m',m+1})\\ &\qquad + \mathcal{O}(T/\tau).\end{aligned} \tag{2.12}$$

The structure of the Floquet matrix is readily understood in the following way: The diagonal entries are the potential energy hypersurfaces "dressed" by (an integer number of) photons. The offdiagonal entries describe the coupling of states differing by one photon. Hence, it is straightforward to interpret transitions with $m' = m \pm 1$ as absorption or emission of one photon. The corresponding matrix representation of the total Hamiltonian is obtained as the sum of the molecular Hamiltonian (2.1) and the photon number operator (2.9)

$$\begin{aligned}\mathcal{H}(R,\omega,t) &= H(R,t) + \hbar N(\omega)\\ &= \mathcal{V}(R,\omega,t)\\ &\quad - \frac{\hbar^2}{2M}\big(\Delta_R + 2C(R)\cdot\nabla_R + T(R)\big).\end{aligned} \tag{2.13}$$

The above equations reflect the properties of the Floquet *ansatz* for the description of photo-induced quantum dynamics [7,46]. For a strictly time-periodic Hamiltonian ($F_0(t) = \text{const}$) the time-dependent Hamiltonian $\widehat{V}$ of Eq. (2.5) is replaced by the (quasi-)stationary Floquet Hamiltonian $\widehat{\mathcal{V}}$ of Eq. (2.13) acting in the extended Hilbert space spanned by "dressed" states.

For the case of shaped light pulses, the main advantage of the Floquet approach (2.13) in comparison with the representation in terms of molecular eigenstates (2.5) is the elimination of the fast carrier oscillations in (2.8) rendering a Hamiltonian with a time-dependence on the slow timescale of the pulse envelope, $F_0(t)$, only. The same applies for the corresponding eigenvalues (instantaneous Floquet states). The variation of the amplitude during an optical cycle gives rise to additional offdiagonal matrix elements. However, the modulation is typically much slower than the oscillations associated with the frequency ω and the additional matrix elements vanish asymptotically with order of $\mathcal{O}(T/\tau)$, see Ref. [47]. One of the goals of this paper is to check the validity of this approximation for shorter and shorter laser pulses down to a single optical cycle and below.

2.4. Coupled Schrödinger equations

In order to treat the photoinduced dynamics of the molecular system, the quantum-mechanical state vector of the system is expanded in the set of molecular or dressed states introduced in (2.4) or (2.10), respectively,

$$\big|\psi(R,t)\big\rangle = \sum_n \phi_n(R,t)\big|n(R)\big\rangle, \tag{2.14}$$

$$\big|\Psi(R,t)\big\rangle\!\big\rangle = \sum_n \sum_m \varphi_{n,m}(R,\omega,t)\big|n,m(R,\omega)\big\rangle\!\big\rangle \tag{2.15}$$

where the expansion coefficients $\phi_n(R,t)$ and $\varphi_{nm}(R,t)$ are readily identified as nuclear wavefunctions. Inserting this *ansatz* into the time-dependent Schrödinger equation (TDSE) leads to a set of coupled partial differential equations. In molecular state representation the vector of nuclear wavefunctions evolves under the influence of Hamiltonian (2.5) or, equivalently, in “dressed state” representation under the influence of the Floquet Hamiltonian (2.13)

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\phi(R,t) = H(R,t)\phi(R,t), \tag{2.16}$$

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\varphi(R,t) = \mathcal{H}(R,\omega,t)\varphi(R,\omega,t). \tag{2.17}$$

These equations are solved numerically using fast Fourier transform (FFT) methods for the transformation between coordinate and momentum space. The corresponding wavefunctions are represented on an equidistant grid in coordinate space [48]. Propagation in time is achieved by the $\mathcal{O}(\Delta t^3)$ Strang splitting (“split-operator”) technique [49,50].

In a typical experimental situation, the molecule is initially prepared in a single electronic state i

$$\big|\psi(R,t=0)\big\rangle = \phi_i(R,t=0)\big|i(R)\big\rangle. \tag{2.18}$$

Then it interacts with (one or more) light pulses, and finally the state of the molecule is probed by a suitable mechanism. While a simulation using the molecular picture of Eq. (2.16) is straightforward, the corresponding strategy in the Floquet picture of Eq. (2.17) deserves some attention. First, the initial molecular wavefunctions has to be lifted to the extended Hilbert space. Note that this procedure is in principle ambiguous [27]. Here the simplest realization is chosen

$$\big|\Psi(R,t=0)\big\rangle\!\big\rangle = \varphi_{i,0}(R,t=0)\big|i,0(R,\omega)\big\rangle\!\big\rangle. \tag{2.19}$$

In order to monitor the population dynamics during or after the interaction of the molecular system with the external field, it is desirable to project extended space vectors back to molecular space again

$$\phi_n(R,t) = \sum_m \varphi_{n,m}(R,t) \tag{2.20}$$

which allows, e.g., to calculate the population of the nth electronic state

$$P_n(t) = \int \big|\phi_n(R,t)\big|^2\,\mathrm{d}R \tag{2.21}$$

by integration over the nuclear degrees of freedom.

The main purpose of this paper is to compare the accuracy and efficiency of computer simulations of photoinduced quantum molecular dynamics in the molecular state picture (2.16) vs. the “dressed state” picture (2.17). In particular, the following questions shall be addressed:

(1) How accurate is the approximation of instantaneous Floquet states (2.12) for the simulation of shorter and shorter pulses?
(2) Where can the expansion in harmonics of ω (summation over m in Eq. (2.15)) be truncated without significant loss of accuracy?
(3) Does the use of the Floquet picture lead to practical advantages in computer simulations, or, is the advantage of a slowly time-dependent Hamiltonian compensated by the higher dimension of the extended Hilbert space?

3. Simulation results

3.1. Model system

As a model system we investigate the photoinduced quantum molecular dynamics of the HCl^+ ion. This choice is motivated by the availability of extensive theoretical [40,43,51–53] and experimental [54–56] data. In particular, there are high quality data available for potential energy curves and transition dipole moments [57] as well as spin-orbit coupling elements [56]. Potential energy curves for the lowest five electronic states of the HCl^+ ion are shown in Fig. 1. Both the electronic ground state ($X^2\Pi$) and the first excited state ($A^2\Sigma^+$) exhibit an attractive potential well. Note that the two states are asymtotically connected to the $H(^2S) + Cl^+(^3P)$ and $H^+ + Cl(^2P^0)$ limit, respectively, where the different charges allow for a relatively simple experimental distinction. Moreover, we consider three repulsive states, $^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$, which are coupled through spin–orbit interaction to the ($A^2\Sigma^+$) state leading to pre-dissociation on a ps time scale for higher vibrational states [53,55,56]. In the present work we consider the interaction of the HCl^+ ion with perpendicularly polarized light in order to exclude the effects of permanent dipole moments while transitions between states of equal multiplicity are dipole allowed, i.e., between the ground state and the two doublet states $A^2\Sigma^+$ and $^2\Sigma^-$, see also the vertical arrows in Fig. 1. Note that in a gas phase experiment the molecules would have to be aligned by external fields before or during the excitation process, see, e.g., Refs. [58,59]. Furthermore, due to the symmetry of the linear molecule, the non-adiabatic coupling (2.6) between any of the five electronic states considered vanishes. In particular, the crossings between the first excited state ($A^2\Sigma^+$) and any of the three repulsive states are not avoided.

In order to further refine the model of photoinduced molecular quantum dynamics of the HCl^+ system, we investigate the frequency dependence of the excitation probability after applying a laser pulse to the molecular ion which is initially in the electronic and vibrational ground state. For typical experiments with pulsed lasers the time-dependence of the envelope is characterized by amplitude F_0 and duration τ

$$F_0(t/\tau) = F_0 \sin^2(\pi t/\tau), \quad 0 \leqslant t \leqslant \tau. \tag{3.1}$$

This envelope is similar to a Gaussian pulse with equivalent full width at half maximum (FWHM) of the pulse intensity, $t_{FWHM} = 0.36\tau$, but the $\sin^2$-like pulse shape offers the advantage of a well defined beginning and end.

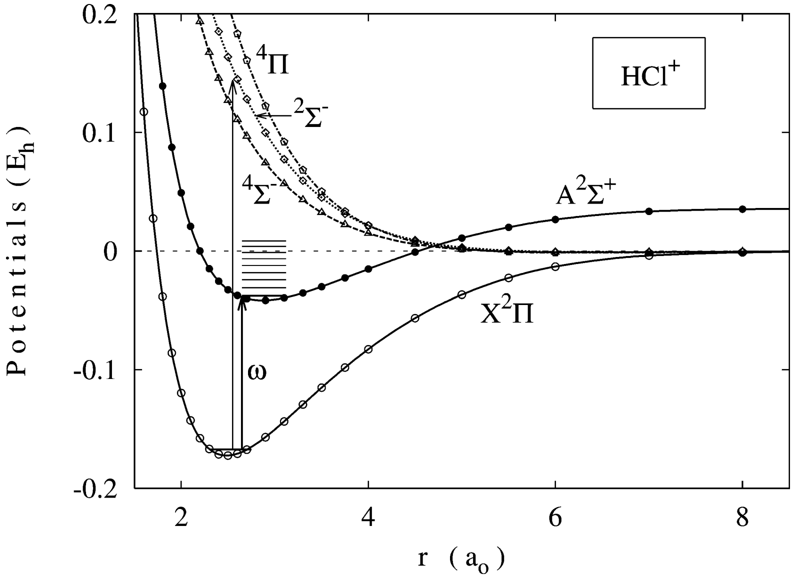


Fig. 1. Potential energy curves for the lowest five electronic states of the HCl^+ ion adapted from Ref. [57]. Dipole allowed transitions (perpendicular polarization) are marked by vertical arrows.

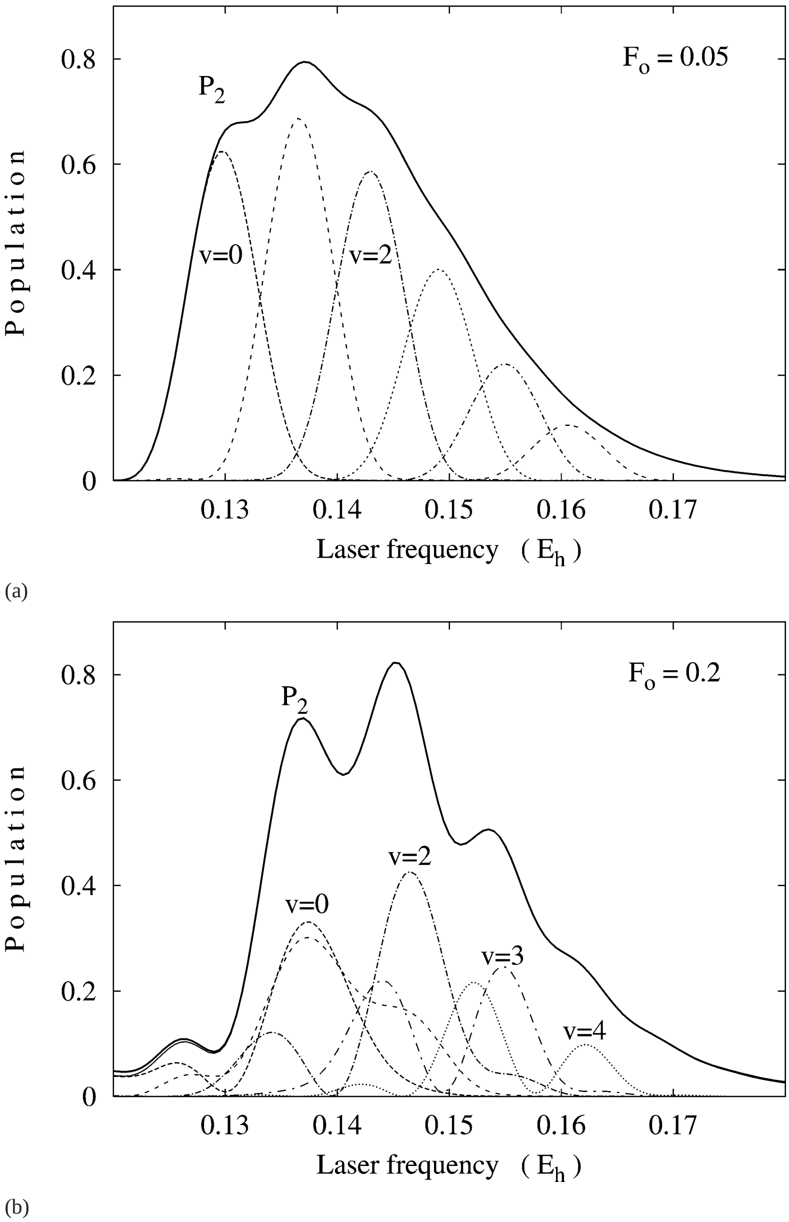
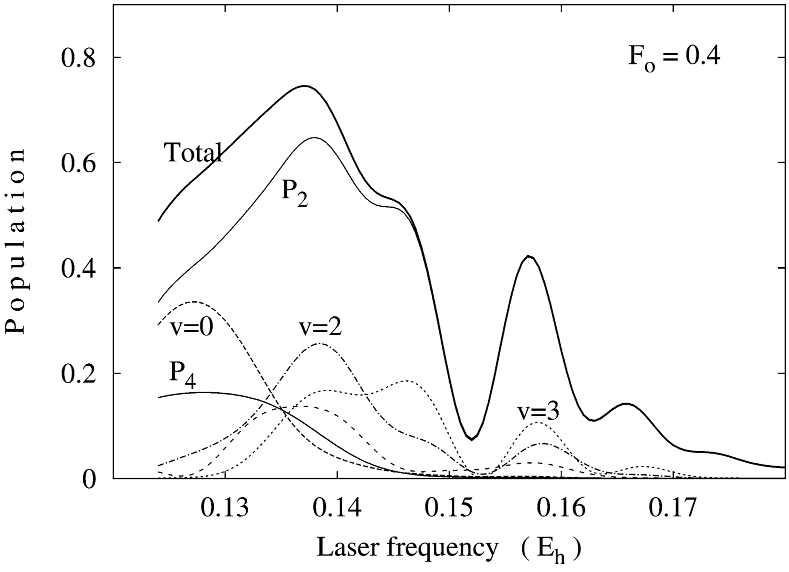


Fig. 2. Frequency dependence of excitation probability at the end of a pulse ($\tau = 30$ fs) for three different field amplitudes: (a) $F_0 = 0.05E_h/(ea_0)$, (b) $F_0 = 0.2E_h/(ea_0)$, (c) $F_0 = 0.4E_h/(ea_0)$. Thick solid curves: Total excitation probabilities. Thin solid curves: Populations of $A^2\Sigma^+$ (labelled P_2) and $^2\Sigma^-$ (P_4) state. Remaining curves: Populations of individual vibrational levels of the bound $A^2\Sigma^+$ state.

Fig. 2 shows results obtained for a numerically exact solution of the TDSE (2.16), i.e., without using a (truncated) Floquet approach. Simulations were carried out for a fixed pulse duration ($\tau = 30$ fs) and for frequencies ranging in the near UV ($0.12 < \hbar\omega/E_h < 0.18$). For a field amplitude of $F_0 = 0.05E_h/(ea_0)$ (intensity of 8.75×10^{13} W/cm^2) one recognizes a broad absorption spectrum. The weak modulation can be traced to the excitation of individual vibrational states which are partially overlapping due to the large



(c)

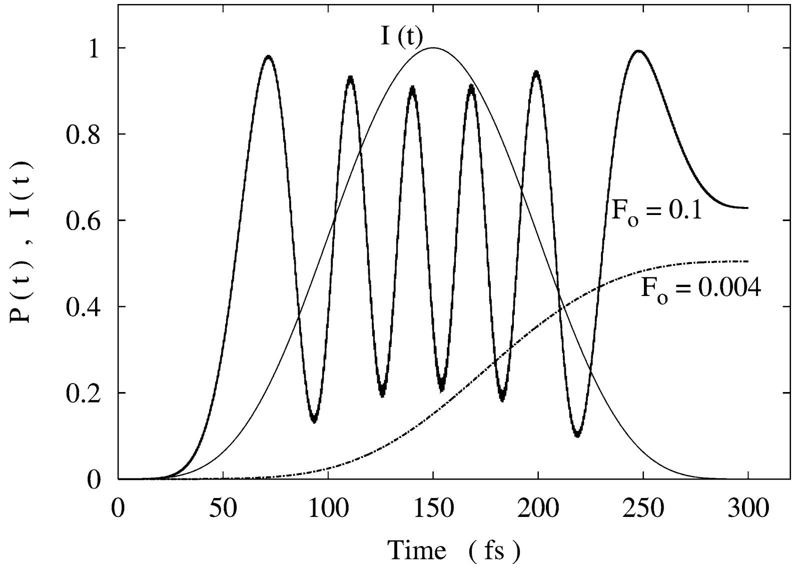
Fig. 2. Continued.

spectral width of the ultrashort pulse. Note that predissociation due to the spin-orbit coupling between the (bound) $A^2\Sigma^+$ state and the three repulsive states occurs only for $v \geqslant 8$, see Refs. [55,56]. For all frequencies below the respective threshold there is no population of any of the repulsive states although the frequencies are—within the spectral pulse width—close to the two-photon resonance for direct excitation of the $^2\Sigma^-$ state which is dipole allowed for the perpendicular polarization considered here. This situation prevails for even stronger fields, e.g., for $F_0 = 0.2E_h/(ea_0)$ but the vibrational state selectivity is practically lost. Only for extreme fields ($F_0 = 0.4E_h/(ea_0)$) there is notable population of the repulsive $^2\Sigma^-$ state, too.

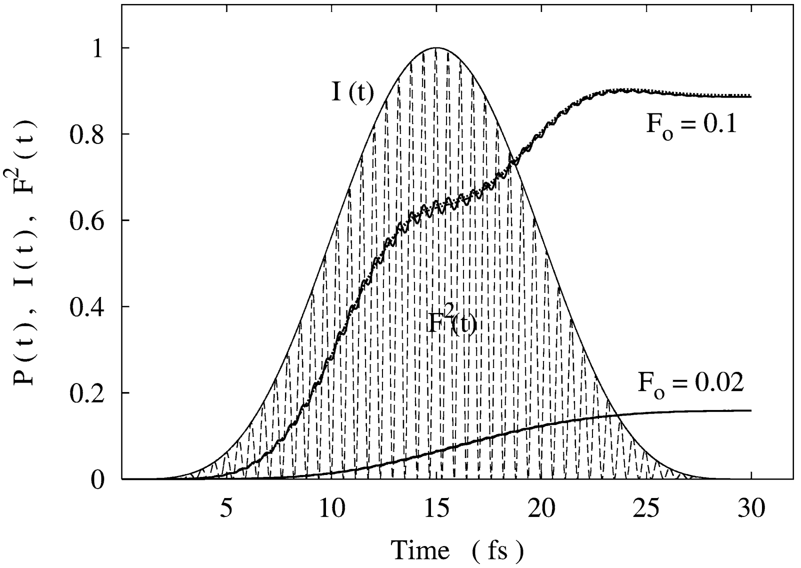
Based on these considerations of the population dynamics we can restrict the simulation model for the investigations presented in the remainder of this work to an effective two-state model consisting of the electronic ground ($X^2\Pi$) and first excited ($A^2\Sigma^+$) state. Furthermore, we choose $\omega = 0.1295E_h/\hbar$ (3.52 eV) which is very close to the resonance frequency, ω_R, for the 0–0 transition. The optical cycle corresponds to $T = 2\pi/\omega = 48.5\hbar/E_h$ (1.17 fs). In the following sections, we shall compare simulation results of the original TDSE (2.16) for those two molecular states with simulations using Floquet basis sets with varying truncation schemes. Assuming only the electronic ground state to be populated initially, the simplest version consists of three “dressed states”, $|1,0\rangle$, $|2,1\rangle$, $|2,-1\rangle$, where the values 1 and 2 of the first quantum number stand for ground ($X^2\Pi$) and excited state ($A^2\Sigma^+$), respectively. The second and third state are coupled to the first one through emission or absorption of one photon, respectively. In a five state basis, we additionally consider the $|1,2\rangle$ and $|1,-2\rangle$ state which corresponds to emission or absorption of a second photon. Finally, we augment the basis by the $|2,3\rangle$, $|2,-3\rangle$ states in order to account for interaction with a third photon as well.

3.2. *Validity of Floquet approach*

In this section we shall compare population dynamics of the two lowest electronic states for a variety of laser pulses using two different approaches, i.e., the numerically exact solution of the TDSE and the solution using a truncated basis set of 3 or 7 Floquet states. Results for a pulse duration of $\tau = 300$ fs are presented in Fig. 3(a). For a medium field amplitude, $F_0 = 0.004E_h/(ea_0)$, we are still in the linear regime with a monotonic increase of the excited state population reaching about 50% at the end of the laser pulse (300 fs); for strong fields, $F_0 = 0.1E_h/(ea_0)$, we are in the highly non-linear regime. The A state popu-



(a)



(b)

Fig. 3. Time dependence of population of $A^2\Sigma^+$ state (together with relative laser intensity and field) for (a) $\tau = 300$ fs and (b) $\tau = 30$ fs pulse duration. Note that the effect of truncation of the Floquet basis is visible only for the case of $\tau = 30$ fs, $F_0 = 0.1E_h/(ea_0)$.

lation oscillates in time with maxima reaching near unity. In either case, the results obtained for the three approaches are in very good quantitative agreement. As could be expected, the Floquet model is almost exact for a relatively long pulse covering more than 250 optical cycles. Results of an analogous set of simulations for a pulse duration of $\tau = 30$ fs are shown in Fig. 3(b). Again, for medium field amplitude, $F_0 = 0.02E_h/(ea_0)$, the truncated Floquet approach is close to exact. For a very strong field, $F_0 = 0.1E_h/(ea_0)$, the slow increase of the excited state population is reproduced correctly. However, the fast oscillations at center of laser pulse which are in phase with the carrier frequency of the pulse, are washed out. They result from a complicated interplay of higher harmonics not included in the truncated basis set. Hence, even for pulses as short as 25 optical cycles the truncated Floquet picture represents a near-quantitative description of photo-induced quantum molecular dynamics.

Although the population of individual Floquet states, $P_{n,m}(t) = \int |\varphi_{n,m}(R,t)|^2 \, \mathrm{d}R$, does not correspond to a molecular observable, it can be instructive to inspect the corresponding population dynamics because it is intimately related to number of emitted or absorbed photons. Typical results for a pulse with $\tau = 30$ fs and $F_0 = 0.1 E_h/(ea_0)$ are displayed in Fig. 4. During the first half of the pulse, we observe buildup of population according to the following scheme: The first states to be populated by the matter-light interaction are the $|2,-1\rangle$ and $|2,1\rangle$ state because the Floquet matrix (2.12) directly couples those states to the initially populated $|1,0\rangle$ state. At the center of the pulse, the population of the former two states differs by more than three orders of magnitude which is due to the resonant ($|2,-1\rangle$) or strongly off-resonant ($|2,1\rangle$) character of the excitation process. A similar ratio is also found for the next two states being populated by absorption/emission of one more photon: This gives rise to transitions from the $|2,-1\rangle$ state to the $|1,-2\rangle$ state as well as from the $|2,1\rangle$ state to the $|1,2\rangle$ state. Analogously, the next pair of states to be populated are $|2,-3\rangle$ state and $|2,3\rangle$. During the second half of the laser pulse the population of the states which were populated by emission, $|2,1\rangle$, $|1,2\rangle$, $|2,3\rangle$, is rapidly decreasing with time until they practically vanish again ($< 10^{-10}$). After the pulse, the remaining population is found in the states $|1,0\rangle$, $|2,-1\rangle$, $|1,-2\rangle$, $|2,-3\rangle$ which corresponds to absorption of zero, one, two, and, three photons. These observations are instrumental in adjusting the size of the truncated Floquet basis. In the present example, the probability of absorption of three photons is below 10^{-6} which gives an upper limit for the error associated with the truncation of the basis.

3.3. Time discretization

Having refined the size of the Floquet basis set, we now turn our attention to the numerical effort for a simulation of photoinduced dynamics. Let us consider the case of M coupled wavefunctions each of which is represented on a spatial grid consisting of N points. To leading order in N and M, the effort for a single evaluation of the Hamiltonian scales with $2MN \log N$ which arises for M pairs of fast Fourier transforms (FFT) to switch forth and back between coordinate

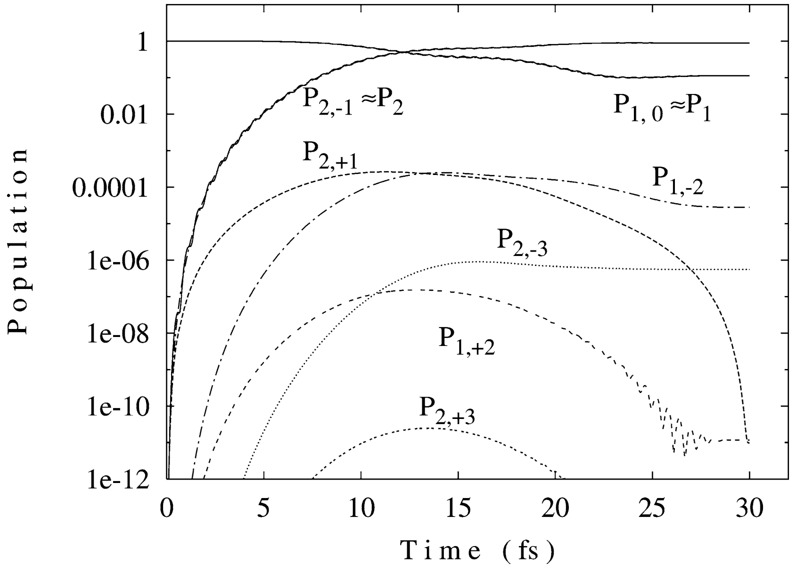
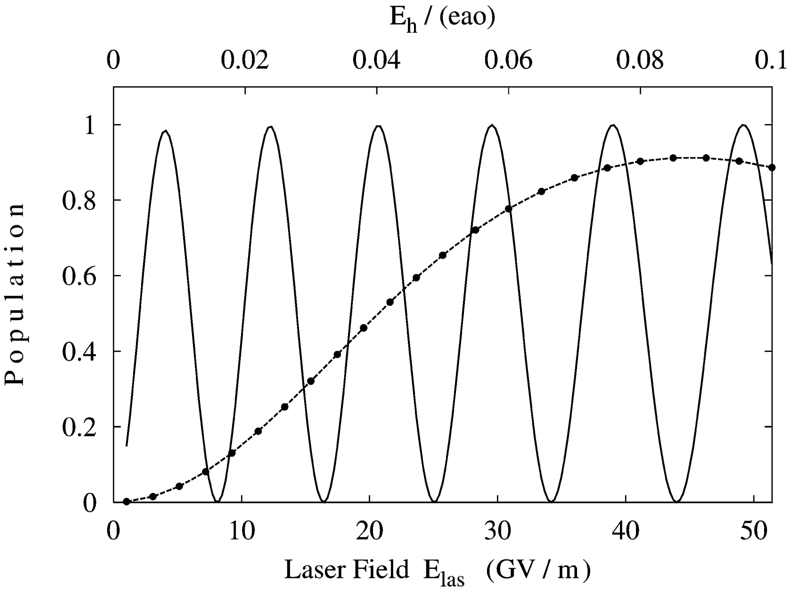
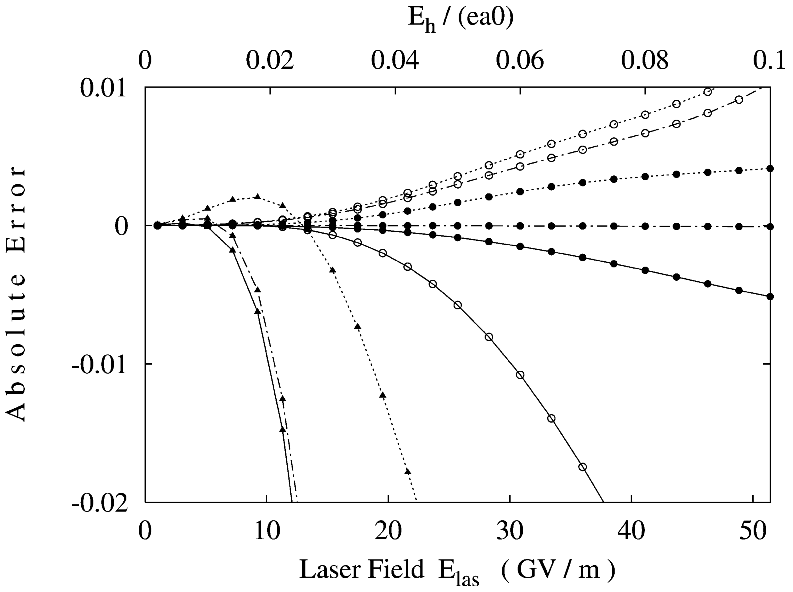


Fig. 4. Time dependence of population of individual Floquet states for a pulse with $\tau = 30$ fs and $F_0 = 0.1 E_h/(ea_0)$. Note the logarithmic scale of the ordinate.



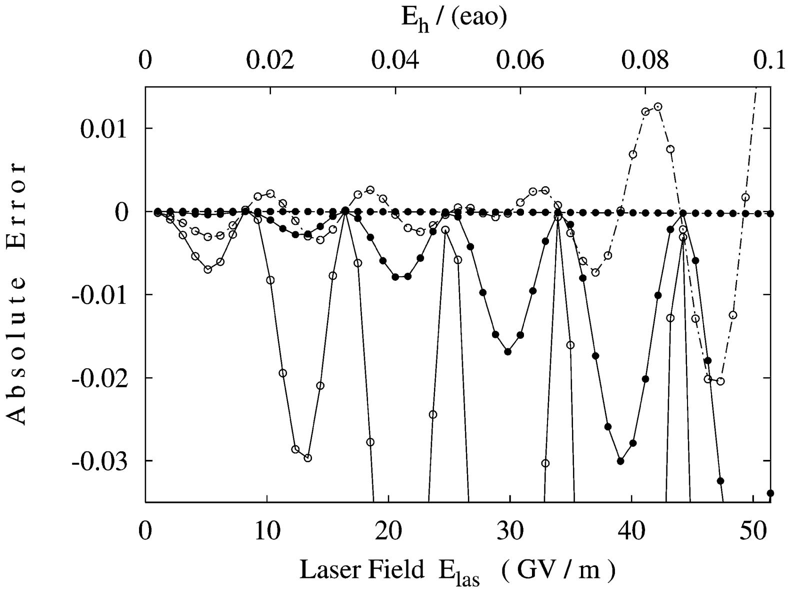
(a)



(b)

Fig. 5. (a) Field dependence of excitation probability at the end of a pulse (dashed: $\tau = 30$ fs, solid: $\tau = 300$ fs). (b) Absolute error for 30 fs pulse: Full calculation (solid curve) versus truncated Floquet approach for 7 states (dash-dotted) and 3 states (dotted) and for a time step of $\Delta t = 1\hbar/E_h$ (full circles), $\Delta t = 5\hbar/E_h$ (empty circles), and $\Delta t = 10\hbar/E_h$ (full triangles). (c) Absolute error for 300 fs pulse: Full calculation (solid curve) versus truncated Floquet approach for 7 states (dash-dotted) and for a time step of $\Delta t = 1\hbar/E_h$ (full circles), $\Delta t = 5\hbar/E_h$ (empty circles).

and momentum space representation. Note that the diagonalization of the M-state Hamiltonian for each of the N grid points is negligible if $N \gg M$. Including one-, two-, three-photon processes in a simulation for two electronic states, with only one state initially populated, leads to $M = 3, 5, 7$. On the one hand, this



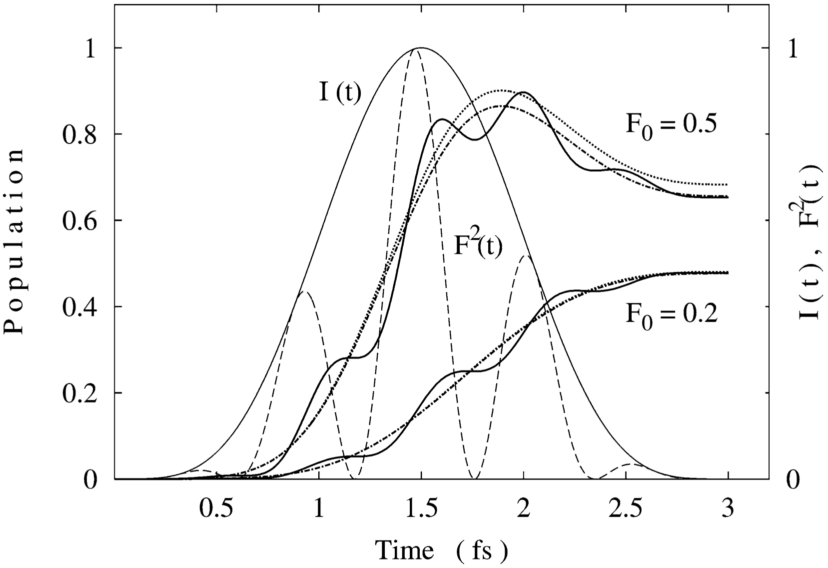
(c)

Fig. 5. Continued.

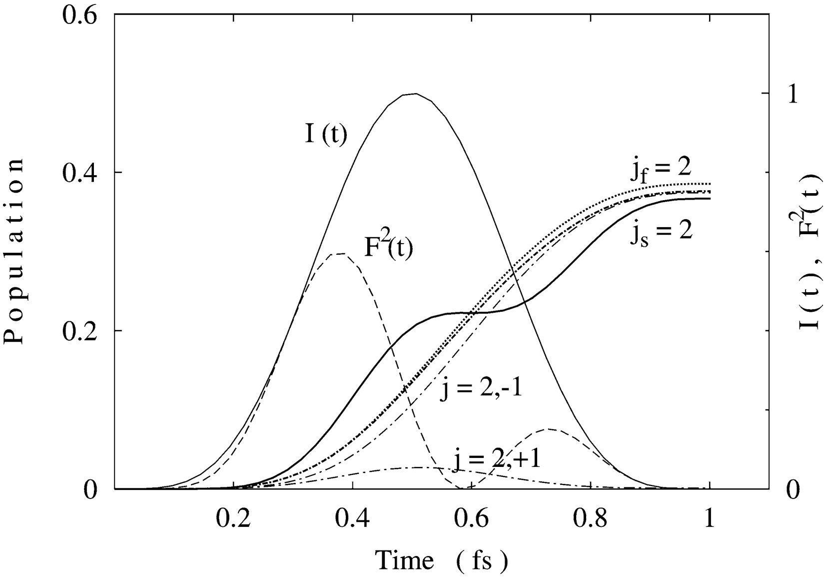
leads to a linearly increasing numerical effort per time step. On the other hand, including the effect of the fast oscillations of the field into the "dressed state" basis leads to a Floquet Hamiltonian (2.13) which is only slowly time-dependent through the modulation of the amplitude $F_0(t)$ which should lead to a reduced number of time steps.

In the following we shall investigate the effect of the time discretization. Fig. 5(a) shows the excited state population at the end of a laser pulse for varying field amplitude, $0.004 < F_0 ea_0/E_h < 0.1$. For a pulse duration of $\tau = 30$ fs there is only a single maximum in the range of amplitudes under consideration while for $\tau = 300$ fs there are several Rabi-type oscillations with amplitudes near unity. To quantify the error, we shall compare simulation results of the excited state population with solutions of the original TDSE (2.16) for an extremely short time step, $\Delta t = 0.01\hbar/E_h$, which is regarded to be numerically exact.

First, let us consider the solution of the TDSE (2.16), i.e., without using a Floquet basis, for $\tau = 30$ fs, see Fig. 5(b). For a short time step of $\Delta t = 1\hbar/E_h$ (24.2 as), there is good agreement with the exact solution within less than half a percent for all fields considered. The situation deteriorates rapidly when going to longer time steps, and for $\Delta t = 10\hbar/E_h$ the simulations reproduce the exact value within a margin of one percent only for relatively weak fields $F_0 < 0.01E_h/(ea_0)$. When comparing these data with the optical period of the carrier, $T = 2\pi/\omega = 48.5\hbar/E_h$ (1.17 fs), this indicates a breakdown of the numerical scheme for less than 10 time steps per period as expected. As a next step, the three-state Floquet picture is discussed (dotted curves in Fig. 5(b)): The magnitude of the error for $\Delta t = 1\hbar/E_h$ is similar as for the solution of the original TDSE. However, this error remains practically the same when reducing the time step down to 0.01. This indicates that the error is rather due to the truncation of the Floquet basis. When considering larger time steps, the advantage of the Floquet approach becomes obvious. For example, the stability for the $\Delta t = 10\hbar/E_h$ is largely improved: For field amplitudes $F_0 < 0.05E_h/(ea_0)$ the results are still within a one percent margin. As discussed above, seven state are practically converged with respect to the size of the Floquet basis (dash-dotted curves in Fig. 5(b)). Accordingly, for $\Delta t = 1\hbar/E_h$ there is hardly any deviation from the numerically exact result. Also for $\Delta t = 5\hbar/E_h$ the error is smaller than for the three-state model. However, for $\Delta t = 10\hbar/E_h$ the numerical accuracy is not better than for the three-state basis.



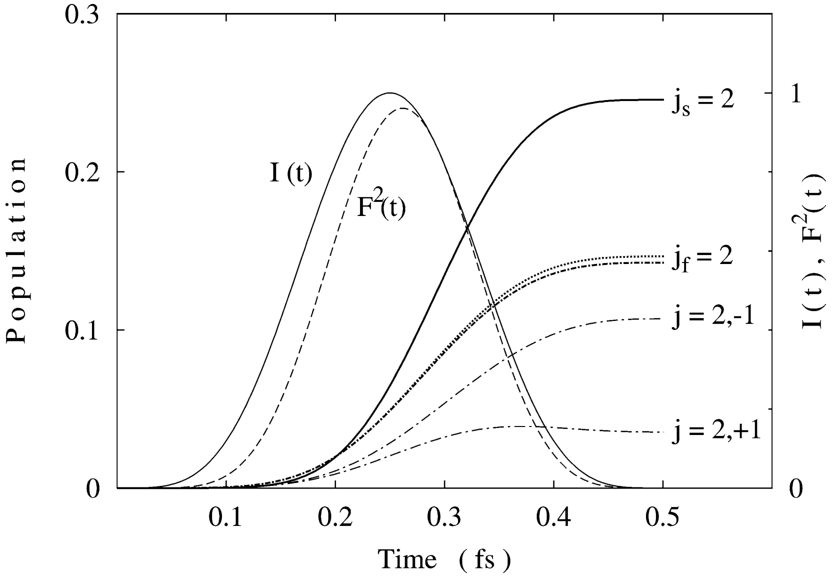
(a)



(b)

Fig. 6. Time dependence of $A^2\Sigma^+$ state population for different pulse durations, (a) $\tau = 3$ fs, (b) $\tau = 1$ fs, (c) $\tau = 0.5$ fs, and for a field amplitude of $F_0 = 0.5E_h/(ea_0)$ (together with relative laser intensity and field): Full calculation (solid curve) versus truncated Floquet approach for 7 states (dash-dotted) and for 3 states (dotted). Additional curves show population of individual Floquet states.

The numerical error for simulations of the 300 fs pulse is illustrated in Fig. 5(c). In contrast to the previous case, the solution of the original TDSE for a time step of $1\hbar/E_h$ already deviates considerably from the numerically exact one ($\Delta t = 0.01\hbar/E_h$) where the periodic behavior of the error correlates with the population as shown in Fig. 5(a). However, the amplitude is rapidly growing with the field amplitude which eventually leads to a divergence for the error. This is remedied efficiently by the Floquet approach (7 states)



(c)

Fig. 6. Continued.

which is practically exact for the same choice of the time step. When enlarging the time step by a factor of five, the results for both approaches show oscillations with monotonically increasing results. While the error of the Floquet result remains below 1% up to a field of $F_0 = 0.08 E_h/(ea_0)$, the TDSE result exceeds that error margin already near $F_0 = 0.02 E_h/(ea_0)$.

To summarize, the elimination of the fast time scale allows for a larger time step in Floquet-based simulations than for numerical solution of the original TDSE. However, the observed enhancement by a factor of approximately ten is considerably below the theoretically expected factor which is of the order of τ/T, i.e., approximately 25 or 250 for the pulse durations considered here. This points at a natural upper limit for the time step which is independent of the time-dependence of the field. For a short-time integrator such as the split operator scheme employed here, the time step is rather limited by the phase oscillations of the quantum-mechanical wave functions [50]. In principle, this could be overcome by the use of long-time integrators such as the Chebychev scheme with its exponential convergence [48,50,60]. In passing we also note that the problem of phase oscillations does not occur for mixed quantum-classical simulations which indeed allow a large time step determined by t_P [47].

3.4. *Limit of ultrashort pulses*

Finally, we would like to investigate the limit of extremely short pulses of a single optical cycle and below. Although in those cases there is no numerical advantage of the Floquet approach, it is nevertheless interesting to explore the limit of a (truncated) Floquet representation of quantum molecular dynamics. The resulting population dynamics for $\tau = 3$ fs shown in Fig. 6(a) is similar to that for longer pulses, see, e.g., Fig. 3(b), but here the amplitude of oscillations at intermediate times is more pronounced. Nevertheless, the final population is reproduced correctly by the Floquet approach. While three states are sufficient for $F_0 = 0.2 E_h/(ea_0)$, seven states are necessary to obtain converged results for $F_0 = 0.5 E_h/(ea_0)$. Even for a pulse duration of 1 fs which is just below one optical cycle we observe only a very small discrepancy between the final excitation probability obtained by solution of the original TDSE (2.16) and that calculated within the Floquet approach (2.17). However, this discrepancy becomes severe when considering even shorter pulses: For a pulse duration of 0.5 fs the excitation probability is underestimated by 40% when using the seven state Floquet model. Note that this shortcoming is not due to the incomplete basis size but is rather connected with the concept of expanding the field in harmonics of ω which necessarily breaks down for pulse lengths of less than one cycle.

4. Conclusions

Apart from the advantage of providing an intuitive physical picture of light-driven molecular quantum dynamics, the main attractiveness of Floquet based models stems from numerical reasons. In the present work, the properties of numerical simulations for a molecular excitation near resonance frequency have been investigated in detail. It has been shown that an approach based on relatively few Floquet "dressed states" is valid even for extremely intense and short pulses. The Floquet technique offers the important advantage of eliminating the highly oscillatory terms associated with the carrier frequency of a light pulse. In most cases, much longer time steps can be used in a numerical integration using dressed states than for bare molecular states. This renders the Floquet representation an efficient tool for the simulation of quantum molecular dynamics driven by light pulses beyond the perturbative regime. Further improvements of the numerical efficiency of Floquet based simulations can be expected if the spatial representation is optimized and if other time propagators such as the Newton or Chebychev schemes are used [48]. This is especially important for multidimensional systems where the computational effort is a critical issue.

One might ask in how far the results presented here can be generalized to other molecules and/or other light pulses. First of all, the potential energy curves as well as the transition dipole moment for the ground ($X^2\Pi$) and excited ($A^2\Sigma^+$) state of the HCl^+ ion are rather typical. Hence, similar scenarios are expected for electronic excitation of other molecules. Second, the variation of field amplitude and pulse duration investigated in this study is rather complete. Moreover, we note that the Floquet approach can also be generalized to cases of multi-color laser fields [8, 13] as well as to the case of frequency modulated ("chirped") pulses [26,27].

However, the present study has been limited to a frequency close to the 0–0 resonance frequency, $\omega_R = 0.1295 E_h/\hbar$, between the ground and excited electronic state. In order to discuss the effect of different frequencies we consider the case of $\omega \approx \omega_R/2$, see Fig. 7. In that case we find that the main contribution to the final excitation probability results from the $|2, -3\rangle$ state. Since the two-photon 0–0 transition is forbidden, this result is indicative for a

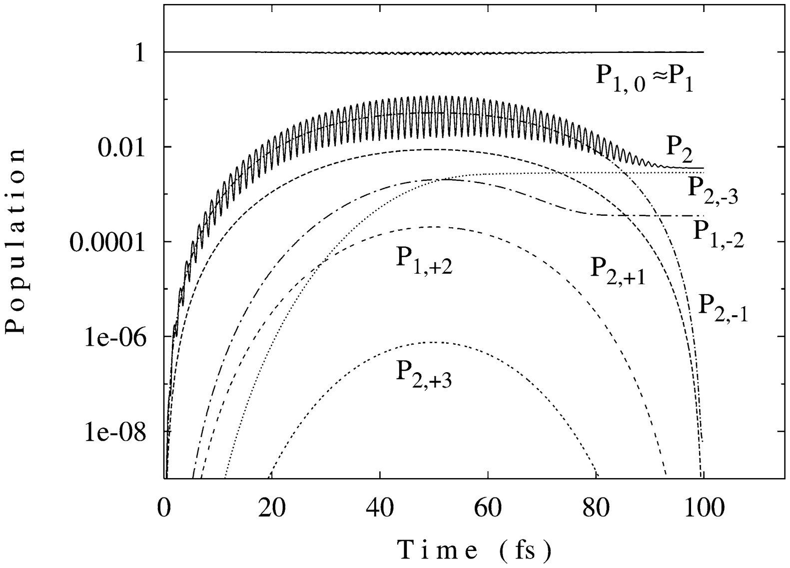


Fig. 7. Population of individual Floquet states for a pulse with $\tau = 100$ fs, $F_0 = 0.3 E_h/(ea_0)$, and $\omega = \omega_R/2$.

three-photon process leading to population of high lying vibrational levels of the excited electronic state.

The use of Floquet-based representations of molecular dynamics is not restricted to fully quantum-mechanical simulations: While the solution of the Schrödinger equation is currently limited to very few atoms, larger molecular systems can be simulated using mixed quantum-classical dynamics [61]. First attempts based on instantaneous adiabatic states were restricted to the long wave-length limit [38–40]. However, this limitation can be overcome by the use of Floquet states as demonstrated in Ref. [47].

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