JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 13 1 OCTOBER 2001

A theoretical model for molecules interacting with intense laser pulses: The Floquet-based quantum-classical Liouville equation

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(Received 18 May 2001; accepted 11 July 2001)

The Floquet-based quantum-classical Liouville equation (F-QCLE) is presented as a novel theoretical model for the interaction of molecules with intense laser pulses. This equation efficiently combines the following two approaches: First, a small but spectroscopically relevant part of the molecule is treated quantum-mechanically while the remaining degrees of freedom are modeled by means of classical molecular dynamics. The corresponding nonadiabatic dynamics is given by the quantum-classical Liouville equation which is a first-order approximation to the partial Wigner transform of full quantum dynamics. Second, the dynamics of the quantum subsystem is described in terms of instantaneous Floquet states thus eliminating highly oscillatory terms from the equations of motion. The resulting F-QCLE is shown to have a well defined adiabatic limit: For infinitely heavy classical particles and for infinitely slow modulation the dynamics adiabatically follows the Floquet quasi-energy surfaces for a strictly time-periodic field. Otherwise, nonadiabtic effects arise both from the motion of the classical particles and from the modulation of the field which is assumed to be much slower than the carrier frequency. A numerical scheme to solve the F-QCLE is based on a Trotter splitting of the time evolution. The simplest implementation can be realized by an ensemble of trajectories stochastically hopping between different Floquet surfaces. As a first application we demonstrate the excellent agreement of quantum-classical and fully quantum-mechanical dynamics for a two-state model of photodissociation of molecular fluorine. In summary, due to the favorable scaling of the numerical effort the F-QCLE provides an efficient tool for the simulation of medium to large molecules interacting with intense fields beyond the perturbative regime. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1398577]

I. INTRODUCTION

One of the ultimate goals in the field of physical chemistry/chemical physics is to understand molecular dynamics in real time. In particular, recent experimental progress connected with the generation of very short and intense laser pulses has lead to novel possibilities to observe, and possibly control, molecular dynamics on a femtosecond time scale by means of various kinds of nonlinear spectroscopy, e.g., pump–probe experiments.[1,2] Currently there is a trend to extend these studies towards larger and, eventually, biologically relevant molecules. The development of corresponding theoretical models is still posing a great challenge. In particular, the requirements for theoretical models of molecular dynamics interacting with strong external fields are the following: First of all, the dynamics of the full molecular system has to be modeled microscopically where at least the most important degrees of freedom ought to be treated quantum-mechanically. Second, the interaction of the molecule with the external field has to be modeled beyond the level of perturbation theory in order to account for high field amplitudes and the corresponding higher-order nonlinear effects.

A pragmatic approach to meet the first of the above requirements is the use of quantum-classical hybrid schemes. On the one hand, a fully quantal model of the dynamics of large molecules is clearly beyond the limits of present computational feasibility. On the other hand, certain quantum effects have to be incorporated in a realistic description of photo-induced processes. However, such effects can often be attributed to a subsystem of the molecule under consideration, e.g., the electronic dynamics in studies of electronic excitation or the proton dynamics in studies of hydrogen transfer systems, whereas it may be sufficient to treat the remaining degrees of freedom by means of standard classical molecular dynamics. The earliest variants of such hybrid schemes are based on the assumption of separability of the wave functions for the two subsystems which are interacting with each other through mean field potentials (Ehrenfest coupling).[3–5] More recently the asymptotic properties of such models have been studied with more mathematical rigor.[6–8] However, the use of such models has to be limited to cases where the dynamics is close to separable. The empirically based surface hopping scheme represents a first attempt to overcome the limitation of separability.[9–11] Owing to the simple concept of surface hopping, modified versions of the original algorithm are still in common use in many studies of nonadiabatic effects in molecular dynamics.[12–17] During the last few years these techniques were given a more rigorous foundation through the advent of the quantum-

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classical Liouville equation (QCLE).[18–22] It can be formally derived as a partial Wigner transform of the original quantum-mechanical Liouville–von Neumann equation (LvNE).[23–25] Other work is devoted to the construction of practical algorithms to solve the QCLE numerically[26–29] using surface-hopping and multithreading schemes.

First attempts to develop quantum-classical models for the coupling between molecular dynamics and external fields are still hampered by serious limitations: The standard technique in the literature is based on perturbation theory[1,30] yielding numerically tractable equations only for specific laser pulses.[31,32] Furthermore, these approaches usually exclude higher order processes prevalent in strong fields. In other work a surface hopping of classical trajectories between instantaneous Stark states is suggested.[33,34] Naturally, such a model is limited to very low frequency fields because of the highly oscillatory behavior of the fields used in typical experiments with pulsed lasers.

In the present work we suggest to overcome these problems by the use of Floquet theory which is well developed for the case of static systems (e.g., atoms). Although originally developed for the interaction of a quantum system with continuous light sources[35,36] it has been adapted in recent years to the treatment of amplitude and frequency modulated light.[37–41] In general, the attractivity of Floquet based models is fourfold: (1) It allows for an adiabatic approximation of the time-dependent Schrödinger equation, possibly including nonadiabatic effects at various levels of approximation.[39,42,43] (2) Since Floquet theory is not based on perturbation theory, it allows for higher-order effects induced by very intense fields. (3) A Floquet description offers the advantage of a straightforward interpretation: The underlying ‘‘dressed state’’ picture allows a direct counting of absorbed or emitted photons.[36] (4) Finally, the elimination of the fast oscillations connected with the carrier frequency of the electric field allows a larger time steps in numerical simulations.

In the present work we introduce a novel approach for the construction of an efficient simulation technique which combines the two approaches mentioned above. In particular, we intend to develop a quantum-classical model for molecular dynamics in the presence of external fields based on Floquet states. This shall be accomplished by means of a Floquet-based quantum-classical Liouville equation (F-QCLE). Such an approach is expected to offer the following advantages: By virtue of the favorable scaling properties of trajectory-based implementations of the QCLE, it can be used for the description of medium to large molecules. At the same time, the use of a Floquet basis allows for description of multiphoton processes while avoiding highly oscillatory nonadiabatic transition probabilities.

The remainder of this paper is organized in the following way: Sec. II presents a fully quantum mechanical model of molecular dynamics based on Floquet states. Subsequently, a quantum-classical description is developed in Sec. III by the use of partial Wigner transforms. Numerical simulations in Sec. IV illustrate the use of these models.

II. QUANTUM DYNAMICS

A. Hamiltonian operator

Let us consider a physical or chemical system consisting of a heavy particle of mass M and a light particle of mass m with $m/M \ll 1$, where generalization to the case of several heavy and/or light particles is straightforward. The quantum dynamics of such a two-component system is described by two sets of position and momentum operators $\hat{R},\hat{P}$ and $\hat{r},\hat{p}$, respectively. Hence, the total Hamiltonian of the system can be written as

$$\hat{H}(\hat{r},\hat{p},\hat{R},\hat{P},t)=\hat{V}(\hat{r},\hat{p},\hat{R},t)+\frac{\hat{P}^2}{2M}, \tag{1}$$

where the first term on the right-hand side is the Hamiltonian of the light particles which can be interpreted as the potential energy governing the dynamics of the heavy particles. In the absence of an external field, we simply have

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

representing the kinetic and potential energy where the latter is depending on the positions of the heavy particles, too. The light–matter interaction can be described in the framework of the semiclassical dipole approximation, i.e., a quantum-mechanical system interacting with a time-dependent classical field[44]

$$\hat{V}(\hat{r},\hat{p},\hat{R},t)=\hat{V}_0(\hat{r},\hat{p},\hat{R})+\hat{\mu}(\hat{r},\hat{R})\cdot F(t), \tag{3}$$

where the electric dipole moment $\hat{\mu}$ of the molecular system interacts with the external electric field $F(t)$. It is noted that the dot product accounts for the vectorial nature of the two quantities and allows for the description of polarization effects. Typically, for modern experiments with conventionally pulsed lasers the time-dependence of the electric field is given by

$$F(t)=F_0(\Omega t)\sin(\omega t) \tag{4}$$

representing fast oscillations with a constant carrier frequency ω with modulated amplitude $F_0(\Omega t)$ defining the envelope (shape) of the light pulse. The time scale of the modulation is assumed to be much slower than that of the carrier frequency $(\Omega/\omega \ll 1)$.

B. Scaled Schrödinger equation

The dynamics of the system is governed by the time dependent Schrödinger equation (TDSE),

$$i\hbar\frac{d}{dt}|\psi(t)\rangle=\hat{H}(t)|\psi(t)\rangle \tag{5}$$

giving the evolution of the quantum-mechanical state vector. In the following we shall use a coordinate representation of the heavy particle operators $\hat{R},\hat{P}$ which allows us to write the Hamiltonian of the total system as

$$\hat{H}(\hat{r},\hat{p},R,t)=\hat{V}(\hat{r},\hat{p},R,t)-\frac{\hbar^2}{2M}\Delta_R, \tag{6}$$

where the heavy particle potential can be written as

$$\hat{V}(\hat{r},\hat{p},R,t)=\frac{\hat{p}^2}{2m}+\hat{U}(\hat{r},R)+\hat{\mu}(\hat{r},R)\cdot F(t). \tag{7}$$

These expressions can be understood as quantum mechanical operators in $\hat{r},\hat{p}$ parametrically depending on the position R of the heavy particle and on the time t. Similarly, the quantum mechanical state vector $|\psi(t)\rangle_{Rr}$ which is a vector in the Hilbert space spanned by R and r can be cast in coordinate representation with respect to R,

$$|\psi(R,t)\rangle_r=\langle R|\psi(t)\rangle_{Rr}, \tag{8}$$

which yields — for each value of R and t — a vector in the reduced Hilbert space $\mathcal{H}_r$ spanned by r only. Later we shall introduce a partial Wigner transform with respect to R while retaining the quantum-mechanical operators in $\hat{r},\hat{p}$ which opens the way towards a quantum-classical model of molecular dynamics.

In order to investigate the asymptotic properties of quantum dynamics, we propose a practical scaling of the quantities of interest. Following earlier work we introduce a scaled time,[6]

$$t'=\frac{\hbar}{\sqrt{mM}}t, \tag{9}$$

while the potential energy as well as the dipole moment scale according to

$$\hat{U}'=\frac{m}{\hbar^2}\hat{U} \text{ and } \hat{\mu}'=\frac{m}{\hbar^2}\hat{\mu}. \tag{10}$$

The corresponding scaling of the high (carrier) and low (modulation) frequencies is then obtained from the de Broglie relation $E=\hbar\omega$,

$$\omega'=\frac{m}{\hbar}\omega \text{ and } \Omega'=\frac{m}{\hbar}\Omega, \tag{11}$$

which leads to the scaled equation of motion (TDSE),

$$i\epsilon\frac{d}{dt'}|\psi(R,t')\rangle=\left[\hat{V}'(R,t')-\frac{\epsilon^2}{2}\Delta_R\right]|\psi(R,t')\rangle, \tag{12}$$

with the scaled potential

$$\begin{aligned}\hat{V}'(R,t')=&\frac{\hat{p}^2}{2\hbar^2}+\hat{U}'(\hat{r},R)+\hat{\mu}'(\hat{r},R)\\&\cdot F_0\left(\gamma\frac{\omega'}{\epsilon}t'\right)\sin\left(\frac{\omega'}{\epsilon}t'\right),\end{aligned} \tag{13}$$

where we have introduced the dimensionless numbers

$$\epsilon=\sqrt{\frac{m}{M}} \text{ and } \gamma=\frac{\Omega}{\omega}, \tag{14}$$

which serve as smallness parameters characterizing the deviation from adiabatic behavior. Note that we will drop the primes on the scaled quantities throughout the remainder of this article for simplicity.

C. Instantaneous Floquet states

In this section we want to construct instantaneous Floquet states which are exact solutions of the time-dependent Schrödinger equation for the light particles subsystem interacting with a strictly time-periodic Hamiltonian ($F_0=\text{const}$), i.e., for a continuous wave (cw) light source. As a first step we derive adiabatic eigenstates $|\phi_n(R)\rangle_r$ of the molecular system in the absence of an external field,

$$\hat{V}_0(R)|\phi_n(R)\rangle_r=E_n(R)|\phi_n(R)\rangle_r, \quad |\phi_n(R)\rangle_r\in\mathcal{H}_r, \tag{15}$$

where E_n are adiabatic eigenenergies of V_0 and where $\mathcal{H}_r$ is the Hilbert space spanned by the light particles. In the limit of an infinitely large number of photons, the state of the external field can be characterized by eigenstates of the (scaled) photon number operator,[36]

$$\hat{N}|\eta_m\rangle_t=-i\epsilon\frac{d}{dt}|\eta_m\rangle_t=m\omega|\eta_m\rangle_t, \quad |\eta_m\rangle_t\in\mathcal{H}_t, \tag{16}$$

where $\mathcal{H}_t$ is the corresponding Hilbert space. Using a coordinate representation in t these states can be expressed as

$$\eta_m(t)=\langle t|\eta_m\rangle_t=\frac{1}{\sqrt{\epsilon\theta}}e^{im(\omega/\epsilon)t}, \quad \eta_m(t)\in L_2(0,\epsilon\theta), \tag{17}$$

yielding square integrable functions which are time-periodic with respect to the optical cycle of the field $\theta=2\pi/\omega$.[45] The corresponding orthogonality relation is given by the scalar product in $\mathcal{H}_t$

$$\langle\eta_{m'}|\eta_m\rangle_t=\int_0^{\epsilon\theta}\eta^*_{m'}(t)\eta_m(t)dt=\delta_{m'm}. \tag{18}$$

Finally, "dressed" states are constructed as tensor products of molecular states (15) and field states (16),

$$\begin{aligned}&|\varphi^{\text{dia}}_{nm}(R)\rangle\rangle:=|\phi_n(R)\rangle_r\otimes|\eta_m\rangle_t,\\&|\varphi^{\text{dia}}_{nm}\rangle\rangle\in\mathcal{H}_{rt}:=\mathcal{H}_r\otimes\mathcal{H}_t,\end{aligned} \tag{19}$$

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,

$$\begin{aligned}\langle\langle\varphi^{\text{dia}}_{n'm'}(R)|\varphi^{\text{dia}}_{nm}(R)\rangle\rangle&=\langle\phi_{n'}(R)|\phi_n(R)\rangle_r\langle\eta_{m'}|\eta_m\rangle_t\\&=\delta_{n'n}\delta_{m'm}.\end{aligned} \tag{20}$$

The quasi-energy operator, or Floquet Hamiltonian, is defined as the sum of the Hamiltonian for the light particles interacting with the field (13), and the photon number operator,

$$\begin{aligned}\hat{\mathcal{V}}(R,F_0)&=\hat{V}(R,F_0,t)+\hat{N}\\&=\hat{V}_0(R)+\hat{\mu}(R)\cdot F_0\sin\left(\frac{\omega}{\epsilon}t\right)-i\epsilon\frac{d}{dt},\end{aligned} \tag{21}$$

where we use calligraphic symbols for operators acting in extended Hilbert space throughout this paper. Using the diabatic basis defined in Eq. (19) the corresponding matrix representation is obtained as an expansion of the

r-dependence in adiabatic molecular states combined with an expansion of the t-dependence in a Fourier series in harmonics of the carrier frequency ω,

$$\begin{aligned}\mathcal{V}_{n'm',nm}(R,F_0) &= \langle\langle \varphi^{\mathrm{dia}}_{n'm'}(R)|\hat{\mathcal{V}}(R,F_0,t)|\varphi^{\mathrm{dia}}_{nm}(R)\rangle\rangle \\ &= (E_n(R)+m\omega)\delta_{n'n}\delta_{m'm}+\mu_{n'n}(R) \\ &\quad\cdot\frac{F_0}{2}(\delta_{m',m-1}+\delta_{m',m+1}). \end{aligned}\tag{22}$$

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 off-diagonal entries couple dressed states which differ by exactly one photon. Hence, it is straightforward to interpret transitions with $m'=m\pm 1$ to absorption or emission of one photon. The coupling strengths are proportional to the matrix elements of the dipole moment operator,

$$\mu_{n'n}(R)=\langle\phi_{n'}(R)|\hat{\mu}(R)|\phi_n(R)\rangle_r . \tag{23}$$

The diagonal or off-diagonal elements are usually referred to as permanent or transition dipole moment functions, respectively. Adiabatic Floquet states are obtained by diagonalization of $\mathcal{V}(\mathcal{R})$,

$$\begin{aligned}\hat{\mathcal{V}}(R,F_0)|\varphi^{\mathrm{adi}}_{\alpha}(R,F_0)\rangle\rangle &= \mathcal{E}_{\alpha}(R,F_0)|\varphi^{\mathrm{adi}}_{\alpha}(R,F_0)\rangle\rangle, \\ |\varphi^{\mathrm{adi}}_{\alpha}\rangle\rangle &\in \mathcal{H}_{rt}, \end{aligned}\tag{24}$$

where the eigenvalues $\mathcal{E}_{\alpha}(R,F_0)$ represent the adiabatic quasi-energies, or Floquet energies, of the light particles of the molecular system driven by a strictly time-periodic field. While the diabatic energies $\mathcal{V}_{nm,nm}(R,F_0)$ generally intersect each other, the codimension of intersections of adiabatic Floquet quasi-energies depends on the symmetry of the problem. For example, for states of equal symmetry the Wigner–von Neumann theorem predicts the existence of avoided crossings or conical intersections for one- or two-dimensional problems, respectively.[46]

It is noted that the above equation reflects the central advantage of the Floquet *ansatz* for the description of quantum systems:[45,47] Instead of solving a time dependent Schrödinger equation for the original Hamiltonian $\hat{V}$ of Eq. (13) one has to solve a time-independent Schrödinger equation for the extended space Floquet Hamiltonian $\hat{\mathcal{V}}$ of Eq. (21). Although the extended space is of higher dimension such approaches are known to be numerically superior.[48]

D. Floquet-based quantum dynamics

In this section we want to return to the original problem of solving the time-dependent Schrödinger equation (12) for the Hamiltonian of the complete molecular system comprising of light and heavy components. Furthermore, we now lift the restriction of a constant field amplitude and consider an oscillating field with varying amplitude. In particular, this affects the Floquet matrix (22) as well as its eigenvalues and eigenvectors (24). In order to estimate the influence of an amplitude modulation, the amplitude F_0 is expanded in a Taylor series in time,

$$F_0\left(\gamma\frac{\omega}{\epsilon}t\right)=F_0\left(\gamma\frac{\omega}{\epsilon}t_0\right)+\gamma\frac{\omega}{\epsilon}\left.\frac{\partial F_0}{\partial t}\right|_{t=t_0}(t-t_0)+\cdots. \tag{25}$$

Restricting the use of this equation to one optical cycle $0\leqslant t-t_0\leqslant \epsilon\theta$ as required for the evaluation of the scalar product in $\mathcal{H}_t$ and $\mathcal{H}_{rt}$ [see Eqs. (18), (20)] provides an upper limit for the linear term,

$$F_0\left(\gamma\frac{\omega}{\epsilon}t\right)=F_0\left(\gamma\frac{\omega}{\epsilon}t_0\right)+\mathcal{O}(\gamma). \tag{26}$$

Hence, neglecting changes of the field amplitude during one optical cycle $\epsilon\theta$ yields an error for the Floquet matrix of Eq. (22),

$$\mathcal{V}(R,F_0(t))=\mathcal{V}(R,F_0(t_0))+\mathcal{O}(\gamma) \tag{27}$$

in case of a modulated field with slowly varying amplitude. It is noted that similar considerations are also possible for frequency modulated ("chirped") pulses.[39]

Next, the quantum-mechanical state vector of the system is expanded in the diabatic basis of dressed states introduced in Eq. (19),

$$|\psi(R,t)\rangle\rangle=\sum_{nm}\chi^{\mathrm{dia}}_{nm}(R,t)|\varphi^{\mathrm{dia}}_{nm}(R)\rangle\rangle, \tag{28}$$

where the coefficients $\chi^{\mathrm{dia}}_{nm}(R,t)$ are readily identified as the heavy particle wavefunction corresponding to the nth adiabatic molecular state dressed with m photons. Inserting this ansatz into the time-dependent Schrödinger equation (TDSE) leads to the diabatic representation of the Floquet-based TDSE. The coupled channel equations describe the evolution of the vector of heavy component wave functions,

$$\begin{aligned}i\epsilon\partial_t\chi^{\mathrm{dia}}(R,t)=\Bigg[&\mathcal{V}(R,F_0)-\frac{\epsilon^2}{2}(\Delta_R+2\mathcal{C}^{\mathrm{dia}}(R)\cdot\nabla_R \\ &+\mathcal{T}^{\mathrm{dia}}(R))\Bigg]\chi^{\mathrm{dia}}(R,t)+\mathcal{O}(\gamma),\end{aligned}\tag{29}$$

where $\mathcal{V}(R,F_0)$ is the Floquet matrix of Eq. (22), but for varying amplitude $F_0=F_0(\gamma\omega t/\epsilon)$. Note that the scalar product has to be understood as $\mathcal{C}^{\mathrm{dia}}_{n'm',nm}(R)\cdot\nabla_R=\Sigma_k\mathcal{C}^{\mathrm{dia}}_{n'm',nm,k}(R)\cdot\nabla_{R_k}$. The matrix elements of the first and second order nonadiabatic operators in extended space,

$$\begin{aligned}\mathcal{C}^{\mathrm{dia}}_{n'm',nm,k}(R)&=\langle\langle\varphi^{\mathrm{dia}}_{n'm'}(R)|\nabla_{R_k}|\varphi^{\mathrm{dia}}_{nm}(R)\rangle\rangle \\ &=C_{n'n,k}(R)\delta_{m'm}, \\ \mathcal{T}^{\mathrm{dia}}_{n'm',nm}(R)&=\langle\langle\varphi^{\mathrm{dia}}_{n'm'}(R)|\Delta_R|\varphi^{\mathrm{dia}}_{nm}(R)\rangle\rangle \\ &=T_{n'n}(R)\delta_{m'm},\end{aligned}\tag{30}$$

can be easily expressed in terms of the kinetic coupling for the field-free molecular system,

$$\begin{aligned}C_{n'n,k}(R)&=\langle\phi_{n'}(R)|\nabla_{R_k}|\phi_n(R)\rangle_r, \\ T_{n'n}(R)&=\langle\phi_{n'}(R)|\Delta_R|\phi_n(R)\rangle_r,\end{aligned}\tag{31}$$

where C is anti-Hermitian with respect to the molecular states $C_{n'n,k}=-C^{*}_{nn',k}$ while there exists no such relation for the second order coupling tensor T.

Alternatively, the state vector can be expanded in adiabatic Floquet quasistationary states introduced in Eq. (24),

$$|\psi(R,t)\rangle\rangle=\sum_{\alpha}\chi_{\alpha}^{\mathrm{adi}}(R,t)|\varphi_{\alpha}^{\mathrm{adi}}(R,F_0)\rangle\rangle, \tag{32}$$

where the coefficients $\chi_{\alpha}^{\mathrm{adi}}(R,t)$ form the heavy particle wave functions corresponding to the αth Floquet state of the light particles interacting with the field. Inserting this ansatz into the time-dependent Schrödinger equation (TDSE) leads to the adiabatic representation of the Floquet-based TDSE,

$$\begin{aligned}i\epsilon\partial_t\chi^{\mathrm{adi}}(R,t)=\Bigg[&\mathcal{E}(R,F_0)-\frac{\epsilon^2}{2}(\Delta_R+2\mathcal{C}^{\mathrm{adi}}(R,F_0)\cdot\nabla_R\\&+\mathcal{T}^{\mathrm{adi}}(R,F_0))-i\Omega\mathcal{G}(R,F_0)\cdot\frac{dF_0}{dt}\Bigg]\\&\times\chi^{\mathrm{adi}}(R,t)+\mathcal{O}(\gamma),\end{aligned} \tag{33}$$

where $\mathcal{E}(R,F_0)$ is a diagonal matrix containing the Floquet quasi-energies of Eq. (24) for varying amplitude $F_0(\gamma\omega t/\epsilon)$. The matrix elements of the first and second order kinetic coupling operators in the Floquet space are given by

$$\begin{aligned}\mathcal{C}_{\alpha'\alpha,k}^{\mathrm{adi}}(R,F_0)&=\langle\langle\varphi_{\alpha'}^{\mathrm{adi}}(R,F_0)|\nabla_{R_k}|\varphi_{\alpha}^{\mathrm{adi}}(R,F_0)\rangle\rangle,\\\mathcal{T}_{\alpha'\alpha}^{\mathrm{adi}}(R,F_0)&=\langle\langle\varphi_{\alpha'}^{\mathrm{adi}}(R,F_0)|\Delta_R|\varphi_{\alpha}^{\mathrm{adi}}(R,F_0)\rangle\rangle.\end{aligned} \tag{34}$$

In addition, the time-dependence of the Floquet states due to the amplitude modulation gives rise to yet another coupling term,

$$\mathcal{G}_{\alpha'\alpha,k}(R,F_0)=\langle\langle\varphi_{\alpha'}^{\mathrm{adi}}(R,F_0)|\nabla_{F_{0,k}}|\varphi_{\alpha}^{\mathrm{adi}}(R,F_0)\rangle\rangle, \tag{35}$$

which is anti-Hermitian with respect to interchange of the Floquet states $\mathcal{G}_{\alpha'\alpha,k}=-\mathcal{G}_{\alpha\alpha',k}^{*}$.

The main advantage of the diabatic or adiabatic Floquet-based time-dependent Schrödinger equation (F-TDSE) over the original TDSE (12) is now obvious. The Fourier decomposition of the time-dependent Hamiltonian serves to eliminate the highly-oscillatory terms connected with the high carrier frequency ω of the electric field. Hence, all terms on the right-hand sides of the two evolution Eqs. (29) and (33), i.e., the Floquet energies and the kinetic and field induced couplings, vary only slowly with time as indicated by the low modulation frequency $\Omega=\gamma\omega$. Furthermore, deviations from the instantaneous Floquet states are of the order of $\mathcal{O}(\gamma)$.

E. Asymptotic analysis

Let us first consider the asymptotic properties of the diabatic F-QCLE as given in Eq. (29). In the limit of a strictly periodic field $(\gamma=0)$, i.e., for the molecular system interacting with a continuous light source, the diabatic Floquet matrix becomes stationary, and the system evolves along the dressed states $E_n(R)+m\omega$ with nondiabatic transitions between them induced by the off-diagonal elements of the Floquet matrix (22) and/or by the first and second order kinetic coupling $\mathcal{C}^{\mathrm{dia}}(R),\mathcal{T}^{\mathrm{dia}}(R)$, see Eq. (30). Note that for symmetric molecules some coupling elements and/or dipole moment functions may vanish due to certain symmetry properties of the molecular eigenstates $|\phi(R)\rangle$.

For the case of vanishing external field $(F_0=0)$ the potential energy matrix in diabatic (dressed state) representation becomes diagonal and the corresponding quantum dynamics is equivalent to that of the noninteracting molecule; The wave functions of the heavy particles evolve along the adiabatic molecular energy levels $E(R)$ obtained as solutions of the time-independent Schrödinger equation (15) for the light particles with nonadiabatic transitions being induced by the first and second order kinetic coupling operators $C(R),T(R)$, see Eq. (31). If in addition the mass ratio of the two components vanishes $(\epsilon\rightarrow0)$ we have the limit of purely adiabatic (Born–Oppenheimer) evolution along $E(R)$.[7]

The adiabatic F-QCLE as given in Eq. (29) describes evolution of the system along the Floquet quasi-energy surfaces with nonadiabatic couplings arising from two different mechanisms. First of all, the first and second order operators $\mathcal{C}^{\mathrm{adi}}(R,F_0),\mathcal{T}^{\mathrm{adi}}(R,F_0)$ stem from the action of the heavy particle kinetic operator on the Floquet states of the light particles. Their effect on the dynamic vanishes in the limit of $\epsilon\rightarrow0$. Second, the change of Floquet states induced by the amplitude modulation of the field is given by the field-induced coupling $\mathcal{G}(R,F_0)$. It ceases to influence the dynamics of the system in the limit of cw light source with $\gamma\rightarrow0$. Finally, if both smallness parameters are infinitely small $(\gamma,\epsilon\rightarrow0)$ the system evolves adiabatically along the stationary Floquet states.

III. QUANTUM-CLASSICAL DYNAMICS

A. Quantum Liouville equation

In the following we shall use density operators instead of state vectors to characterize the evolution of the molecular system under consideration. Apart from the possibility to describe also mixed states, this description allows us to explore the transition from quantum dynamics to classical mechanics through the method of Wigner transforms, see below. In particular, the technique of partial Wigner transforms is instrumental in the construction of quantum-classical models. In the density picture, a quantum mechanical system evolves in time according to the Liouville–von Neumann (or quantum Liouville) equation (LvNE),

$$\partial_t\hat{D}(t)=-\frac{i}{\epsilon}[\hat{H}(t),\hat{D}(t)], \tag{36}$$

where the scaling of Eqs. (9)–(11) has been used.

In order to solve the LvNE numerically, a specific representation of the density and Hamiltonian operator has to be used. In the present work these shall be the diabatic (dressed state) or adiabatic (Floquet state) representation of wave functions in Eqs. (28) and (32), respectively, from which the density matrices can be constructed in a straightforward manner.[29] The corresponding matrix representations of the Hamiltonian operator can be found inside the square brackets on the r.h.s. of the diabatic (29) and adiabatic (33) formulation of the TDSE.

B. Partial Wigner transforms

The Wigner transform is a well established tool to represent quantum dynamics in phase space.[49,50] In particular, it can be shown that the equations of motion for Wigner distribution functions have a well-defined classical limit. In order to derive a quantum-classical formulation for the dynamics of a system comprising of light and heavy particles, a partial Wigner transform with respect to the heavy particle coordinates has to be carried out. This technique allows for a description of the degrees of freedom of the heavy particles, *R*, in the classical limit while maintaining the quantum mechanical nature in the degrees of freedom, *r*, connected with the dynamics of the light particles.[23,25] Using the scaling introduced above, the partial Wigner transform $A_W(R,P,t)$ of the (diabatic or adiabatic) matrix representation of a quantum-mechanical operator $\hat{A}(R,R',t)$ can be written as the Fourier transform of an off-diagonal element of the respective density matrix in *R*,

$$A_W(R,P,t)=\int_{R^N}\hat{A}\left(R-\frac{\epsilon}{2}Y,R+\frac{\epsilon}{2}Y,t\right)e^{iP\cdot Y}dY, \tag{37}$$

where an additional factor $(2\pi)^{-N}$ has to be used to obtain correct normalization for the Wigner distribution function D_W which is defined as the Wigner transform of the density operator $\hat{D}$. When using a particular (diabatic or adiabatic) basis for the representation of the quantum subsystem in $\hat{r},\hat{p}$, the partial Wigner transform takes the form of a matrix of functions in classical phase space spanned by R,P.

First, we define the heavy particles density matrix,

$$\mathcal{K}^{\mathrm{dia}}_{n'm',nm}(R,R',t)=\chi^{\mathrm{dia}}_{n'm'}(R,t)(\chi^{\mathrm{dia}}_{nm}(R',t))^*. \tag{38}$$

Using a result of Ref. 25, the transform of the density operator in the diabatic (dressed state) picture (28) is given by

$$\mathcal{D}^{\mathrm{dia}}_W(R,P,t)=\mathcal{K}^{\mathrm{dia}}_W(R,P,t)+\frac{i\epsilon}{2}[\mathcal{C}^{\mathrm{dia}},\nabla_P\mathcal{K}^{\mathrm{dia}}_W]_++\mathcal{O}(\epsilon^2), \tag{39}$$

where $[\mathcal{C}^{\mathrm{dia}},\nabla_P\mathcal{K}^{\mathrm{dia}}_W]_+=\Sigma_k[\mathcal{C}^{\mathrm{dia}}_k,\nabla_{P_k}\mathcal{K}^{\mathrm{dia}}_W]_+$ stands for a generalized form of the anticommutator $[A,B]_+=AB+BA$. Note that the first (and higher) order correction(s) are due to the fact that the dressed state basis inherits the dependence on the coordinates *R* of the heavy particles through the adiabatic basis of the field-free molecule of Eq. (15). An analogous relation holds for the partial Wigner transform of the density operator in the basis of adiabatic (Floquet) states.

The partial Wigner transform of the diabatic Hamiltonian on the r.h.s. of Eq. (29) can be expressed as

$$\mathcal{H}^{\mathrm{dia}}_W(R,P,F_0)=\mathcal{V}(R,F_0)+\tfrac{1}{2}|P|^2-i\epsilon\mathcal{C}^{\mathrm{dia}}(R)\cdot P+\mathcal{O}(\epsilon^2,\gamma), \tag{40}$$

where the terms of second order in ϵ arise both from a second order contribution of the product $\mathcal{C}\cdot P$ as well as from the second order kinetic coupling in Eq. (29). Similarly, the partial Wigner transform of the adiabtic Hamiltonian in Eq. (33) is given by

$$\begin{aligned}\mathcal{H}^{\mathrm{adi}}_W(R,P,F_0)=&\mathcal{E}(R,F_0)+\tfrac{1}{2}|P|^2-i\epsilon\mathcal{C}^{\mathrm{adi}}(R,F_0)\cdot P\\&-i\Omega\mathcal{G}(R,F_0)\cdot\frac{dF_0}{dt}+\mathcal{O}(\epsilon^2,\gamma).\end{aligned} \tag{41}$$

Again it has to be noted that the extended space representation of the Hamiltonian operator offers the advantage that there are no highly oscillatory terms connected with the carrier frequency ω. The only time-dependence in the two equations above arises from the slowly varying amplitude of the field $F_0=F_0(t)$.

C. Floquet-based quantum-classical Liouville equation

In order to obtain a quantum-classical equation of motion for the system under consideration, we have to calculate the partial Wigner transform of the quantum Liouville equation. Replacing all expressions in Eq. (36) by the respective transforms and using a first order approximation in ϵ for the Wigner transform of products of operators,[25,50–52] one readily obtains the quantum-classical Liouville equation (QCLE),

$$\begin{aligned}\partial_t D_W&=-\frac{i}{\epsilon}((HD)_W-(DH)_W)\\&=-\frac{i}{\epsilon}[H_W,D_W]_--\frac{1}{2}(\{H_W,D_W\}\\&\quad-\{D_W,H_W\})+\mathcal{O}(\epsilon).\end{aligned} \tag{42}$$

As will become more evident in the following section, the commutator in the first term on the r.h.s. of the above equation describes pure quantum dynamics of the light particles while the Poisson brackets in the second term contain both the classical dynamics of the heavy particles as well as genuinely quantum-classical terms.

Choosing the diabatic representation of the transformed Hamiltonian H_W (40) and properly evaluating the commutator and the Poisson brackets we obtain the **diabatic F-QCLE**,

$$\begin{aligned}\partial_t\mathcal{D}^{\mathrm{dia}}_W(R,P,t)=&-\frac{i}{\epsilon}[\mathcal{V}(R,F_0)-i\epsilon\mathcal{C}^{\mathrm{dia}}(R)\\&\cdot P,\mathcal{D}^{\mathrm{dia}}_W(R,P,t)]_--P\cdot\nabla_R\mathcal{D}^{\mathrm{dia}}_W(R,P,t)\\&+\tfrac{1}{2}[\nabla_R\mathcal{V}(R,F_0),\nabla_P\mathcal{D}^{\mathrm{dia}}_W(R,P,t)]_+\\&+\mathcal{O}(\epsilon,\gamma).\end{aligned} \tag{43}$$

Analogously, the **adiabatic F-QCLE** can be derived from Eq. (41),

$$\begin{aligned}\partial_t\mathcal{D}^{\mathrm{adi}}_W(R,P,t)=&-\frac{i}{\epsilon}\Bigg[\mathcal{E}(R,F_0)-i\epsilon\mathcal{C}^{\mathrm{adi}}(R,F_0)\cdot P\\&-i\Omega\mathcal{G}(R,F_0)\cdot\frac{dF_0}{dt},\mathcal{D}^{\mathrm{adi}}_W(R,P,t)\Bigg]_-\\&-P\cdot\nabla_R\mathcal{D}^{\mathrm{adi}}_W(R,P,t)\\&+\tfrac{1}{2}[\nabla_R\mathcal{E}(R,F_0),\nabla_P\mathcal{D}^{\mathrm{adi}}_W(R,P,t)]_+\\&+\mathcal{O}(\epsilon,\gamma).\end{aligned} \tag{44}$$

These equations describe the evolution of a matrix of distribution functions in classical phase space spanned by the coordinates *R* and momenta *P* of the heavy particles. Each of the diagonal or off-diagonal elements of this matrix corresponds to a density or a coherence, respectively, of the quantum system formed by the light constituents of the molecular system.

D. Numerical realization

In the following, let us consider the solution $\rho(t)$ of the first order approximation to the adiabatic F-QCLE (44), i.e., neglecting quadratic and higher terms in the two smallness parameters ϵ, γ. We are using the concept of superoperators in Liouville space,[1]

$$\partial_t \rho(t) = -\frac{i}{\epsilon}\mathcal{L}\rho(t) \quad \text{with} \quad \mathcal{L} = \mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_3, \tag{45}$$

where the superoperator on the r.h.s. of the adiabatic F-QCLE is split into three contributions,[25]

$$-\frac{i}{\epsilon}\mathcal{L}_1\rho(R,P,t) = -\frac{i}{\epsilon}[\mathcal{E}(R,F_0),\rho(R,P,t)]_-, \tag{46}$$

$$-\frac{i}{\epsilon}\mathcal{L}_2\rho(R,P,t) = -\left[\mathcal{C}^{\mathrm{adi}}(R,F_0)\cdot P + \frac{\Omega}{\epsilon}\mathcal{G}(R,F_0) \cdot \frac{dF_0}{dt}, \rho(R,P,t)\right]_-, \tag{47}$$

$$-\frac{i}{\epsilon}\mathcal{L}_3\rho(R,P,t) = -P\cdot\nabla_R\rho(R,P,t) + \tfrac{1}{2}[\nabla_R\mathcal{E}(R,F_0),\nabla_P\rho(R,P,t)]_+. \tag{48}$$

A straightforward approach to approximate the general solution of Eq. (45) utilizes a Trotter splitting of the Liouvillian into three parts. Hence, for a small time step $\tau = O(\epsilon)$ we find

$$\rho(t+\tau) = \exp\left(-\frac{i}{\epsilon}\mathcal{L}_1\tau\right)\exp\left(-\frac{i}{\epsilon}\mathcal{L}_2\tau\right) \times \exp\left(-\frac{i}{\epsilon}\mathcal{L}_3\tau\right)\rho(t) + \mathcal{O}(\epsilon^2). \tag{49}$$

This factorization allows for a relatively simple interpretation of the individual constituents of the adiabatic F-QCLE as described in the following:

1. Oscillatory phases

The superoperator $\mathcal{L}_1$, Eq. (46) can be traced back to the purely quantal dynamics of the light particle subsystem. The corresponding time evolution is given by

$$\rho_{\alpha\beta}(t+\tau) = \exp\left(\frac{i}{\epsilon}(\mathcal{E}_\beta - \mathcal{E}_\alpha)\tau\right)\rho_{\alpha\beta}(t). \tag{50}$$

While the coherences acquire a complex phase factors which is proportional to the Bohr frequency of the transition between the instantaneous Floquet states, densities are not effected by this propagator.

2. Exchange of population

The Liouville operator $\mathcal{L}_2$, Eq. (47) is of genuinely quantum-classical nature. For the sake of simplicity, let us consider two dressed states only. Moreover, we assume that the diabatic Floquet matrix $\mathcal{V}(R,F_0)$ has two real, nondegenerate eigenvalues $\mathcal{E}_1(R,F_0)$ and $\mathcal{E}_2(R,F_0)$, so that the first order kinetic coupling $\mathcal{C}^{\mathrm{adi}}(R,F)$ and the field coupling $\mathcal{G}(R,F_0)$ are real antisymmetric matrices with zeroes on the diagonal. Hence, the total nonadiabaticity can be characterized by the sum of the off-diagonal contributions,

$$\zeta(R,P,F_0) = \mathcal{C}^{\mathrm{adi}}_{12}(R,F_0)\cdot P + \frac{\Omega}{\epsilon}\mathcal{G}_{12}(R,F_0)\cdot\frac{dF_0}{dt}. \tag{51}$$

The corresponding time evolution can be described by an exchange of population between Floquet states

$$\rho(t+\tau) = \mathcal{S}(-\zeta\tau)\rho(t)\mathcal{S}(\zeta\tau)$$

with

$$\mathcal{S}(\zeta\tau) = \begin{pmatrix} \cos(\zeta\tau) & \sin(\zeta\tau) \\ -\sin(\zeta\tau) & \cos(\zeta\tau) \end{pmatrix}, \tag{52}$$

which is equivalent to a rotation of the quantum-mechanical state vector by the angle $\zeta\tau$.

3. Classical transport

Finally, the purely classical Liouville operator $\mathcal{L}_3$, Eq. (48) is equivalent to a classical Liouville equation for each entry of the density matrix,

$$\partial_t \rho_{\alpha\beta}(t) = -\frac{i}{\epsilon}\left\{\mathcal{W}_{\alpha\beta} + \frac{1}{2}|P|^2, \rho_{\alpha\beta}(t)\right\}, \tag{53}$$

where the dynamics is governed by the effective potential,

$$\mathcal{W}_{\alpha\beta}(R,F_0) = \frac{\mathcal{E}_\alpha(R,F_0) + \mathcal{E}_\beta(R,F_0)}{2}, \tag{54}$$

i.e., densities are transported along the corresponding Floquet quasi-energy surfaces while coherences are subject to an arithmetic mean potential.

4. Surface hopping implementation

Although there exists more sophisticated algorithms in the recent literature for the numerical solution of the QCLE,[27–29] we will sketch here only a very simple approach leading to the surface hopping algorithm which was originally derived empirically.[10] Assuming that the system is initially prepared in a single Floquet-state α, the initial probability distribution $\rho_{\alpha\alpha}(R,P,t=t_0)$ is modeled by an ensemble of points in classical phase space sampled from the Wigner distribution function $\mathcal{D}_W(R,P,t=t_0)$ of Eq. (39). If there is a nonvanishing density in more than one of the (diabatic or adiabatic) states in certain regions of phase space, the trajectories are distributed accordingly while coherences are neglected. Associated with each of the trajectories there is a density matrix the initial value of which is one in the corresponding diagonal element and zero elsewhere. Then time-dependent ensembles representing the multistate density at subsequent times are calculated by iterating the following propagation steps for each member of the ensemble:

(1) To model the purely quantal time evolution associated with $\mathcal{L}_1$, update the phase of the coherences according to Eq. (50);

(2) To model the quantum-classical time evolution associated with $\mathcal{L}_2$, update the density matrix following Eq. (52). For more than two states this has to be replaced by an appropriate numerical solution of Eq. (47). After linearization of the trigonometric functions in Eq. (52) the change of the diagonal elements reads

$$P_{\alpha\beta}(t)=\rho_{\alpha\alpha}(t+\tau)-\rho_{\alpha\alpha}(t)=-2\zeta\tau\,\Re(\rho_{\alpha\beta}(t)), \tag{55}$$

which determines the probability for a sudden hop of a trajectory from quantum state β to state α;[10]

To model the classical time evolution associated with $\mathcal{L}_3$, transport the members of the ensemble along the respective potential energy surface (54). This can be achieved by any algorithm commonly used in classical molecular dynamics simulations,[53] e.g., the Verlet algorithm.

Note that this simple surface hopping algorithm does not correctly account for the transport of coherences. Instead it is assumed that a complete density matrix is propagated with each of the trajectories in the ensemble. This leads to the problem of overcoherence[54] which is circumvented in advanced numerical integrators for the QCLE.[27–29]

E. Discussion

As illustrated above, the purely quantal ($\mathcal{L}_1$), the quantum-classical ($\mathcal{L}_2$), and the purely classical ($\mathcal{L}_3$) parts of the adiabatic F-QCLE (44) are straightforward to understand and can be easily realized in a computer simulation using the surface hopping techniques discussed above. However, a problem arises if the amplitude $F_0(t)$ of the electric field becomes very small, e.g., at the beginning and at the end of a laser pulse. In that case both the kinetic coupling $\mathcal{C}^{\mathrm{adi}}(R,F_0)$ and the field induced coupling $\mathcal{G}(R,F_0)$ may become singular in the vicinity of (avoided) crossings of Floquet states. Hence, the hopping probability of Eq. (55) diverges. As an alternative we suggest to use the diabatic F-QCLE (43) in those cases. It is noted that for a propagation in the diabatic picture there are two main differences compared to the adiabatic formulation. First, replacing the diagonal matrix $\mathcal{E}$ by the full matrix $\mathcal{V}$ in all Liouville operators shifts the population transfer from $\mathcal{L}_2$ to $\mathcal{L}_1$. Second, exchange of density would also occur in the Hamiltonian flow operator $\mathcal{L}_3$ (48) through the off-diagonal elements of $\mathcal{V}(R,F_0)$, see Eq. (22). However, we can neglect this population transfer to first order in ϵ when the inequality

$$\nabla_R \mu_{n'n}(R) \leqslant \frac{2\epsilon}{F_0(t)} \tag{56}$$

is fulfilled. Typically, in practical simulations of molecules the gradient of the molecular transition dipole moment is found to be relatively small even permitting the use of the Condon approximation, i.e., $\mu_{n'n}(R)=\mathrm{const}$. In conclusion, a practical strategy for the simulation of photoinduced processes should be as follows: For the beginning and the end of the laser pulse, i.e., when estimate (56) is fulfilled, one should propagate the F-QCLE diabatically, whereas in the middle of the pulse one should switch to an adiabatic representation.

IV. EXAMPLE: PHOTODISSOCIATION OF THE F_2 MOLECULE

A. Model

As a typical example let us consider the photoexcitation process of a (nonrotating) fluorine molecule in gas phase. Naturally, we separate the electronic degrees of freedom, r, from the (relative) motion of the two nuclei, R, which leads to a value for the first nonadiabaticity parameter of $\epsilon=\sqrt{m/M}=7.57\times 10^{-3}$ which is typical for electronically nonadiabatic effects. Note that in this section we return to unscaled variables and all quantities are given in atomic units ($m_e=e=\hbar=1$) unless stated otherwise.

Initially the molecule is assumed to be in its vibrational and electronic ground state. For simplicity, we will consider only the ground (${}^1\Sigma_g^+$) and the first excited state (${}^1\Pi_u$) in our quantum-mechanical description of the electronic system. The corresponding molecular eigenenergies $E_\Sigma(R), E_\Pi(R)$ as well as the (perpendicular) transition dipole moment $\mu_{\Pi\Sigma}(R)$ are taken from the literature.[55,56] Due to the $D_{\infty h}$ symmetry of the molecule there is no nonadiabatic coupling for the field-free molecule $[C_{\Pi\Sigma}(R)\equiv 0]$, see Eq. (31). The corresponding Floquet matrix is constructed from the ${}^1\Sigma_g^+$ and ${}^1\Pi_u$ levels "dressed" with an integer number of photons,

$$\mathcal{V}(R,F_0)=\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \cdots \\ \cdots & E_\Pi(R)-\omega & \mu_{\Pi\Sigma}(R)\cdot F_0/2 & 0 & 0 & \cdots \\ \cdots & \mu_{\Pi\Sigma}(R)\cdot F_0/2 & E_\Sigma(R) & 0 & 0 & \cdots \\ \cdots & 0 & 0 & E_\Pi(R) & \mu_{\Pi\Sigma}(R)\cdot F_0/2 & \cdots \\ \cdots & 0 & 0 & \mu_{\Pi\Sigma}(R)\cdot F_0/2 & E_\Sigma(R)+\omega & \cdots \\ \cdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \tag{57}$$

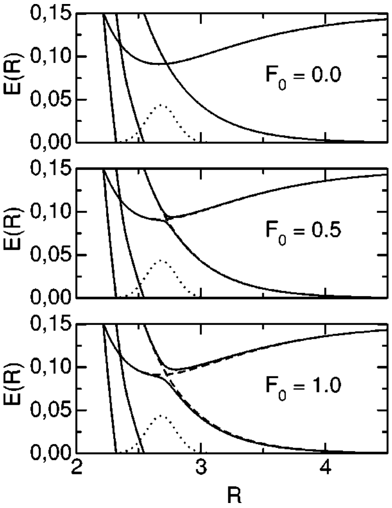

FIG. 1. Selected Floquet states for the ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$ photoexcitation of the F_2 molecule for $\omega = 0.15$ and for three different amplitudes of the electric field. Dashed curves: Diabatic “dressed” states corresponding to the ground state $E_\Sigma(R)$ and the electronically excited state $E_\Pi(R) + m\omega$ with $m = -1, -2, -3$. Solid curves: Adiabatic Floquet states $\mathcal{E}(R, F_0)$. For comparison, the dotted curve shows the vibrational ground state density (all quantities in atomic units).

where couplings occur only for dressed states differing by ±1 photon. A graphical representation of the dressed states is shown in Fig. 1 for a carrier frequency $\omega = 0.15$ which is close to the center of the Franck–Condon region for the ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$ transition, i.e., the crossing of the dressed states $E_\Pi(R_c) - E_\Sigma(R_c) = \omega$ coincides with the maximum of the ground state vibrational density. Furthermore, crossings with other dressed states $[E_\Pi(R) - \omega, E_\Pi(R) - 2\omega]$ are well outside the classically allowed region. These considerations justify the use of the above effective two-state model for the frequency range investigated in the present work $(0.1 \leqslant \omega \leqslant 0.2)$ effectively permitting only one-photon transitions. The corresponding adiabatic states are also shown in Fig. 1. In particular, the Floquet states exhibit an avoided crossing with an energetic gap of $\mathcal{E}_2(R_c) - \mathcal{E}_1(R_c) = \mu_{\Pi\Sigma}(R_c) F_0$.

We consider a light pulse with an envelope which is obtained as one half cycle of the $\sin^2$ function,

$$F_0(t) = \begin{cases} F_0 \sin^2(\Omega t) & 0 \leqslant t \leqslant \pi/\Omega \\ 0 & \text{else}, \end{cases} \tag{58}$$

the polarization of which is assumed to be perpendicular to the molecular axis. A total duration of the pulse of $\pi/\Omega = 100$ fs is chosen to match modern experiments with ultrashort light pulses. For the central Franck–Condon frequency $(\omega = 0.15)$ we have an optical cycle of $\tau = 2\pi/\omega = 1.01$ fs which yields a value of $\gamma = 5.1 \times 10^{-3}$ for the second nonadiabaticity parameter.

B. Numerical results

Quantum-classical simulations of the photodissociation of the F_2 molecule upon ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$ transition were carried out in the following way: The initial density $\rho_\Sigma(R, P, t = 0)$ of the vibronic ground state is obtained as a Wigner transform of the corresponding bound state wave function $\psi_\Sigma(R, t = 0)$ which can be well approximated by a Gaussian wave packet. Then phase-space points are sampled in a pseudo-random manner from this distribution function. Starting from these initial conditions, trajectories are propagated using the surface hopping algorithm outlined above. The molecule interacts with the laser pulse specified in Eq. (58) with a carrier frequency $\omega = 0.15$ and a relatively strong amplitude $(F_0 = 0.6)$ which is far outside the perturbative regime.

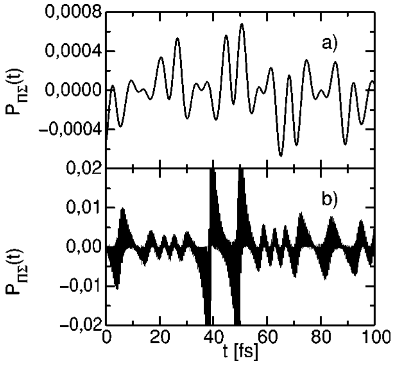

FIG. 2. Hopping probability for a single trajectory. The trajectory is chosen such that it does not hop during the interaction with the 100 fs laser pulse of Eq. (58). (a) Probability computed from adiabatic F-QCLE according to Eq. (55). (b) Corresponding probability for a QCLE using an adiabatic basis constructed from instantaneous Stark states (Refs. 33, 34).

A typical result for the hopping probability (55) from the ${}^1\Sigma_g^+$ to the ${}^1\Pi_u$ state is illustrated in Fig. 2(a), where a trajectory has been picked that is initially very close to the minimum of the molecular potential energy curve $E_\Sigma(R)$. It undergoes small amplitude vibrations without hopping to the excited state during the simulation time of 100 fs. It is apparent that the variations of the hopping probability are smooth; in particular the oscillations occur on a time scale which is much larger than the optical cycle of the carrier frequency $2\pi/\omega \approx 1$ fs. It is very instructive to compare this result with the approach of Thachuk *et al.* who use instantaneous Stark states instead of Floquet states in order to describe the long wavelength limit.[33,34] As can be seen from Fig. 2(b), the oscillations are much faster essentially following the fast time scale of the carrier frequency. Moreover, the absolute value of the hopping probability is much higher. This leads to very many hops forth and back between the states involved which may lead to serious numerical problems.

The photo-induced quantum-classical dynamics of the F_2 molecule is displayed in Fig. 3 which gives snapshots of the (diabatic) position space densities,

$$\rho_\Sigma(R,t) = \int dP \rho_\Sigma(R,P,t), \quad \rho_\Pi(R,t) = \int dP \rho_\Pi(R,P,t) \tag{59}$$

for both the ground $({}^1\Sigma_g^+)$ and electronically excited $({}^1\Pi_u)$ state. The ground state density is largely depleted by the interaction with the laser pulse without notable vibrational excitation. At the same time there is a build-up of excited state density rapidly traveling towards larger internuclear distances which is typical for a direct photodissociation pro-

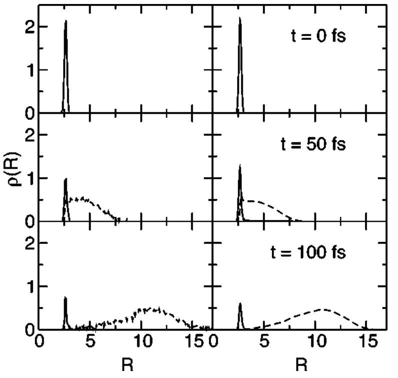

FIG. 3. Snapshots of ground state (solid curve) and excited state (dashed curve) diabatic nuclear densities during the interaction of the F_2 molecule with the laser pulse of Eq. (58). Left panels: Numerical solution of Floquet-based quantum-classical Liouville equation (F-QCLE), see Eqs. (43), (44). Right panel: Numerical solution of the corresponding Schrödinger equation for comparison, see Eqs. (29), (33).

cess occurring through a purely repulsive state. The densities are in excellent agreement with the results of quantum mechanical simulations which were obtained by numerically solving the time-dependent Schrödinger equation (TDSE). In passing we note that the use of the Floquet-based TDSE (29) in extended Hilbert space offers substantial numerical advantages over the original TDSE (12). The elimination of the fast oscillations in the former allows an increase in the time step by $1/\gamma$ which is two orders of magnitude for the example considered here.

Finally, the resulting population dynamics upon interaction of F_2 with the above laser pulse is investigated. We consider here the population of the electronically excited state

$$\Theta_\Pi(t)=\int dR\int dP\rho_\Pi(R,P,t) \tag{60}$$

which is simply calculated from the (relative) number of trajectories in the ${}^1\Pi_u$ state, see Fig. 4. We see a monotonic increase of population with time. This is easy to understand since each trajectory rapidly leaves the region of the crossing of the dressed states on a time scale which is much shorter than a Rabi cycle (≈ 10 fs). For the field amplitude considered here, this population transfer can be substantial. For the central Franck–Condon frequency ($\omega = 0.15$) the transfer reaches up to almost unity (97%). Although this is far from the perturbative regime, the quantum-mechanical results are very well reproduced by the quantum-classical simulations. Furthermore, the figure illustrates the decrease of statistical errors when increasing the number of trajectories by one order of magnitude. The remaining, very small discrepancies are due to the approximate treatment of the coherences using the simple surface hopping approach. They can be remedied by advanced QCLE propagators.[29]

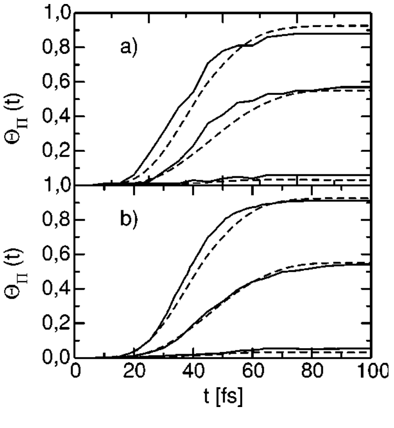

FIG. 4. Population of the electronically excited state (${}^1\Pi_u$) during the interaction of the F_2 molecule with the 100 fs laser pulse of Eq. (58). The three pairs of curves correspond to $\omega = 0.10$, $\omega = 0.20$, $\omega = 0.15$ (bottom to top). (a) 100 trajectories. (b) 1000 trajectories. Quantum-classical results (solid curves) are compared with results of purely quantum-mechanical simulations (dashed curves).

V. CONCLUSIONS

In the present work, a quantum-classical description of large molecules interacting with intense, pulsed light has been worked out. More specifically, the Floquet-based quantum-classical Liouville equation (F-QCLE) has been derived as a first order approximation to the partial Wigner transform of the quantum Liouville equation in the two nonadiabaticity parameters (ϵ,γ) yielding well-defined asymptotic properties. In particular, for $\epsilon \to 0$ and $\gamma \to 0$ we have adiabatic evolution along Floquet states of the molecule interacting with a periodically oscillating field while for finite values of ϵ and γ nonadiabatic effects are caused by the motion of the heavy particles or by modulation of the field amplitude, respectively.

As a first example, photodissociation of the F_2 molecule upon electronic excitation has been investigated yielding excellent agreement of quantum-classical with purely quantum-mechanical results. Although the specific example is relatively simple, it nevertheless serves to demonstrate the capabilities of the F-QCLE approach to photoinduced molecular dynamics, and generalization to more sophisticated applications is obvious:

(1) The use of instantaneous Floquet states to model the dynamics of the quantum subsystem interacting with pulsed light eliminates the time scale of the fast oscillations connected with the carrier frequency from the equations of motion which have to account only for the slow time scales of the modulations of the external field. Furthermore, the Floquet basis allows for the description of multiphoton transitions by including higher harmonics in the dressed state basis. Consequently, nonlinear spectroscopic effects well beyond the perturbative regime can be included in a straightforward manner.

(2) The use of trajectory-based methods to model the dynamics of the classical subsystem opens the way towards higher dimensionality because of the favorable scaling of the numerical effort with increasing number of degrees of freedom. Moreover, replacing the simple surface hopping scheme by more elaborate approaches for the numerical solution of the QCLE allows for a correct description of the light particle coherences.

In summary, the F-QCLE represents a novel and efficient model for photo-induced processes in medium to large molecular systems.

ACKNOWLEDGEMENT

Financial support by the *Deutsche Forschungsgemeinschaft* through Grant De 293/6-3 in the framework of a program on ‘‘Time-dependent phenomena in quantum systems of physics and chemistry’’ is gratefully acknowledged.

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