Constrained Adiabatic Trajectory Method[†]

Georges Jolicard,*,[‡] David Viennot,[‡] and John P. Killingbeck[‡,§]

Laboratoire d'Astrophysique de l'Observatoire de Besançon (CNRS UMR 6091),
41 bis Avenue de l'Observatoire, BP1615, 25010 Besançon Cedex, France, and Mathematics Department,
University of Hull, Hull HU6 7RX, U.K.

Received: January 6, 2004; In Final Form: May 28, 2004

The nonadiabatic temporal evolution which is associated with inelastic collisions and photoreactive processes typically produces a final state distribution that differs markedly from the initial state distribution. Nevertheless an adiabatic formalism is often used in a zeroth-order description of the processes; for time-periodic perturbations the Floquet theory has been used within an adiabatic framework to provide a compact dynamical theory which requires a basis composed of only a small number of Floquet eigenstates. The use of the generalized Floquet theory or of the concept of a super-adiabatic basis allows the adiabatic approach to be further extended to handle systems with quasi-periodic Hamiltonians. The present work proposes a new approach, in which the time duration of the interaction is artificially prolonged and special absorbing boundary conditions are introduced asymptotically over the lengthened time interval in such a way as to force the adiabaticity of the process. The method involves what can be thought of as time-dependent optical potentials. Some trial applications to semiclassical inelastic collisions and to photodissociation effects have shown that the use of the new technique permits a description of the dynamical processes which is so economical that the use of a single generalized Floquet eigenvector will suffice. The main technical feature of this constrained adiabatic trajectory method is that it converts the problem of solving the TDSE with an explicitly time-dependent potential into that of solving a static complex eigenvalue problem.

1. Introduction

The study of molecular dynamical systems is often characterized by two contrasting features. First, the nonlocal character of the interactions, which requires a global description of all the molecular phase space, increases the sizes of the vector spaces involved and so increases the memory and CPU time needed in numerical calculations. Second, in many such large scale calculations it emerges that the dynamical processes are in fact well described by using only a small number of the eigenvectors in the large space, so that only a small effective subspace of the original large space turns out to be important. This observation has led to a renewed interest in adiabatic or quasi-adiabatic approaches and in effective Hamiltonian methods, which are conceptually simple and which use only spaces of small dimension.

The interest of the effective Hamiltonian formalisms is evident when studying the laser control of molecular dynamical processes, which is today one of the major goals of photochemistry. The possibility of reaching large radiation field intensities using short-pulsed lasers has motivated an increasing amount of experimental and theoretical work.[1−4] To describe the nonlinear effects induced by intense and ultrashort laser pulses it is essential to possess a nonperturbative theory which describes the nonlinear effects occurring during all of the interaction period and which facilitates the repetitive calculation of many propagations, in which the small number of coupling parameters involved can be varied to find the optimum values required to achieve the desired control process. The analysis of laser control processes is also an appropriate field for the application of Floquet theory, which permits an adiabatic separation between the fast field oscillation dynamics and the slow time modulation of the field envelope. In this framework, appropriate adiabatic representations can be constructed by considering instantaneous Floquet eigenvector basis sets,[5−7] and a detailed understanding of the inelastic and dissipative processes induced by the field-matter interaction can be obtained. For example, the importance of the laser-induced avoided crossings is clearly revealed in this approach, and dissociation processes or inelastic transitions are characterized by the presence or absence of nonadiabatic jumps at the avoided crossings of instantaneous Floquet states.[8,9] For high laser frequencies a high frequency approximation can be implemented by neglecting the rapidly oscillating parts of the eigenfunctions. This approximation was proposed by Gavrila[10] and has been tested with success in the study of the ionization produced by high-frequency short pulses.[11]

One crucial consequence of the near-adiabatic nature of the above and other processes is that an active space of few dimensions suffices to describe the dynamical evolution of the system concerned. This advantage justifies the use of effective Hamiltonian theories and in particular that of the time-dependent wave operator theory (TDWOPT),[12] which has several valuable features: It is consistent with the Floquet theory, it is applicable without change to non-Hermitian Hamiltonians, and various robust algorithms have been proposed for the integration of the wave operator equation.

Clearly, the most simple dynamical evolution to describe is that involving a purely adiabatic evolution and a one-dimensional active space. One of the important trends in modern theory is the attempt to construct representations which will

---

[†] Part of the "Gert D. Billing Memorial Issue".

[‡] Laboratoire d'Astrophysique de l'Observatoire de Besançon (CNRS UMR 6091)

[§] University of Hull.

10.1021/jp0499373 CCC: $27.50

make it possible to start from a system which apparently undergoes nonadiabatic transitions involving large spaces and to transform it so as to reduce it as nearly as possible to one undergoing an adiabatic evolution. The use of a generalized Floquet basis set[13] and of Berry's super-adiabatic basis concept,[14,15] belong to this trend of ideas. Nevertheless great difficulties arise in putting such ideas into practice. The main one is that of choosing the dimension of the active space needed to obtain a given degree of accuracy of the results. The necessity of choosing a priori the instantaneous Floquet eigenstates involved in describing a nonadiabatic process is a severe handicap because one does not generally have precise indications about the degree of nonadiabaticity before solving the problem.

To remedy this, we tackle this problem by adopting another point of view. We do not try to define a new more efficient representation but we modify the Hamiltonian over an artificially prolonged time interval so as to transform the primary dynamical problem into a pure eigenvalue problem (which of course represents the extreme limit of adiabaticity). The paper is organized as follow.

Section 2 analyses the adiabaticity concept in molecular dynamics by paying careful attention to the case of periodic and quasi-periodic Hamiltonians. The concept is developed in the framework of the Floquet theory by first presenting a standard formulation using the instantaneous Floquet state concept and then introducing a generalized Floquet formalism. The correlation between the adiabaticity of a process and the asymptotic behavior of the generalized Floquet eigenstates is investigated.

Section 3 presents the constrained adiabatic trajectory method (CATM) by developing a theoretical analysis of the asymptotic behavior of the Floquet eigenstates in the presence of local time-dependent optical potentials.

Section 4 illustrates the theory by treating two examples which both involve short time interactions, since the CATM in its present version is limited to such problems. The first concerns the semiclassical treatment of the He$-$N$_2$ inelastic collision, a system which was investigated many years ago by Gert Billing.[16,17] The second is the photodissociation of the H_2^+ ion subjected to a short and intense laser pulse. Particular emphasis is given to the beneficial dispersion of the eigenvalue spectrum produced by the introduction of a time-dependent absorbing potential, with a consequent notable improvement in the rate of convergence of the iterative calculations.

Section 5, the conclusion, analyses the merits and defects of this new method and describes some planned improvements to it.

2. Adiabaticity and Floquet Theory

We consider in this paper the case of quantum systems for which the time-dependent Hamiltonian includes a perturbation $V(t)$

$$V(t) = \sum_i A^i\left(q, \frac{\partial}{\partial q}\right) F^i(t) \qquad (1)$$

where the terms $A^i(t)$ represent quantum mechanical operators depending both on the quantum coordinates q and on the associated momenta $-i\hbar\partial/\partial q$ and the $F^i(t)$ are pure time functions introduced by the semiclassical treatment of the interaction. In our first example, the semiclassical treatment of a diatom$-$atom collision, q represents the molecular vibration coordinate, and the time functions describe the translational and rotational parts of the couplings, including the coriolis terms, in a description in which the relative translation and the molecular rotational motions are obtained by integration of the classical Hamilton differential equations. In the second example, the photodissociation of H_2^+, the use of the dipole approximation and of the length gauge in a semiclassical description leads to the Hamiltonian:

$$H(r,\theta_o + \omega t) = H_o(r) - \vec{\mu}(r)\vec{E}_o(t)\cos(\theta_o + \omega t) \qquad (2)$$

where the field-matter interaction is assumed to be turned on at $t = 0$. The initial phase θ_o appears as a parameter and r, which plays the role of q in eq 1, is the interfragment axis coordinate.

2.1. The Instantaneous Floquet Eigenstates Basis Set. The standard adiabatic theorem[18] cannot be applied for these two chosen applications. In the case of semiclassical collisions the translational and rotational couplings are not generally adiabatic functions of time. The difficulty appears to be more severe for the second example, since eq 2 exhibits rapidly oscillating terms which remove the possibility of expanding the wave function using a few instantaneous eigenvectors of $H(\theta_o + \omega t)$ at each time t. However, this last problem can be partially solved by using an enlarged Hilbert space

$$\mathbf{K} = \mathbf{H} \otimes \mathbf{L}^2(S^1, d\theta/2\pi) \qquad (3)$$

where $\mathbf{L}^2$ denotes the space of square integrable functions on the circle of length 2π and $\mathbf{H}$ is the molecular Hilbert space. On this enlarged space the Floquet Hamiltonian is defined as

$$H_F = H(\theta) - iV_{opt}(r) - i\hbar\omega\frac{\partial}{\partial\theta} \qquad (4)$$

where H_F is 2π-periodic as a consequence of going from t to θ and where the local optical potential $V_{opt}(r)$ allows dissipative systems to be treated using finite L^2 representations. In the following the system will be described equally by using θ or t.

The advantage of the Floquet Hamiltonian (eq 4) arises from the fact that the Floquet dynamics in $\mathbf{K}$ and the semiclassical dynamics in $\mathbf{H}$ are essentially identical. A precise demonstration of this equivalence can be found in the review paper of Guérin and Jauslin.[19] A complementary result is that of the equivalence between the purely quantum approach and the Floquet formulation under some precise conditions in the strong field regime, as expressed in the symbolic formula

$$(H^{mol} + H^{rad} + V) - \hbar\omega\bar{n} \rightarrow H_F \qquad (5)$$

where the photon average $\bar{n}$ is assumed to be very large and where the symbol $\rightarrow$ in eq 5 relates to a model of a quantized field in a cavity V taken at the limits $V \rightarrow \infty$, $\bar{n} \rightarrow \infty$, with $\rho = \bar{n}/V = C^{te}$. The idea of the equivalence between the quantum dressed state dynamics in $\mathbf{H} \otimes \mathbf{F}$ (the tensorial product of the Hilbert space of the molecule and the Hilbert space of the photons) and the Floquet dynamics in the $\mathbf{K}$ space was present in the pioneering work of Shirley,[5] and was developed more explicitly by Bialynicki-Birula and Van[20] and by Guérin et al.[21] The use of the Floquet Hamitonian H_F then appears as the intermediate step necessary to demonstrate the equivalence of the pure quantum and the semiclassical treatments in the strong field limit.

The Floquet dynamics also provides a new complete basis set at each instant, formed by the instantaneous eigenvectors of $H_F(t)$ (i.e., the eigenvectors $|\lambda^{\alpha(t)}\rangle$ of $H_F(t)$ in which the adiabatic parameters $\alpha(t)$ of the field are frozen at their instantaneous values). This basis possesses a strongly adiabatic character when compared with the H-eigenvectors basis. This is a direct consequence of the quasi-stationary character of the spectrum of H_F in the complex plane when working in the enlarged $\boldsymbol{K}$ space; by comparison the $H(t)$ spectrum makes fortuitous temporary resonances appear during the time evolution. In favorable situations only a single Floquet eigenstate participates in the dynamics, which can then be treated by using the following adiabatic conjecture:

If $\Psi(t = 0)$ *is identical to a Floquet state* $|\lambda^{\alpha(0)}\rangle$ *and if the Floquet state is isolated during the evolution, then the system remains in the instantaneous Floquet eigenstates* $|\lambda^{\alpha(t)}\rangle$ *continuously connected to* $|\lambda^{\alpha(0)}\rangle$

When the system introduces resonance effects, this purely adiabatic approach should be generalized by combining adiabatic trajectories with local diabatic evolution. The treatment of Guérin et al.[22] (see also ref 19) relates the efficiency of the population transfer to the topology of the dressed state energy surfaces, which varies as a function of the time-dependent external field parameters.

2.2. The Generalized Floquet Basis Set. The small dimension of the active space into which the dynamics is projected in the framework of the Floquet theory has led to the rapid development of new attemps to extend the standard Floquet theory. These include the exact adiabatic representation of Nguyen-Dang,[23,24] the time dependent density functional theory (TDDFT)−Floquet formalism,[25] which provides a general time-independent approach for the treatment of multiphoton processes of many-electron quantum systems, and the Floquet treatment of Dresse and Holthaus,[15] which uses the framework of Berry's superadiabatic basis concept[14] and introduces an iterative scheme of unitary transformations to construct basis sets which describe the fast part of the dynamics.

If the perturbation $V(t)$ in eq 1 vanishes at the two boundaries of the time interval $[0, T]$ on which the interaction is represented then one can regard $V(t)$ as the first cycle of a periodic function with period T.[13] This is just a mathematical artifact; its principal consequence is the existence of a complete set of Floquet eigenvectors $|\lambda_\eta\rangle$ in $\mathbf{K} = \mathbf{H} \otimes \mathbf{L}^2(S^1, d\theta/2\pi)$ where the period $\theta = 2\pi$ now corresponds to *the full duration of the interaction* (i.e., a much larger period than the optical period). These eigenvectors obey the eigenvalue equation

$$H_F\left(q, \frac{\partial}{\partial q}, t\right)|\lambda_\eta(q, t)\rangle = E_\eta|\lambda_\eta(q, t)\rangle \qquad (6)$$

and satisfy the orthonormality condition[7]

$$\langle\langle\lambda_\eta|\lambda_{\eta'}\rangle\rangle = \frac{1}{T}\int_0^T \mathrm{d}t\, \langle\lambda_\eta(q, t)|\lambda_{\eta'}(q, t)\rangle = \delta_{\eta\eta'} \qquad (7)$$

A convenient labeling of the Floquet eigenstates $|\lambda_{j,n}\rangle$ can be produced by using the two indices j and n referring to the H_o-molecular eigenstates and to the Fourier functions (with $\langle t|n\rangle = \exp(in\omega t)$. By taking into account the periodicity of the Hamiltonian, one can rigorously expand the wave function using the group of Floquet eigenvectors which belong to the first Brillouin zone ($n = 0$)

$$|\Psi(t)\rangle = \sum_j \mathrm{e}^{-iE_{\lambda_{j,0}}t/\hbar}|\lambda_{j,0}(t)\rangle\, \langle\lambda_{j,0}(t = 0)|i\rangle \qquad (8)$$

where $|i\rangle$ designates the initial molecular state.

This new basis possesses a highly adiabatic character, since the introduction of the identity $|\lambda_{j,0}(t = 0)\rangle = |\lambda_{j,0}(t = T)\rangle$ in eq 8 leads to the result

$$\Psi(t) = \sum_k c_k(t)|k\rangle$$

with

$$c_k(0) = \sum_j \langle k|\lambda_{j,0}(0)\rangle\, \langle\lambda_{j,0}(0)|i\rangle$$

and

$$c_k(T) = \sum_j \mathrm{e}^{-iE_{\lambda_{j,0}}t/\hbar}\langle k|\lambda_{j,0}(0)\rangle\, \langle\lambda_{j,0}(0)|i\rangle \qquad (9)$$

In the context of the adiabatic picture using instantaneous eigenstates, Barash et al.[11] make a distinction between "adiabatic ionization" (caused by the presence of complex energies) and "nonadiabatic ionization" (caused by nonadiabatic transitions). This distinction also exists in the present picture. The eigenvalues $E_{\lambda j,0}$ in eq 9 are complex in photoreactive processes and so produce a temporal decrease of the norm of the wave function. When a single resonance Floquet state is much longer lived than all the others, one can have cases in which this single surving state controls the long-time development, even if the short-time dynamics is largely nonadiabatic. Nevertheless the use of generalized Floquet eigenstates identifies more clearly the presence of purely adiabatic processes. When an instantaneous basis set is used, one has in every case $\langle\lambda_{j,o}(t = 0)|i\rangle = \delta_{i,j}$, because the instantaneous Floquet state is initially proportional to the free molecular state. On the contrary, when the generalized basis set is used, the same equation is the exclusive signature of an adiabatic process. The T periodicity of the eigenvectors means that, at the adiabatic limit, a unique state $|\lambda_{i,0}\rangle$ is present, characterized by the asymptotic conditions $\langle k|\lambda_{i,0}(0)\rangle = \langle k|\lambda_{i,0}(T)\rangle = \delta_{i,k}$. At this limit the generalized Floquet eigenvectors are the simple juxtaposition at successive instants of the instantaneous Floquet eigenstates (see refs 12 and 26 for a rigorous demonstration). Outside the adiabatic limit the relationship between instantaneous and generalized Floquet eigenvectors is more intricate. One can simply affirm that when several eigenstates are present in the sum appearing in eq 8 then the process is nonadiabatic, since one cannot simultaneously satisfy the requirement $c_k(0) = \delta_{i,k}$ imposed by the initial conditions and also the final condition $c_k(T) = \delta_{i,k}$; this impossibility is due to the presence of the complex phase factors $\exp(-iE_{\lambda j,0}T/p)$ in eq 9. The case of adiabatic ionization (or adiabatic dissociation) defined by Barash et al.[11] represents an intermediate case for which the final wave function is on the state $|i\rangle$ but with a weight $|c_i(T)|^2$ which is strictly smaller than unity. One can finally summarize these results as follows:

There exists a direct correlation between the adiabatic character of the dynamics, the number of eigenstates in the Floquet eigenstates expansion (eq 8) and the asymptotic conditions satisfied by the generalized Floquet eigenvector $|\lambda_{i,0}\rangle$.

3. The Constrained Adiabatic Trajectory Method

When a few generalized Floquet states compose the wave function (cf. eq 8) the treatment should involve the degenerate active space spanned by these Floquet states. The time-dependent wave operator $\Omega(t, 0)$ $(= U(t, 0)[P_oU(t, 0)P_o]^{-1})$ can be used to select the corresponding model space $S_o(P_o)$ at $t = 0$ by implementing the wave operator sorting algorithm.[27,28]

The wave operator formalism has some similarities with the well-known theory of the nonlocal optical potential.[29,30] The two theories try to represent the exact dynamics of the quantum system by working in the restricted model space. This simplified dynamics is obtained in the two schemes by suppressing any reflected quantum flux from the complementary space S_o^+ back to the S_o space. Other close similarities exist with the (t, t') theory of Peskin and Moiseyev,[31,32,33] and have been analyzed in ref 12.

The basic equation of the wave operator theory can be written in the **K** space as

$$H_F(t)\Omega(t) = \Omega(t)H_F(t)\Omega(t) = \Omega(t)H_F^{eff}(t) \qquad (10)$$

If the model space includes all the unperturbed states continuously connected to the generalized Floquet eigenstates which initially have a nonzero overlap with the wave function then the integration of eq 10 (e.g., by using the recursive distorted wave approximation,[34,35] or the single cycle method[36]) gives a complete basis of the active space This active (or target) space is composed of a single Floquet state $|\lambda_{i,n=0}\rangle$ in the adiabatic limit, since $\langle k|\lambda_{i,n=0}(0)\rangle = \delta_{i,k}$ and the dynamical problem in the Hilbert space is thus equivalent to a pure nondegenerate eigenvalue problem in the extended Hilbert space. On the contrary, eq 10 becomes a degenerate eigenvalue problem in the general nonadiabatic case, and so represents a larger computational task when the active space is large.

3.1. The Concept of the Local Absorbing Potential. In this section, we will artificially modify the investigated system in order to give to the general case the simplicity of the adiabatic case. Our analysis is limited to a study of the evolution of a quantum system characterized by $H(t) = H_o + V(t)$ over a short time interval $[0, T_o]$. The perturbation satisfies the condition $V(0) = V(T_o) = 0$, and the system is initially in an eigenstate $|i\rangle$ of H_o, i.e., $\langle k|\Psi(0)\rangle = \delta_{k,i}$.

This basic problem can be summarized as follows:

If the initial condition $\langle k|\lambda(0)\rangle = \delta_{k,i}$ *is satisfied then equivalent results are obtained by solving either the Schrödinger equation in the Hilbert space or the Floquet eigenequation in the extended Hilbert space:*

$$H_F(t)|\Psi(t)\rangle = 0 \Leftrightarrow (H_F - E)|\lambda\rangle = 0 \qquad (11)$$

One then has a linear correspondence at any time between the solutions:

$$\left|\Psi(t)\right\rangle = \exp\left\{\frac{1}{i\hbar}Et\right\}\left|\lambda(t)\right\rangle \qquad (12)$$

Unfortunately the simple initial condition is never satisfied, unless the dynamics issuing from $|i\rangle$ is purely adiabatic (in this case one has $\langle k|\lambda_{i,n=0}(0)\rangle = \langle k|\lambda_{i,n=0}(T_o)\rangle = \delta_{k,i}$). The impossibility of representing the solution of the TDSE by using a single generalized Floquet state on $[0, T_o]$ follows then from the boundary conditions. The periodicity of the Floquet states on $[0, T_o]$ is inconsistent with the existence of any inelastic solution. To overcome these difficulties without increasing the numerical task, we propose to solve the problem by artificially forcing adiabatic behavior within a one-dimensional space, using the procedure described below.

The initial time interval $[0, T_o]$ on which the interation $V(t)$ is nonzero is prolonged using an additional time interval $[T_o, T]$ on which absorbing local potentials are introduced. These potentials are present on the different channels (dissociative or bound channels) but not on the initial one (i). The initial state on the channel (i) has in our example the simple Fourier basis expansion $|\Psi(t = 0)\rangle = |i, n = 0\rangle$. The choice ($n = 0$) corresponds to an initial phase θ_o (the relative phase between the molecular state and the perturbation) which is uniformly averaged over $[0, 2\pi]$.

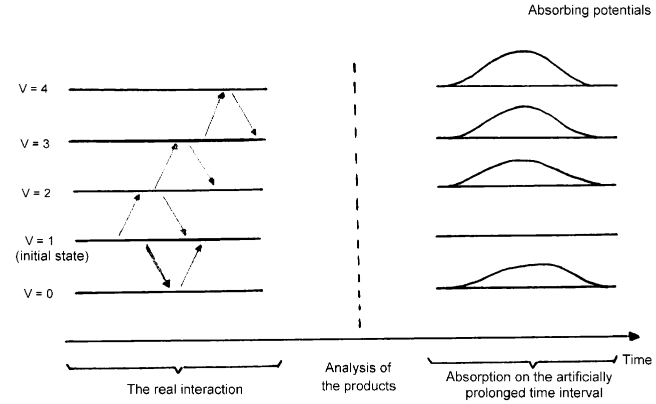

Figure 1. Schematic representation of the constrained adiabatic trajectory method.

To simplify our scheme, the same Gaussian optical potential is introduced on each channel except the initial one.

$$-iV_{opt}(t) = \sum_l |l\rangle\langle l|\left\{-iA\exp\left[-\left(\frac{t-\bar{T}}{\tau}\right)^2\right]\right\}(1-\delta_{l,i}) \qquad (13)$$

$\bar{T}$ is equal to $(T_o + T)/2$, and τ is chosen such that V_{opt} is negligible both at $t = T_o$ and at $t = T$. The CATM is presented schematically in Figure 1.

3.2. Asymptotic Analysis of the Modified Floquet States. The optical potentials are introduced to recover the final conditions $\langle f|\lambda(T)\rangle = 0$ if $f \neq i$ and finally to recover the initial conditions $\langle f|\lambda(0)\rangle = 0$ if $f \neq i$ as a consequence of the periodicity of the Floquet states. Between the times T_o and T, only the derivative term $-i\hbar\partial/\partial t$, the free molecular Hamiltonian, and the optical potentials are present in the TDSE. One can then recover the exact influence of $-iV_{opt}(t)$, since in this interval the Floquet states have a simple analytical expression, namely

$$|\lambda_E(t)\rangle = \sum_f |f\rangle\, |\lambda_E(t)\rangle_f \qquad (14)$$

with

$$\begin{cases} |\lambda_E(t)\rangle_{f\neq i} = |\lambda_E(T_o)\rangle_f \exp^{i/\hbar\int_{T_o}^{t}(\mathrm{Re}(E)-E_f)\mathrm{d}t'}\exp^{-1/\hbar\int_{T_o}^{t}(\mathrm{Im}(E)+V_{opt})\mathrm{d}t'} \\ |\lambda_E(t)\rangle_i = |\lambda_E(T_o)\rangle_i \exp^{i/\hbar\int_{T_o}^{t}(\mathrm{Re}(E)-E_i)\mathrm{d}t'}\exp^{-1/\hbar\int_{T_o}^{t}\mathrm{Im}(E)\mathrm{d}t'} \end{cases} \qquad (15)$$

where E_f is the asymptotic energy which characterizes the channel (f).

The main effect of V_{opt} is to produce the absorption of the asymptotic components $|\lambda_E(t)\rangle_{f\neq i}$ which are produced by the exponentially decreasing term $\exp\{-1/\hbar\int_{T_o}^{t} V_{opt}\, \mathrm{d}t'\}$ The analysis of eq 15 is nevertheless not straightforward, because the optical potentials V_{opt} which are explicitly present in this equation also indirectly influence the eigenvalue E by inducing complex shifts. Their contributions are equal to $\langle\langle\lambda^\dagger| - iV_{opt}\lambda\rangle\rangle$ where the eigenfunctions $|\lambda^\dagger\rangle$ of $H_F^\dagger$ together with the Floquet eigenstates form a biorthogonal basis set.[37] By using eq 15 and the identity $(|\lambda_E^\dagger\rangle = |\lambda_E\rangle^*)$, one obtains the result

$$\langle\langle\lambda_{\mathrm{E}}^{\dagger}| - iV_{\mathrm{opt}}\lambda_{\mathrm{E}}\rangle\rangle = \sum_{f\neq i}(|\lambda_{\mathrm{E}}(T_{\mathrm{o}})\rangle_f)^2\int_{T_{\mathrm{o}}}^{T} -iV_{\mathrm{opt}}(t)\,\exp^{2i/\hbar\int_{T_{\mathrm{o}}}^{t}(\mathrm{Re}(E)-E_f)\mathrm{d}t'}\,\exp^{-2/\hbar\int_{T_{\mathrm{o}}}^{t}(\mathrm{Im}(E)+V_{opt})\mathrm{d}t'}\,\mathrm{d}t \qquad (16)$$

Except for the trivial (closed channel) case for which $|\lambda(T_{\mathrm{o}})\rangle_f$ is equal to zero the value of this integral principally depends on the Fourier frequencies ($\omega_f = \mathrm{Re}(E) - E_f$). Two different cases can be distinguished, denoted by the numbers 1 and 2 below.

1. Re(E) is quite different from all the inelastic channel energies $E_{f\neq i}$. In a perturbative scheme this situation manifests itself via the vector $|\lambda_{i,n=0}\rangle$, which is continuously connected to the initial nonperturbed state $|i, n = 0\rangle$ when one assumes a state-to-state correspondence between the nonperturbed states, (i.e., the eigenvectors of $H_{\mathrm{o}} - i\hbar\partial/\partial t$ and the Floquet eigenstates: $(k, n) \leftrightarrow \lambda_{k,n}$). The integral on the right of eq 16 then tends to zero, since all the Fourier frequencies ω_f take large values. The contribution of the optical potential to the eigenvalue is negligible, so that

$$|\int_{T_{\mathrm{o}}}^{t}\mathrm{Im}(E)\,\mathrm{d}t'| \ll |\int_{T_{\mathrm{o}}}^{t}V_{\mathrm{opt}}\,\mathrm{d}t'| \qquad (17)$$

The “increasing” effect due to Im(E) < 0 is thus totally canceled by the “decreasing” effect due to $V_{\mathrm{opt}} > 0$. If the state $|\lambda_{\mathrm{E}}\rangle$ is a resonance, then Im(E) is related to a natural width which is independent of V_{opt}. It is nevertheless possible to take large amplitudes of V_{opt} in order to satisfy (17). By introducing (17) into (15), one easily concludes that all the asymptotic components $|\lambda_{\mathrm{E}}(T)\rangle_{\mathrm{f}}$ take negligible values, except the component corresponding to the initial channel (i). As the periodicity of $|\lambda\rangle$ imposes the same values at $t = 0$, one finally obtains the result that this modified Floquet eigenvector obeys the expected boundary conditions $|\lambda(0)\rangle_k = \delta_{k,i}$. By taking into account eqs 11 and 12, one can thus affirm that the selected eigenvector $|\lambda_{\mathrm{E}}(t)\rangle$ is proportional to the true wave function on the time interval [0, T_0], or more exactly that the expansion (eq 8) requires only a single term $|\lambda_{i,0}(t)\rangle$. This affirmation takes into account the time-arrow (from the past to the future) introduced by the TDSE so that the extra time-perturbation introduced after T_0 cannot retrospectively influence the true system before T_0. In other words, the calculation of a unique eigenstate in the **K** space takes the place of the integration of the TDSE.

2. Re(E) is about equal to at least one inelastic channel energy E_{f}. The corresponding Fourier frequency ω_{f} becomes very small in eq 16 and the direct consequence is a large contribution of V_{opt} to E which acquires a large negative imaginary part Im(E). By introducing this result into (15), one observes that the component $|\lambda_{\mathrm{E}}\rangle_i$ increases exponentially with the term exp($-1/\hbar \int Im(E)$ dt). As |Im(E)| itself increases with V_{opt}, it rapidly becomes impossible to satisfy the periodicity condition $\langle i|\lambda_E(0)\rangle = \langle i|\lambda_{\mathrm{E}}(T)\rangle$. This implies that $|\lambda_{\mathrm{E}}(T_{\mathrm{o}})\rangle_i \simeq 0$ and consequently that $|\lambda_{\mathrm{E}}(0)\rangle_i \simeq 0$. For the other components with $f \neq i$, the two contributions Im(E) and V_{opt} have opposite signs and can compensate to give finite asymptotic amplitudes. In this case the boundary condition is not consistent with eq 11, and the eigenvector $|\lambda_{\mathrm{E}}\rangle$ is not proportional to the wave function.

4. Two Simple Examples

Two simple examples will be treated in this section to test the predictions presented in the previous section and to analyze the performance of the constrained adiabatic trajectory method.

The first example concerns the semiclassical treatment of an inelastic molecular collision. This example proves that the application of the formalism is not limited to photoreactive processes but can be applied more generally to systems characterized by a periodic time-dependent potential $V(t)$ (eq 1) whatever may be the origin of this explicit time dependence. The second example concerns the photodissociation of a molecule subjected to a short and intense laser pulse. This example illustrates the capacity of our model to treat open dissipative systems.

4.1. The Characteristics of the New Approach. Before investigating two examples, we summarize the main characteristics of our approach.

The implementation of the new treatment is simple. The Floquet Hamiltonian is formed by prolonging the time duration of the interaction [0, T_{o}] from T_{o} to T and by introducing over the lengthened time interval [T_{o}, T] the optical potentials (eq 13). Then the Floquet eigenstate which is continuously related to the initial state $|i, n = 0\rangle$ is calculated. The wave function, simply obtained by multiplying the eigenstate by the phase term exp{$1/i\hbar\ Et$} (eq 12), is finally used to analyze the products at the intermediate time T_{o}.

In our first example the basis set is very small and the small size of the Floquet matrix (N < 10^3) makes it is possible to obtain, by diagonalization, not only the eigenvalue $E_{\lambda i,n=0}$ but also the full spectrum in the complex plane and thus to monitor the direct influence of $V_{\mathrm{opt}}(t)$ on this complete spectrum. This example then permits a direct illustration and analysis of the theoretical developments presented in section 3.2. Nevertheless we note that the calculation of the final eigenstate $|\lambda_{i,n=0}\rangle$ need not be done by full diagonalization in the case of larger systems; it can be done more simply by using filter-diagonalization[38] methods, a Chebyshev expansion of a projection operator,[39] or a wave operator diagonalization method. The wave operator option has been selected in our second example, using a recent new algorithm which performs the iterative RDWA integration of the Bloch equation ($H_{\mathrm{F}}\Omega = \Omega H_{\mathrm{F}}\Omega$) and which incorporates nonlinear Padé approximant techniques.[40] The calculation is completed by testing for obedience to the initial condition $\langle k|\lambda(t = 0)\rangle = \delta_{k,i}$ imposed by V_{opt}.

The main principle of our formulation is the transformation of the task of solving the Schrödinger equation of evolution into that of solving a nondegenerate eigenvalue problem. This approach opens up interesting new questions about the status of the time variable in quantum mechanics and about the concept of adiabaticity. The calculation artificially suppresses the constraint of periodicity on the generalized Floquet eigenstate on the interval [0, T_{o}]. This periodicity is incompatible with the inelastic character of the process and is responsible for the dispersion described in eq 8.

Two obvious advantages result from the introduction of the absorbing potentials. First, the solution separates a fast oscillating term exp{$1/i\hbar\ Et$} and a slowly varying term $|\lambda(t)\rangle$ (even if $|\lambda(t)\rangle$ defined on [0, T] exhibits more rapid variations on [0, T_{o}] near the instants which correspond to the avoided crossings of the instantaneous eigenstates). Second, the precision of the result is related solely to the precision of obedience to the asymptotic condition $\langle k|\lambda(t = 0)\rangle = \delta_{k,i}$ (forced by the optical potential) and not to the composition of the degenerate model space. It is thus not necessary to repeat detailed calculations many times in order to determine a suitable dimension for the model space.

The present version of the CATM is devoted to the study of short time interactions. Our second example, which involves a pulse with 100 optical cycles, is thus an upper limit case; larger pulses would require too large a Fourier basis. This constraint is evidently a severe limitation and will be removed in a future version (some details are given in the conclusion). The two examples examined correspond to short interactions ($T_o < 10^{-13}$ s). For such systems there exist numerous techniques, e.g, second order differencing schemes, split operator methods, a short iteration Lanczos technique, the (t, t') method. However, our second example reveals that the CATM is faster than the second order differencing scheme (for the same quality of solution). This result is not obvious since the CATM requires the calculation of internal eigenstates in the dense spectra of large nonhermitian matrices. This is a severe test which often induces slow convergences of the iterative algorithms used in eigenvalue calculations. The good calculational performance arises from an interesting effect: the time-dependent absorptions produce a beneficial dispersion of the eigenvalues around the initial one, with a significant increase in the distance between $E_{i,n=0}$ and the other nearest eigenvalues. This induces a convergence of the algorithm after less than 50 iterations and explains the very small CPU time required. Another advantage of the CATM appears when many calculations need to be repeated with slight modifications of the couplings, to test for example the sensitivity of the results as a function of the perturbative parameters. The iterative nature of the method makes possible the rapid generation of new solutions (after only one or a few iterations) by applying the iterative algorithms starting from the previous solution.

4.2. The Semiclassical Treatment of the He—N$_2$ Molecular Collision. For the semiclassical treatment of inelastic molecular collisions, Gert Billing introduced many years ago the so-called $V_qR_cT_c$ method, in which both rotation and translation are treated classically and vibration is treated quantum mechanically. This approach reduces the quantum dimensionality of the problem and for heavy diatomic molecules such as CO and N$_2$, it gives results which for a wide range of energies are much better than the quantum infinite order sudden (IOS) approximation, when both are compared to the coupled-states (CS) results as a standard. Billing[41] tested this approach on the system He−N$_2$ by using the potential energy surface (PES) of Banks et al.[42] The PES is given by the following expression

$$V(R, r,\gamma) = \sum_{i=0}^{2} V_i(R,\gamma)(r - \bar{r})^i/\bar{r}^i \qquad (18)$$

where

$$V_i(R,\gamma) = \frac{\partial^i}{\partial r^i}\Big(\sum_{j=1}^{2} C_j \exp(-\alpha_j R_j) - a_j R_j^{-6}\Big) \qquad (19)$$

for $i = 0$ and $i = 1$; for $i = 2$ only the short-range term is included in eq 19. R is the distance from He to the center of mass of N$_2$, r is the N$_2$ interatomic distance and γ is the angle between R and r.

The time-dependent Hamiltonian which drives the quantum oscillator is given by the Hamiltonian $H_o(r)$ of the isolated N$_2$ molecule plus a time-dependent perturbation relating to the matrix elements of the potential (eq 18) and the Coriolis coupling. The classical equations of motion are integrated to give five different functions $F^i(t)$ (cf. eq 1) which describe, on a common fixed time interval, the translational and rotational parts of these couplings.

They are represented in Figure 2 for a particular choice of the initial conditions as randomly selected by a Monte Carlo procedure. For consistency, all the results presented here correspond to this particular collision. Nevertheless, these restricted results do correctly characterize the CATM since all the numerous other simulations, not presented here, finally lead to the same conclusions.

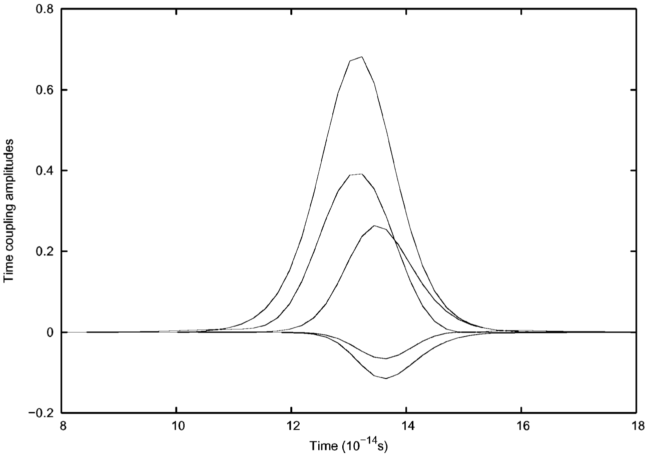

Figure 2. Five functions $F_i(t)$ representing the translational and rotational parts of the potential and Coriolis coupling for a He + N$_2$ collision as a function of time.

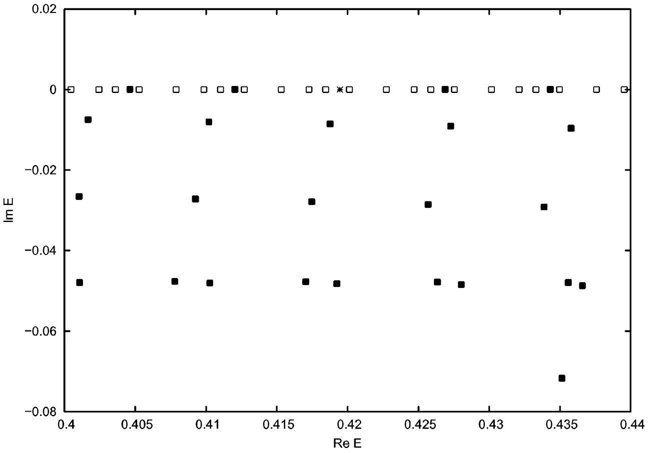

Figure 3. Part of the spectrum of H_F for the He + N$_2$ collision which is near the eigenvalue corresponding to the initial state. The symbol + and the squares correspond to an Hamiltonian without optical potential. The symbols × and the black squares refer to the same Hamiltonian with optical potentials.

The Floquet Hamiltonian is formed for this selected collision by prolonging the time duration of the interaction [0, T_o] from T_o to T with $(T - T_o) = T_o = 25.0 \times 10^{-14}$s. The basis of the extended Hilbert space is the product of the 5 first vibrational states of N$_2$ and of 128 Fourier states used to describe the time interval from 0 up to T. The diagonalization of H_F gives a complex spectrum; the part of the spectrum around the eigenvalue of the initial state ($E^{o}_{v=1,n=0}$) is presented in Figure 3. This figure shows the spectrum of H_F for two cases.

The first case introduces an amplitude A of the optical potentials equal to zero (eq 13). The symbol + represents the eigenvalue $E_{\lambda v=1,n=0}$ connected to the initial state $|v = 1, n = 0\rangle$ and the squares represent the other eigenvalues. All these eigenvalues are on the real axis since in this case H_F is an Hermitian matrix.

In the second case the amplitude of the optical potentials is finite. The symbol × is used for $E_{\lambda v=1,n=0}$, and black squares refer to the other states. In accordance with our analysis, $E_{\lambda v=1,n=0}$ is not affected by the introduction of $V_{opt}(t)$. The two

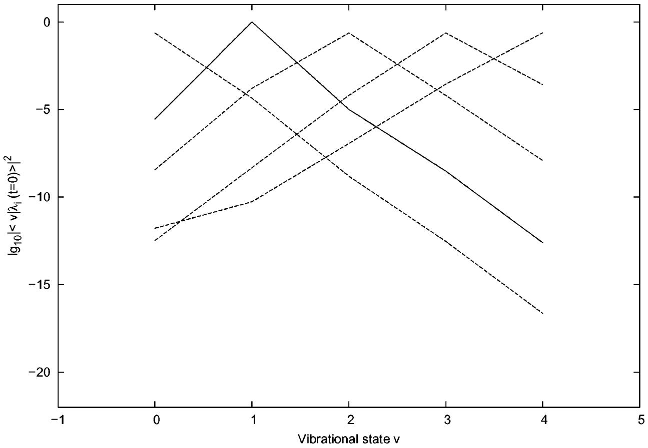

Figure 4. Representation on a logarithmic scale of the boundary components of different Floquet eigenstates on the five vibrational channels $lg_{10}|\langle v|\lambda(t=0)\rangle|^2$. The full line corresponds to the Floquet state which is continuously connected to the initial state, namely $|\lambda_{v=1,n=0}\rangle$. The dashed lines correspond to the four other Floquet states of the first Brillouin zone, $|\lambda_{v\neq 1,n=0}\rangle$. The common amplitude of the optical potentials is equal to $A = 0.2$.

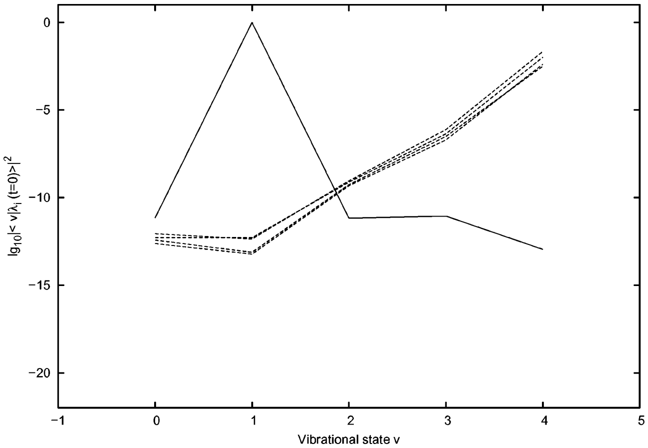

Figure 5. Same as Figure 4 but for $A = 25.0$.

corresponding eigenvalues are perfectly merged. Other states situated on the real axis are also unaffected by the introduction of V_{opt}. The eigenvalues $E_{\lambda v=1,n\neq 0}$ corresponding to the two cases (with and without optical potentials) are also perfectly merged. This arises from the periodic properties of the Floquet eigenstates and eigenvalues

$$\begin{cases} \langle\langle\lambda_{j,m}|i,n\rangle\rangle = \langle\langle\lambda_{j,0}|i,\, n-m\rangle\rangle \\ E_{\lambda_{j,m}} = E_{\lambda_{j,o}} + n\hbar 2\pi/T \end{cases} \qquad (20)$$

This periodicity is evident in Figure 3.

All the other eigenvalues move in the complex plane according to our predictions (see section 3.2). To confirm our analysis, we present in Figures 4 and 5 the components at the initial time $t = 0$ of some eigenvectors on the vibrational channels, namely $(|\langle v|\lambda(t=0)\rangle|)$ for two extreme amplitudes of the optical potentials: $A = 0.2$ and $A = 25.0$. On these figures, the full line corresponds to $|\lambda_{v=1,n=0}\rangle$ and the four dashed lines to the four other Floquet states of the same Brillouin zone $|\lambda_{v\neq 1,n=0}\rangle$.

Figure 4 reveals that the amplitude $A = 0.2$ is manifestly too small. The square moduli of the components $\langle v=0|\lambda_{v=1,n=0}\rangle$ and $\langle v=2|\lambda_{v=1,n=0}\rangle$ are equal to about 10^{-5}. This is too large an error and reveals a noncomplete absorption on these two channels. The perturbation introduced by the optical potential is also relatively small and one can recognize the different eigenstates $|\lambda_{v\neq 1,n=0}\rangle$ by simply looking at the several largest components.

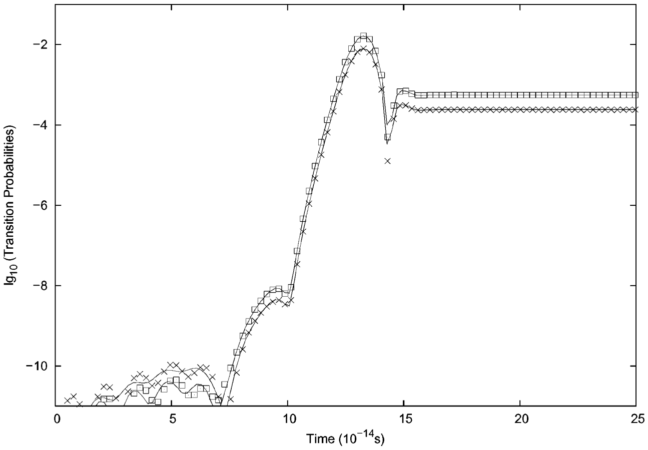

Figure 6. Transition probabilities $P_{1\to 0}$ and $P_{1\to 2}$ on a logarithmic scale as a function of time. The symbols × and the squares are the "exact" semiclassical results obtained by integration of the TDSE for 1 → 0 and 1 → 2, respectively. The solid lines correspond to the CATM results. The optical potential amplitude is equal to $A = 25.0$.

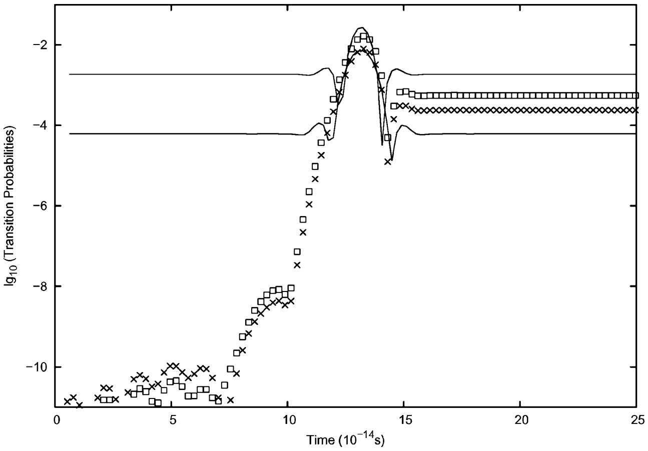

Figure 7. Same as Figure 6 but without the asymptotic optical potential.

The error has vanished in Figure 5. For $A = 25.0$, the square modulus of the largest boundary components $\{\langle v'|\lambda_{v=1,n=0}(0)\rangle\}_{v'\neq 1}$ is smaller than 10^{-11}. According to eq 12, this Floquet state is proportional to the solution of the Schrödinger equation.

For the four other eigenstates of the same Brillouin zone with eigenvalues possessing large imaginary parts, the squared amplitudes $|\langle v=1|\lambda(0)\rangle|^2$ are very small ($<10^{-12}$), in conformity with our analysis. Note that for these states the optical potentials give such strong perturbations that it is impossible to recognize the unperturbed states $|v,\, n=0\rangle$ which are continuously connected to these Floquet states.

The vibrational transition probabilities $P_{1\to 0}$ and $P_{1\to 2}$ are represented for this collision on a logarithmic scale as a function of time in Figures 6 and 7. The relative value of the two probabilities $P_{1\to 0}$ and $P_{1\to 2}$ is not significant because they do not correspond to the same total energy after the symmetrization procedure of the initial + kinetic rotational energy U which is introduced in the ($V_qR_cT_c$) method. In Figure 6, the CATM results obtained by using eq 12 are in perfect agreement with the results coming from the integration of the Schrödinger equation.

Figure 7 confirms that this success is due to the artificial boundary conditions introduced over the lengthened time interval. It reveals that calculations working with only one unperturbed generalized Floquet eigenvector and without optical potentials fail to produce the correct final probabilities and even gives inconsistent results (for example nonzero values at the time origin before the molecular couplings can produce transitions).

4.3. The Photodissociation of H_2^+. We consider as a second example the photodissociation of H_2^+ via an excitation and a dissociation step.

$$H_2^+(^2\Sigma_g^+, v = 0, J = 0) + n\hbar\omega_o \rightarrow H_2^+(^2\Sigma_u^+) \rightarrow H^+ + H(1s) \qquad (21)$$

The sudden switching on of intense laser pulses tuned to the transition ($^2\Sigma_g^+ \rightarrow {}^2\Sigma_u^+$) produces multiphoton processes with stimulated emissions during the interaction period and finally induces dissociation and inelastic transitions between vibrational states of the ground surface.[43] In our example the electric field is described by a Gaussian envelope of the form

$$E(t) = \begin{cases} \epsilon_o \exp\left[-\left(\dfrac{t - t_1}{\tau}\right)^2\right] & \text{for } t \geq t_1 \\ \epsilon_o & \text{for } t_1 \leq t \leq t_2 \\ \epsilon_o \exp\left[-\left(\dfrac{t - t_2}{\tau}\right)^2\right] & \text{for } t \geq t_2 \end{cases} \qquad (22)$$

with a rise time of $\tau = 5fs$ and a plateau duration of ($t_2 - t_1 = 25fs$). The pulse is represented in Figure 8.

This particular system has been studied recently in the framework of the generalized Floquet approach for a carrier wave frequency equal to $\omega_o = 0.295868$ au (corresponding to a wavelength $\lambda_o = 154$ nm) and a maximum amplitude ϵ_o corresponding to the intensity $I = 10^{12}$ W cm^{-2}.[44] It was found that the dissociation probabilities can be accurately described by a single generalized Floquet eigenstate but that an accurate description of inelastic transitions requires more than one generalized Floquet state.

This system is an interesting test for the CATM for two reasons. First, in contrast to the first example, this is an open and dissipative system which does not conserve the norm of the wave function. Conventional asymptotic radial absorbing potentials are used along the two dissociative potential surfaces, and it is interesting to know whether their presence is compatible with the introduction of time-dependent optical potentials.

Second, it introduces a complicated time dependence. Despite the short duration of the pulse, the time variation of the coupling (see Figure 8) includes about 100 optical oscillations. Whether our model has the capacity to take into account such complicated time-dependencies is a first interesting question. A second question relates to the large basis set produced by the long time variations in the extended Hilbert space. The complete product basis is constituted by 204 800 states (200 grid states to represent the two surfaces and 1024 Fourier states to span the large time interval). Within this basis the CATM requires the calculation of the generalized Floquet eigenstate $|\lambda_{v=0,n=0}\rangle$ (associated with the first vibrational state of the ground surface) after the introduction of asymptotic optical potentials. This eigenvector is calculated in our treatment within the framework of the Bloch wave operator theory, using a recent new algorithm.[40] The efficiency of this iterative procedure which calculates the perturbed eigenvector $|\lambda_{v=0,n=0}\rangle$ from the nonperturbed one $|v = 0, n = 0\rangle$ evidently depends on the spectrum of H_F. From this point of view the CATM is very interesting because it concentrates the dynamics into a single eigenstate and simultaneously isolates the corresponding eigenvalue. For our first test problem this second effect of the optical potential is obvious in Figure 3. The addition of absorbing boundaries increases the distance between the initial eigenvalue and its neighbors. In our second application the basis set is too large to permit calculation of the full spectrum of H_F but the analysis[40] made on the same system reveals a large increasing of the distance between the unperturbed initial eigenvalue and its neighbors (without field-matter interaction) as compared with the distortion of the spectrum due to the field-matter interaction. The optical potential approach concentrates the expansion of the wave function onto a single eigenstate and consequently, it cannot easily handle near or exact degeneracies which would produce mixing of different eigenstates.

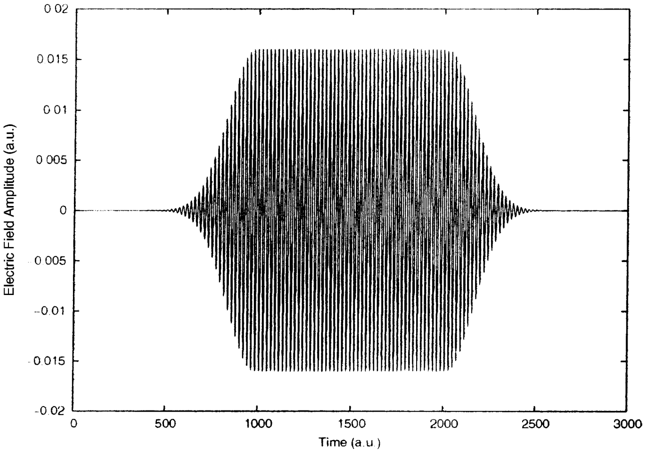

Figure 8. Laser pulse as a function of time.

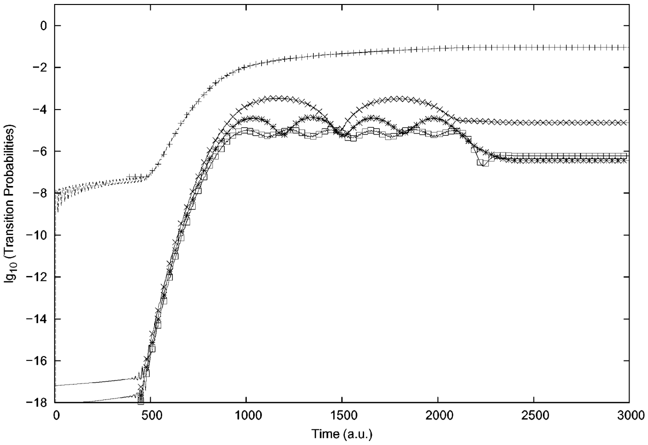

Figure 9. Dissociation probability and vibrational transition probabilities on a logarithmic scale as a function of time for an intensity equal to 10^{12} W/cm^2. The dots correspond to the integration of the Schrödinger equation: (+) dissociation probability; (×) $P_{0\rightarrow1}$; (*) $P_{0\rightarrow2}$; (squares) $P_{0\rightarrow3}$. The dashed and full lines correspond to the results of the CATM.

We present in Figures 9 and 10 the results of this procedure for an intensity of the field equal to 10^{12} W/cm^2. The dissociation probability and the inelastic transition probabilities $P_{0\rightarrow1}$, $P_{0\rightarrow2}$ and $P_{0\rightarrow3}$ are compared with the corresponding results obtained by a direct integration of the Schrödinger equation. Figure 9 shows a perfect agreement of the CATM results with the "exact" results. Moreover the perturbative calculation of the Floquet eigenstate with the iterative RDWA procedure uses less CPU time than the propagation of the wave packet with a second order differencing scheme. This is a consequence of the influence of the optical potentials on the spectrum. The greater

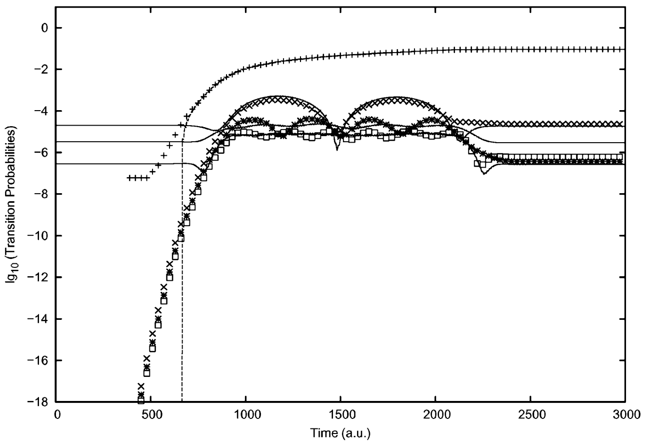

Figure 10. Same as Figure 9 but without optical potentials.

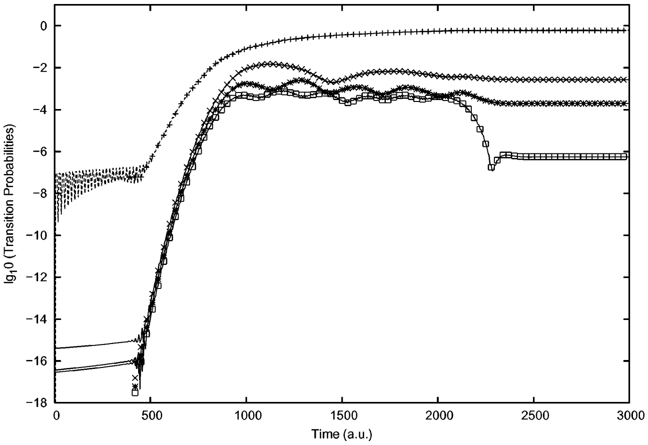

Figure 11. Same as Figure 9 but for an intensity $I = 9. \times 10^{12}$ W/cm^2.

isolation of $E_{\lambda v=0,n=0}$ significantly increases the speed of convergence of the RDWA procedure.

Figure 10 reveals the main importance of the use of absorbing boundaries. Without optical potentials the Floquet solution fails to produce the correct bound state to bound state transition probabilities and even gives nonzero values at the time origin. The dissociation probability remains correct; this is consistent with a preceding study which concluded that a single Floquet resonance is sufficient to describe the photodissociation.[44] The indirect positive effect of the optical potentials in increasing the radius of convergence and the speed of convergence of the eigenvalue integration procedure permits the solution of this reactive problem for stronger field amplitudes. For an intensity of $I = 9. \times 10^{12}$ W/cm^2 Figure 11 reveals the same perfect agreement between our results and the exact ones.

5. Conclusions and Perspectives

This work has explored the joint use of the stationary wave operator theory to solve the generalized Floquet eigenvalue problem and of time-dependent absorbing potentials to force adiabatic behavior. This approach provides a compact dynamical theory in which the calculation of a single generalized Floquet eigenvector suffices to describe correctly the dynamics induced by the TDSE. Our study has revealed that this new method presents several advantages. It is consistent with the Floquet theory and can be applied both to the semiclassical description of inelastic collisions and to photoreactive processes due to the interaction between matter and pulsed laser fields. In the latter case, it is perfectly consistent with the use of the non-Hermitian Hamiltonians generated by analytical continuations in the complex plane when L^2 representations of the continua are used. The precision of the results is limited by the degree of obedience to the exact initial condition $\langle k|\lambda(t = 0)\rangle = \delta_{i,k}$ which is imposed by the time-dependent optical potentials. In our second example this condition is satisfied with a precision of about 10^{-11} (see Figure 5) and the inelastic transitions probabilities, the survival, and the dissociation probabilities thus have a similar error factor (extra errors can also arise from the finite dimension of the basis).

On the other hand, the optical potentials modify the Floquet spectra by making them more sparse; this effect improves the efficiency of the iterative algorithms which are used to solve the Floquet eigenvalue problem.

The CATM is well adapted to describe the time evolution of large quantum systems over short time intervals and makes possible the rapid repetition of perturbative calculations when physical parameters are slightly modified. It is thus of interest in studies of the laser control of molecular dynamics, which often require many simulations to choose the few adiabatic parameters which govern the efficiency of the control process.

In its present version the method can only be applied to systems for which the initial wave function is a single instantaneous eigenstate of the initial Floquet operator. Consequently it cannot be used for the propagation of wave packets on grids, since the associated states initially have a large dispersion on the DVR basis set. This defect has been analyzed and will be removed in a new version which is currently in development. This new version introduces an evolutive active space and a nonorthogonal basis in order to propagate wave packets and to construct new propagators.

Acknowledgment. This article is written in memory of Gert Billing, who was a valuable collaborator, a considerate friend and a scientist who contributed widely to the new methods which have made molecular dynamics such an attractive field for the last twenty years.

References and Notes

(1) Corkum, P. B. *IEEE J. Quantum Electron.* **1985**, *21*, 216.

(2) Cornaggia, C.; Normand, D.; Morellec, J.; Mainfray, G. Manus, C. *Phys. Rev. A* **1986**, *34*, 207.

(3) Bandrauk, A. D.; Wallace, S. C. *Coherence Phenomena in Atoms and Molecules in Laser Fields*; Nato Advanced Study Institute, Series B: Physics B287; 1992.

(4) Chelkowski, S.; Bandrauk, A. D.; Corkum, P. B. *Phys. Rev. Lett.* **1990**, *65*, 2355.

(5) Shirley, J. H. *Phys. Rev. B* **1965**, *138*, 979.

(6) Chu, S. I. *Adv. At. Mol. Phys.* **1985**, *21*, 197.

(7) Chu, S. I. *Adv. Chem. Phys.* **1989**, *73*, 739.

(8) Guérin, S. *Phys. Rev. A* **1997**, *56*, 1458.

(9) Guérin, S.; Jauslin, H. R. *Phys. Rev. A* **1997**, *55*, 1262.

(10) Gavrila, M. *Atoms in Intense Laser fields*; Academic: New York, 1992; p 435.

(11) Barash, D.; Orel, A. E.; Baer, R. *Phys. Rev. A* **1999**, *61*, 013402.

(12) Jolicard, G.; Killingbeck, J. P. *J. Phys. A: Math. Gen.* **2003**, *36*, R411.

(13) Jolicard, G.; Balakrishnan, N. *J. Chem. Phys.* **1997**, *106*, 3613.

(14) Berry, M. V. *Proc. R. Soc.* **1990**, *429*, 61.

(15) Dresse, K.; Holthaus, M. *Eur. Phys. J. D* **1999**, *5*, 119.

(16) Billing, G. D. *Chem. Phys.* **1975**, *9*, 359.

(17) Billing, G. D. *Chem. Phys.* **1978**, *30*, 387.

(18) Messiah, A. *Mécanique Quantique*; Dunod: Paris, 1964; Vol. II.

(19) Guérin, S.; Jauslin, H. R. *Adv. Chem. Phys.* **2003**, *125*, 1.

(20) Bialynicki-Birula, I.; Van, C. L. *Acta Phys. Pol.* **1980**, A *57*, 599.

(21) Guérin, S.; Monti, F.; Dupont, J. M.; Jauslin, H. R. *J. Phys. A: Math. Gen.* **1997**, *30*, 7193.

(22) Guérin, S.; Thomas, S.; Jauslin, H. R. *Phys. Rev. A* **2002**, *65*, 023409.

(23) Nguyen-Dang, T. T. *J. Chem. Phys.* **1989**, *90*, 2657.

(24) Nguyen-Dang, T. T.; Manoli, S.; Abou-Rachid, H. *Phys. Rev. A* **1991**, *43*, 5012.

(25) Telnov, D.; Chu, S. I. *Phys. Rev. A* **1998**, *58*, 4749.

(26) Viennot, D.; Jolicard, G.; Killingbeck, J. P. Manuscript in preparation.

(27) Wyatt, R. E.; Iung, C.; Leforestier, C. *J. Chem. Phys.* **1992**, *97*, 3458.

(28) Wyatt, R. E., Iung, C. In *Dynamics of Molecules and Chemical Reaction*, Wyatt, R. E., Zhang, J. H. M. Dekker Inc.: New York, 1997.

(29) Austern, N. *Ann. Phys. N.Y.* **1967**, *45*, 113.

(30) Lüdde, H. J.; Henne, A.; Salin, A.; Toepfer, A.; Dreizler, R. M. *J. Phys. B: Atm. Mol. Opt. Phys.* **1993**, *26*, 2667.

(31) Peskin, U.; Moiseyev, N. *J. Chem. Phys.* **1993**, *99*, 4590.

(32) Peskin, U.; Alon, O. E.; Moiseyev, N. *J. Chem. Phys.* **1994**, *100*, 7310.

(33) Peskin, U.; Kosloff, R.; Moiseyev, N. *J. Chem. Phys.* **1994**, *100*, 8849.

(34) Jolicard, G.; Grosjean, A. *Phys. Rev. A* **1985**, *32*, 2051.

(35) Jolicard, G.; Billing, G. D. *J. Phys. B: At. Mol. Opt.* **1990**, *23*, 3457.

(36) Périé, J.; Jolicard, G.; Killingbeck, J. P. *J. Chem. Phys.* **1993**, *98*, 6344.

(37) Dennery, Ph.; Krzywicki, A. *Mathematics for physicists* Harper & Row **1967.**

(38) Wall, M. R.; Neuhauser, D. *J. Chem. Phys.* **1995**, *102*, 8011.

(39) Baer, R.; Head-Gordon, M. *J. Chem. Phys.* **1997**, *107*, 10003.

(40) Jolicard, G.; Viennot, D.; Killingbeck, J. P.; Zucconi, J. M. *Phys. Rev. E*, submitted for publication.

(41) Billing, G. D. *Chem. Phys.* **1986**, *107*, 39.

(42) Banks, A. J.; Clary, D. C.; Werner, H. *J. Chem. Phys.* **1986**, *84*, 3788.

(43) Numici, R.; Keller, A.; Atabek, O. *Phys. Rev. A* **1997**, *56*, 772.

(44) Jolicard, G.; Atabek, O.; Dubernet-Tuckey, M. L.; Balakrishnan, N. *J. Phys. (Paris) B: At. Mol. Opt. Phys.* **2003**, *36*, 2777.