Adiabatic theorem for the time-dependent wave operator

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The application of time-dependent wave operator theory to the development of a quantum adiabatic perturbation theory is treated both theoretically and numerically, with emphasis on the description of field-matter interactions which involve short laser pulses. It is first shown that the adiabatic limit of the time-dependent wave operator corresponds to a succession of instantaneous static Bloch wave operators. Wave operator theory is then shown to be compatible with the two-time Floquet theory of light-matter interaction, thus allowing the application of Floquet theory to cases which require the use of a degenerate active space. A numerical study of some problems shows that the perturbation strength associated with nonadiabatic processes can be reduced by using multidimensional active spaces and illustrates the capacity of the wave operator approach to produce a quasiadiabatic treatment of a nominally nonadiabatic Floquet dynamical system.

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I. INTRODUCTION

The numerical study of the interaction of a molecule with a strong laser field leads to a need for long computational times and large computer memory capacity, if use is made of a wave-packet approach which involves a direct integration of the time-dependent Schrödinger equation. This problem is even greater for the study of control processes, since the repetition of many propagations is needed to find the optimum values of several adjustable parameters which describe the nonlinear effects due to ultrashort laser pulses. Provided that some of the parameters do not vary too rapidly, adiabatic techniques [1] have some value within the contex of Floquet theory; Guérin and Jauslin [2] and Drese and Holthaus [3] have proposed adiabatic Floquet methods. To take into account the nonadiabatic effects which are inevitably present for short laser pulses, Guérin and Jauslin [2] assumed them to be localized, in the sense that the adiabatic transport can be considered as made up of lengthy adiabatic passages along eigenstate trajectories, with local diabatic evolution near conical intersections between these trajectories. In the work of Drese and Holthaus [3] the nonadiabatic couplings were treated approximately using first-order perturbation theory. The principal difficulty in treating the nonadiabatic effects is due to the large representation spaces used in the Floquet formalism [2–6], since a large extended Hilbert space $\mathcal{H}\otimes L^2(S^1, d\theta/2\pi)$ is used, involving a product of the bare molecule Hilbert space with the space of square integrable functions on the circle of length 2π [2,3].

Fortunately, it turns out that a reasonable description of the matter-field interaction can often be made by using an active space of small dimension, provided that the basis sets used consist of instantaneous Floquet eigenvectors [7] or generalized Floquet eigenvectors [8]. This feature makes an effective Hamiltonian approach attractive and Guérin and Jauslin [2] have proposed such an approach, based on the quantum analog of the Kolmogorov-Arnold-Moser (KAM) transformation [9], with resonant effects being treated by a rotating wave approximation. The superadiabatic Floquet approach [3], which uses a sequence of unitary transformations to produce bases which follow the nonadiabatic evolution, is also very similar to an effective Hamiltonian approach. The time-dependent wave operator theory (TDWOT) is a third example of effective Hamiltonian theory for time-dependent systems. It has long been used to describe photoreactive processes [10,11] and has several features which make it useful in the search for an efficient description of nonadiabatic effects. It is consistent with Floquet theory and enables a generalization to the degenerate case of the adiabatic conjecture for Floquet states. It proceeds by using an evolving target space within which the description of the nonadiabatic transitions is concentrated. The several iterative techniques which have been proposed to integrate the wave operator equation of motion are sufficiently robust to work with Hamiltonians which are rotated in the complex plane or which include extra complex absorbing potentials. However, some basic theoretical properties of the TDWOT have not been rigorously demonstrated. The theoretical part of the present work looks in particular at the adiabatic limit of the time-dependent wave operator and at the link between the two-time Floquet theory and wave operator theory.

Section II of this work demonstrates an adiabatic theorem for the wave operator, after recalling the basic points of wave operator theory and of the earlier adiabatic theorem of Nenciu [12]. This section also introduces the adiabatic principle of Drese and Holthaus [3], which uses two time variables (like the (t,t') method of Peskin and Moiseyev [13]) and shows how to generalize this earlier principle involving the wave function so as to apply it to the wave operator. In Sec. III numerical applications illustrate our adiabatic theorem for one-dimensional and degenerate active subspaces and deal with electronic transitions produced by short laser pulses.

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They show how the effective adiabaticity of a dynamical process can be increased by projecting the fast nonadiabatic effects into a multidimensional target space. Section IV summarizes the work, with a comment about further possible applications.

II. THEORY

TDWOT allows a generalization to the degenerate case of the adiabatic conjecture for Floquet states, when the Floquet spectrum satisfies some not very onerous conditions. TDWOT can isolate the description of the diabatic part of the dynamics by restricting it to a relatively small target space, with the strong nonadiabatic effects which affect the initial state being included inside this target space. Although the above features have been abundantly illustrated by numerical calculations on a range of particular systems, we regard it as useful to give a more careful theoretical proof of their general validity. In a recent review [14] we made a heuristic conjecture that the adiabatic limit of the time-dependent wave operator is a succession of instantaneous stationary wave operators. In this section we demonstrate this theoretically, after giving a brief review of some necessary details of previous work.

A. Wave operator concept

1. Time-dependent wave operator

We consider a separable Hilbert space $\mathcal{H}$ which is used to describe the states of a quantum system. The dynamical system is described by a time-dependent Hamiltonian $H(t)$ and its associated time-dependent Schrödinger equation and has the time evolution operator $U(t)$ ($\forall\ t \in [0,T]$). The idea of TDWOT is to consider an *active subspace* S_0 of $\mathcal{H}$, such that the dynamics projected into this subspace can be integrated using an effective Hamiltonian. S_0 should be chosen to describe the strong and fast part of the dynamics issuing from the initial state. Its choice has been made previously by using artificial intelligence approaches [15,16] and a wave operator sorting algorithm [11,17]. After solution of the Schrödinger equation in the active space S_0 the wave operator Ω which generates H_{eff} is used to transform the solution in S_0 into the true solution in the Hilbert space $\mathcal{H}$. The above description can be summarized as follows:

$$\forall\ t, \quad \Omega(t): \begin{array}{c} S(t) \to \mathcal{H} \\ \psi_0(t) \mapsto \psi(t) \end{array}, \tag{1}$$

where $\psi(t)$ is a solution of the Schrödinger equation

$$\imath\hbar\partial_t\psi(t) = H(t)\psi(t) \tag{2}$$

and where $\psi_0(t)$, defined as the projection of ψ into S_0, is a solution of the equation

$$\imath\hbar\partial_t\psi_0(t) = H_{\text{eff}}(t)\psi_0(t). \tag{3}$$

The effective Hamiltonian (which describes the approximate dynamics in S_0) is defined by $H_{\text{eff}}(t) = P_0 H(t)\Omega(t)$ and the target space is $S(t) = P_0 U(t) S_0 \subset S_0$, P_0 being the projector on S_0. The time-dependent wave operator can be written as

$$\Omega(t) = U(t)[P_0 U(t) P_0]^{-1}, \tag{4}$$

where $[P_0 U(t) P_0]^{-1} = P_0[P_0 U(t) P_0]^{-1} P_0$ is the inverse of $U(t)$ within S_0 $\{\text{dom}[P_0 U(t) P_0]^{-1} = S_0\}$, dom is the domain of an operator.

One can split the wave operator as follows:

$$\Omega(t) = P_0 + X(t), \tag{5}$$

where the reduced wave operator $X(t)$ satisfies the intermediate normalization condition $Q_0 X P_0 = X$. This operator is governed by a nonlinear partial differential equation

$$\imath\hbar\partial_t X(t) = [1 - X(t)]H(t)[1 + X(t)]. \tag{6}$$

By introducing the Floquet Hamiltonian $H_F = H - \imath\hbar\partial/\partial t$ and a generalized Hilbert space, formed by the product of the Hilbert space $\mathcal{H}$ with the vector space arising from the time variable t, this partial differential equation can be rewritten as

$$H_F(t)\Omega(t) = \Omega(t)H_F(t)\Omega(t). \tag{7}$$

2. Stationary wave operator

We will now consider (in the same separable Hilbert space $\mathcal{H}$) the operator H and the eigenvalue equation

$$H\psi = \lambda\psi. \tag{8}$$

We consider two subspaces S_0 and S of $\mathcal{H}$ such that $S_0 \cap S \neq \emptyset$. We call them the active and target subspaces and we denote the projectors of these subspaces by P_0 and P. We are interested in eigenvectors included in S such that $P\psi = \psi$. As for the previous time-dependent problem, we reduce the problem to one within the active subspace. We introduce the Bloch wave operator:

$$\Omega: \begin{array}{c} S_0 \to S \\ \psi_0 \mapsto \psi \end{array}, \tag{9}$$

where ψ is a solution of the eigenvalue equation (8) and ψ_0 is a solution of

$$H_{\text{eff}}\psi_0 = \lambda\psi_0. \tag{10}$$

The effective operator is defined by $H_{\text{eff}} = P_0 H\Omega$. The wave operator is formally given by the expression

$$\Omega = P(P_0 P P_0)^{-1}, \tag{11}$$

where $(P_0 P P_0)^{-1}$ is the inverse of P within S_0. It is a solution of the generalized eigenvalue equation,

$$H\Omega = \Omega H\Omega = \Omega H_{\text{eff}}. \tag{12}$$

It is important to note that Eq. (7), which describes a time evolution, is identical in form to Eq. (12), except that the Floquet Hamiltonian H_F is taken in place of H. This similarity indicates the compatibility of the TDWOT with the Floquet treatment of periodic or quasiperiodic dynamical processes. More details about the wave operator theory can be found in the review articles [8,14] and in Refs. [4,5,10,11].

B. Adiabatic theorem for the wave operator

This section considers the adiabatic limit of the time-dependent wave operator when the active subspace S_0 (defined at time $t=0$) and the target subspaces $\{S(t)\}_{t\in]0,T]}$ can be considered as instantaneous spectral subspaces which are isolated permanently from the rest of the spectrum. This assumption is central and holds throughout our treatment. To demonstrate this wave operator adiabatic theorem we need an adiabatic theorem which does not investigate the eigenvalues separately, as does the standard adiabatic theorem (see, for example, Ref. [1]), but which considers some subspectrum. Such a theorem was proposed by Nenciu [12] and is recalled here.

Theorem 1. Let $s\mapsto H(s)$ be a family of self-adjoint Hamiltonians. We write $s=t/T$ for the reduced time on the interval $[0,T]$. We suppose that the $\{H(s)\}_{s\in[0,1]}$ have a dense common domain in $\mathcal{H}$, and that the equation

$$i\hbar\partial_s U_T(s) = TH(s)U_T(s)$$

admits a strongly continuous solution $s\mapsto U_T(s)$ of unitary operators (to fulfill this assumption see Ref. [18]). We suppose that

(i) there exist real functions $a_j(s)$ and $b_j(s)$ for $j=1,\ldots,N-1<+\infty$, defined on [0,1], such that

$$a_j(s) < b_j(s) < a_{j+1}(s), \quad \forall\ j, \forall\ s,$$

$$\min_j \inf_s [b_j(s) - a_j(s)] \geqslant d > 0,$$

and

$$\sigma(H(s)) = \bigcup_{j=1}^{N} \sigma_j(s),$$

$$\sigma_1(s) \subset]-\infty, a_1(s)]$$

$$\sigma_j(s) \subset [b_{j-1}(s), a_j(s)], \quad \forall\ j=2,\ldots,N-1,$$

$$\sigma_N(s) \subset [b_{N-1}(s), +\infty[;$$

(ii) $P_j(s)\in\mathcal{C}^2([0,1];\mathcal{B}(\mathcal{H}))$;

(iii) $R(s,z)=[H(s)-z]^{-1}$ is differentiable with respect to s and $\forall\ \delta>0$, $\exists\ K_\delta\in\mathbb{R}^+$ such that

$$\|\partial_s R(s,z)\| \leqslant \frac{K_\delta}{\mathrm{dist}(z,\sigma(H(s)))}$$

$\forall\ s$ such that $\mathrm{dist}(z,\sigma(H(s)))>\delta$. Also, $\forall\ j=2,\ldots,N-1$, we have

$$\lim_{T\to+\infty} U_T(s)P_j(0) = P_j(s)\lim_{T\to+\infty} U_T(s) \tag{13}$$

(the limits are norm limits).

The first assumption supposes that the spectrum is decomposed into N isolated subspectra; the case where the spectrum has a continuous part is not excluded. Eigenvalue crossings are permitted within each subspectrum. The third assumption supposes that the variations of the resolvent are slow far from the spectrum.

The active space which participates in the definition of the time-dependent wave operator can be identified with one of the spectral subspaces introduced by the Nenciu theorem. Indeed, suppose that the wave function is

$$|\psi(s)\rangle = U_\infty(s)|i\rangle, \tag{14}$$

where $U_\infty(s)$ is a simplified notation for $\lim_{T\to\infty} U_T(s)$. Generally a suitable normed vector $|\lambda\rangle\in\mathcal{H}$ must be included in the active space if $\exists\ \sigma\in[0,1]$ to ensure that $|\langle\lambda|\psi(\sigma)\rangle|$ is large. This criterion is consistent with the wave operator sorting algorithm proposed by Wyatt and Iung [17], which considers the wave operator $\Omega^0(s)$ associated with the one-dimensional active space generated by $|i\rangle$ and which selects a vector λ if $\exists\ \sigma\in[0,1]$ such that $|\langle\lambda|X^0(\sigma)|i\rangle|$ is large, namely,

$$\Omega^0(s) = \frac{|\psi(s)\rangle\langle i|}{\langle i|\psi(s)\rangle} \tag{15}$$

and

$$|\langle\lambda|X^0(s)|i\rangle| = \left|\frac{\langle\lambda|\psi(s)\rangle}{\langle i|\psi(s)\rangle}\right|. \tag{16}$$

This criterion thus also involves the same amplitude $|\langle\lambda|\psi(s)\rangle|$. If the conditions of Nenciu's theorem are fulfilled and if the initial state satisfies $|i\rangle\in\mathrm{Ran}\,P_I(0)$, where $P_I(s)$ is one of the spectral projectors of Nenciu's theorem (or a sum of spectral projectors), then

$$\langle\lambda|\psi(s)\rangle = \langle\lambda|U_\infty(s)|i\rangle = \langle\lambda|U_\infty(s)P_I(0)|i\rangle = \langle\lambda|P_I(s)U_\infty(s)|i\rangle. \tag{17}$$

The amplitude $|\langle\lambda|\psi(s)\rangle|$ is large only if $|\lambda\rangle\in\mathrm{Ran}\,P_I(s)$ since $|\langle\lambda|P_I(s)U_\infty(s)|i\rangle|=0$ if $|\lambda\rangle\in\mathrm{Ran}\,P_I(s)^\perp$. Thus a good choice for the active space would be $\int_{[0,1]}^{\oplus}\mathrm{Ran}\,P_I(s)ds$, but unfortunately this space can be very large. By assuming that the couplings are not strong enough to rotate significantly the target space at each instant, i.e., $\forall\ s\,\mathrm{Ran}\,P_I(0)\cap\mathrm{Ran}\,P_I(s)^\perp=\{0\}$, a reasonable choice for the active subspace is $\mathrm{Ran}\,P_I(0)$.

We can now formulate and prove an adiabatic theorem for the time-dependent wave operator.

Theorem 2. Let $s\mapsto H(s)$ be a family of self-adjoint Hamiltonians, where $s=t/T$ is the reduced time on the interval $[0,T]$. We suppose that the $\{H(s)\}_{s\in[0,1]}$ have a dense common domain in $\mathcal{H}$, and that the equation

$$\imath\hbar\partial_s U_T(s) = TH(s)U_T(s)$$

admits a strongly continuous solution $s\mapsto U_T(s)$. We suppose that the instantaneous spectra of $H(s)$ have the decomposition

$$\sigma(H(s)) = \sigma_0(s)\cup\sigma_\perp(s)$$

with the properties

(i) $\exists\ d>0$, $\forall\ s\in[0,1]$, $\mathrm{dist}(\sigma_0(s),\sigma_\perp(s))\geqslant d$;

(ii) $\sigma_0(s)$ is bounded $\forall\ s$ and has a finite number of connected parts in $\sigma(H(s))$;

(iii) $P(s),Q(s)\in\mathcal{C}^2([0,1];\mathcal{B}(\mathcal{H}))$, where $P(s)$ is the spec-

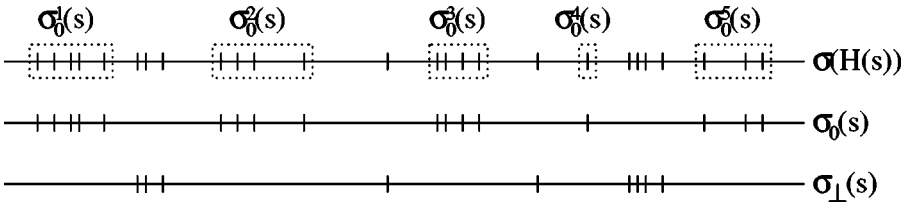

FIG. 1. Example of the decomposition of $\sigma(H(s))$.

tral projector associated with $\sigma_0(s)$: and $Q(s)$ is that associated with $\sigma_\perp(s)$;

(iv) $\forall\ s\in[0,1]$, Ran $P(s)\oplus$ Ran $Q(s)=\mathcal{H}$;

(v) Ran $P(0)\perp$ Ran $Q(0)$;

(vi) $\forall\ s\in[0,1]$, Ran $P(s)^\perp\cap$ Ran $P(0)=\{0\}$;

(vii) $R(s,z)=[H(s)-z]^{-1}$ is differentiable with respect to s and $\forall\ \delta>0$, $\exists\ K_\delta\in\mathbb{R}^+$ such that

$$\left\|\frac{dR}{ds}\right\|\leqslant\frac{K_\delta}{\mathrm{dist}(z,\sigma(H(s)))},$$

$\forall\ z\,|\,\mathrm{dist}(z,\sigma(H(s)))>\delta$.

Let $\Omega_T(s)=U_T(s)[P(0)U_T(s)P(0)]^{-1}$ be the wave operator with Ran $P(0)$ as associated active space. Then $\lim_{T\to+\infty}\Omega_T(s)$ is a succession of instantaneous stationary wave operators with Ran $P(0)$ as associated active space and Ran $P(s)$ as target space. We thus have

$$\lim_{T\to+\infty}\Omega_T(s)=P(s)[P(0)P(s)P(0)]^{-1}. \tag{18}$$

Demonstration. We decompose $\sigma(H(s))$ as follows: The spectral values of $\sigma_0(s)$ and of $\sigma_\perp(s)$ are ordered and grouped from the smallest value up to the largest one. The spectra thus have the decomposition $\sigma(H(s))=\cup_i\sigma_0^i(s)\cup\cup_j\sigma_\perp^j(s)$ (cf. Fig. 1).

Because of the condition $\mathrm{dist}(\sigma_0(s),\sigma_\perp(s))\geqslant d$, all the parts of the decomposition are isolated and separated by a distance equal to or larger than d. We can thus apply the Nenciu adiabatic theorem

$$\forall\ i\quad\lim_{T\to\infty}U_T(s)P_i(0)$$

$$=P_i(s)\lim_{T\to\infty}U_T(s)\Rightarrow\lim_{T\to\infty}U_T(s)\sum_i P_i(0)$$

$$=\sum_i P_i(s)\lim_{T\to\infty}U_T(s),$$

$\Sigma_i P_i(s)=P(s)$, $\forall\ s$, then

$$\lim_{T\to\infty}U_T(s)P(0)=P(s)\lim_{T\to\infty}U_T(s),$$

$$\Omega_T(s)=U_T(s)[P(0)U_T(s)P(0)]^{-1},$$

$$\Omega_T(s)=U_T(s)P(0)[P(0)U_T(s)P(0)]^{-1},$$

$$\Omega_T(s)P(0)U_T(s)P(0)=U_T(s)P(0),$$

$$\lim_{T\to+\infty}[\Omega_T(s)P(0)U_T(s)P(0)]=\lim_{T\to\infty}U_T(s)P(0).$$

We also have:

$$\lim_{T\to+\infty}\Omega_T(s)P(0)\lim_{T\to+\infty}U_T(s)P(0)=\lim_{T\to+\infty}U_T(s)P(0),$$

$$\lim_{T\to+\infty}\Omega_T(s)P(0)P(s)\lim_{T\to+\infty}U_T(s)=P(s)\lim_{T\to+\infty}U_T(s).$$

Since $\forall\ T\ U_T(s)$ is invertible, then $\lim_{T\to\infty}U_T(s)$ is invertible,

$$\lim_{T\to+\infty}\Omega_T(s)P(0)P(s)=P(s),$$

$$\lim_{T\to+\infty}\Omega_T(s)P(0)P(s)P(0)=P(s)P(0),$$

$$\lim_{T\to+\infty}\Omega_T(s)=P(s)P(0)[P(0)P(s)P(0)]^{-1}.$$ ■

It is important to note that it is the different subspaces which globally evolve adiabatically and not the states individually. Inside each subspace nonadiabatic transitions can occur at the conical intersections or near avoided crossings, since this generalized theorem refers to subspaces and not just to individual levels. Theorem 2 [Eq. (18)] shows an adiabatic limit of the wave operator which is a pure stationary operator without any rapid phase, by contrast with the equivalent adiabatic limit of the wave function, which includes both dynamical and Berry phases. This should be related to the fact that the basic equations of the time-dependent wave operator [Eq. (7)] and of the stationary wave operator [Eq. (12)] are identical in form.

C. Wave operator in the Floquet (s,ϕ) treatment of laser pulses

Calculations treating photoreactive processes and the control of molecular dynamics by laser fields generally involve large vector spaces. However, the number of eigenvectors effectively contributing to the dynamical processes can be reduced if suitably adapted representations are used, thus offering favorable circumstances for the use of adiabatic treatments. In the case of field-matter interactions the semiclassical picture of the interaction of a laser pulse with a molecule makes use of a periodic or a quasiperiodic Hamiltonian. The above adiabatic theorem obviously cannot be applied directly. It is first necessary to separate dynamically the fast oscillating terms from the adiabatic evolution of parameters such as the chirped frequency and the electric field envelope. In the standard adiabatic approach this separation is the goal of the theories using two time variables. This concept of two times was introduced by Breuer *et al.* [19] and by Peskin and Moiseyev in the (t,t') theory [13], where it avoided the introduction of the time-ordering operator and allowed the use of techniques originally developed for time-independent

Hamiltonians. In the Floquet theory of Drese and Holthaus [3] the same concept is used together with perturbation theory to construct adiabatic trajectories plus nonadiabatic corrections.

We must adapt these two-time variables theories to the TDWOT in order to make the wave operator theory consistent with the Floquet treatment of quasiperiodic dynamics. To illustrate this formal development we consider an atom or a molecule interacting with a classical radiation pulse. The Hamiltonian of the system is taken to be

$$H(t) = H_0 + \mu f(t)\sin[\omega(t)t], \tag{19}$$

where H_0 is the Hamiltonian of the free molecule defined in the Hilbert space $\mathcal{H}$, μ is the electric dipole, $f(t)$ is the field envelope, and $\omega(t)$ is the instantaneous radiation frequency (possibly chirped). We suppose that the envelope variations and frequency chirping are slow with respect to the instantaneous frequencies. Our aim is to separate (in the framework of the wave operator formulation) the slow dynamics correlated to the adiabatic parameters and the fast dynamics produced by the periodic terms. To this end, we introduce the phase ϕ,

$$\frac{\partial\phi(t)}{\partial t} = \omega_{\text{eff}}(t) = \omega(t) + \dot{\omega}(t)t, \tag{20}$$

and take this phase as the time variable corresponding to the fast dynamics. We then have

$$H(s,\phi) = \frac{T}{\hbar\omega_{\text{eff}}(s)}[H_0 + \mu f(s)\sin(\phi)], \tag{21}$$

where s is the reduced time $s=t/T$ and T is the duration of the pulse. Note that $s\in[0,1]$ and $[0,1[\simeq S^1\backslash\{2\pi\}$.

As a consequence of going from the variable t to the variable ϕ, $H(s,\phi)$ is periodic with respect to ϕ even if the frequency is chirped. We can then use Floquet theory. ϕ is considered as a parameter of the configuration space, and $H_F(s,\phi)=H(s,\phi)-\imath\partial_\phi$ is an operator of the space $\mathcal{H}\otimes L^2(S^1,d\phi/2\pi)$ which depends on the s time. For more details about this Floquet theory, see Refs. [2,3,6].

We suppose that $H(s,\phi)$ considered as a function of s is adiabatic, i.e., we assume that the time intervals during which ω and the envelope amplitude f change significantly are large compared to the instantaneous oscillation period. We investigate this adiabatic dynamics by applying the wave operator adiabatic theorem (with respect to s) and by working with $H_F(s,\phi)$ in the extended Hilbert space $\mathcal{H}\otimes L^2(S^1,d\phi/2\pi)$. This approach first requires us to define a convenient well isolated active space $S_0\otimes L^2(S^1,d\phi/2\pi)$ and the corresponding target space $S(s)=P_0\otimes 1_{L^2(S^1)}U_F(s)S_0\otimes L^2(S^1,d\phi/2\pi)$. This construction will be described later. A second important question concerns the relationship of the generalized wave operator $X_F(\phi,s)$ defined in the Floquet space to the wave operator $X(\phi)$ corresponding to the real time-dependent problem. This question, which appeared in the (t,t') theory for the wave function, is important, since we wish to extract physical results from $X_F(\phi,s)$. The question can be formulated as follows: *Can the wave operator* $X(\phi)$ *be identified with* $X_F(\phi,s=\phi)$? This is the subject of the following theorem.

Theorem 3. Let $X(\phi)$, the reduced wave operator in $\mathcal{H}$, be a solution of

$$\imath\partial_\phi X(\phi) = [1-X(\phi)]H(\phi,\phi)[1+X(\phi)]. \tag{22}$$

Let $X_F(\phi,s)$, the reduced wave operator in $\mathcal{H}\otimes L^2(S^1)$, be a solution of

$$\imath\partial_s X_F(\phi,s) = [1-X_F(\phi,s)]H_F(s,\phi)[1+X_F(\phi,s)] \tag{23}$$

with

$$H_F(s,\phi) = H(s,\phi) - i\partial_\phi.$$

Then, $X_F(\phi,\phi)$ is a solution of Eq. (22), such that $X_F(\phi,\phi)=X(\phi)$.

Proof:

$$X_F: S_0\otimes L^2(S^1)\to S_0^\perp\otimes L^2(S^1).$$

Let $\{|\alpha\rangle\}_\alpha$ be a basis in $\mathcal{H}$ and $\{|m\rangle\}_{m\in\mathbb{Z}}$ a basis in $L^2(S^1)$,

$$X_F(\phi,s) = \sum_{\alpha\in S_0}\sum_{\beta\in S_0^\perp}\sum_{n=-\infty}^{+\infty}\sum_{m=-\infty}^{+\infty}|\beta\rangle\langle\phi|n\rangle\chi_{\beta n,\alpha m}(s)\langle m|\phi\rangle\langle\alpha|$$

with

$$\begin{aligned}\chi_{\beta n,\alpha m}(s) &= \langle\beta|\otimes\langle n|X_F(\phi,s)|\alpha\rangle\otimes|m\rangle\\ &= \int_0^{2\pi}\langle\beta|X_F(\phi,s)|\alpha\rangle\langle n|\phi\rangle\langle\phi|m\rangle\frac{d\phi}{2\pi}.\end{aligned}$$

Let $I=\{\alpha,\beta,n,m\}_{\alpha\in S_0,\beta\in S_0^\perp,n\in\mathbb{Z},m\in\mathbb{Z}}$. We find, using Eq. (23),

$$\begin{aligned}&\imath\sum_I|\beta\rangle\langle\phi|n\rangle\dot{\chi}_I(s)\langle m|\phi\rangle\langle\alpha|\\ &\quad=[1-X_F(\phi,s)]H(s,\phi)[1+X_F(\phi,s)]\\ &\qquad-\imath[1-X_F(\phi,s)]\sum_I|\beta\rangle\chi_I(s)(\langle\phi|n\rangle'\langle m|\phi\rangle\\ &\qquad+\langle\phi|n\rangle\langle m|\phi\rangle')\langle\alpha|.\end{aligned}$$

We have $X_F|\beta\rangle=0$ because $X_F=Q_0X_FP_0$ and $|\beta\rangle\in S_0^\perp$; then we have

$$\begin{aligned}&\imath\sum_I|\beta\rangle[\langle\phi|n\rangle'\langle m|\phi\rangle\chi_I(s)+\langle\phi|n\rangle\langle m|\phi\rangle'\chi_I(s)\\ &\qquad+\langle\phi|n\rangle\langle m|\phi\rangle\dot{\chi}_I(s)]\langle\alpha|\\ &\qquad=[1-X_F(\phi,s)]H(s,\phi)[1+X_F(\phi,s)].\end{aligned}$$

The previous property is true, $\forall\ \phi$, $s\in S^1$; in particular it is true for $s=\phi$, so that

$$\begin{aligned}&\imath\sum_I|\beta\rangle[\langle\phi|n\rangle'\langle m|\phi\rangle\chi_I(\phi)+\langle\phi|n\rangle\langle m|\phi\rangle'\chi_I(\phi)\\ &\qquad+\langle\phi|n\rangle\langle m|\phi\rangle\dot{\chi}_I(\phi)]\langle\alpha|\\ &\qquad=[1-X_F(\phi,\phi)]H(\phi,\phi)[1+X_F(\phi,\phi)]\\ &\qquad\Leftrightarrow\imath\partial_\phi X_F(\phi,\phi)\\ &\qquad=[1-X_F(\phi,\phi)]H(\phi,\phi)[1+X_F(\phi,\phi)].\end{aligned}$$

Then $X_F(\phi,\phi)$ is the solution of Eq. (22). ■

Thus the two-time wave operator $X_F(\phi,s)$ can be used to extract the physical results by considering the limit $s=\phi$. The interest of the Floquet approach is that the time-dependent dynamics is described by using a stationary formalism. We can then use a spectral criterion to justify the use of the wave operator adiabatic theorem. If at each time the spectrum of the instantaneous target space is isolated sufficiently far from the rest of the spectrum of $H_F(\phi,s)$ in $\mathcal{H}\otimes L^2(S^1)$, then we can write

$$\lim_{T\to+\infty}\Omega_F^T(s)=P(s)[P_0\otimes 1_{L^2(S^1)}P(s)P_0\otimes 1_{L^2(S^1)}]^{-1}, \tag{24}$$

where the target space $S(t)$ is a subspace of $\mathcal{H}\otimes L^2(S^1)$, and Ω_F^T is an operator of the same space.

III. ILLUSTRATION: A MEASURE OF ADIABATICITY

This section illustrates the wave operator theorem and the two-time formalism by analyzing two simple models of molecules subjected to an ultrashort laser pulse. Both models are represented by Eq. (21). The numerical study of these two systems has the double objective of illustrating the adiabatic theorem (that the generalized wave operator is, at the adiabatic limit, a succession of instantaneous wave operators) and also of demonstrating the decrease of the nonadiabatic effects outside the active space when an appropriate multidimensional active space is used. The two systems are treated in the two-time (s,ϕ) formulation so that our illustration simultaneously accords with the two original theorems, theorem 2 and theorem 3. In other words, it correctly obeys Eq. (24) which is a condensed form of the two theorems. The atomics units (a.u.) are used in these applications.

A. A pure adiabatic case

The first system involves the photodissociation of H_2^+, via the process

$$H_2^+(^2\Sigma_g^+,v=0,J=0)+\hbar\omega\rightarrow H_2^+(^2\Sigma_u^+)\rightarrow H^+ + H(1s). \tag{25}$$

The two electronic potential-energy surfaces and the transition dipole moment are taken from Bunkin and Togov [20]. The laser is characterized by its carrier wave frequency $\omega_o=0.295\,868$ a.u., a maximum intensity of $I=10^{12}$ W/cm^2 and a Gaussian envelope of the form

$$f(t)=\begin{cases}\epsilon_o\exp\left[-\left(\dfrac{t-t_1}{\tau}\right)^2\right] & \text{for } t\leqslant t_1\\ \epsilon_o & \text{for } t_1\leqslant t\leqslant t_2\\ \epsilon_o\exp\left[-\left(\dfrac{t-t_2}{\tau}\right)^2\right] & \text{for } t\geqslant t_2\end{cases} \tag{26}$$

with a rise time of $\tau=25$ a.u. and with a large plateau between $t_1=200$ a.u. and $t_2=300$ a.u.

This system has been extensively studied in the literature. The photodissociation process is a direct transition from the ground surface (Σ_g^+) to the upper structureless surface (Σ_u^+). For strong enough laser intensities stimulated emissions of photons appear during the interaction, involving the Σ_g^+ continuum, so that the two molecular continua participate in the dynamics. The spectrum of the Floquet Hamiltonian $H_F(s,\phi)=H(s,\phi)-i\partial_\phi$ consists then of discrete bound states embedded in the molecular and photonic continua. The theorems demonstrated in the previous section cannot be applied directly in this case [21]. The dissipative character of the process is not really a handicap because one can use biorthogonal basis sets to reproduce the outgoing quantum fluxes. It might appear to be impossible to define isolated subspaces including the initial state. One can, nevertheless, recover correct conditions by discretizing both the photonic and the molecular continua. The discretization of the photonic continuum is simply obtained by using a finite basis set $\exp(\imath n\phi)$ to span the space $L^2(S^1,d\phi/2\pi)$. This approximation is consistent with the Floquet formalism itself since the Floquet Hamiltonian is identical, up to an additive constant, to the quantum Hamiltonian of the field-matter interaction if one assumes that the number of photons exchanged during the field-molecule interaction is small compared to the average photon number [2]. Preliminary tests reveal that a basis set of $N=256$ states, namely, $\{\exp(\imath n\phi)\}_{n=-170-n=+85}$, is sufficient to represent the full laser pulse and to give well converged results in the space $\mathcal{H}\otimes L^2(S^1)$. The initial Floquet state is taken to be $|i\rangle=|v=0,n=0\rangle$, where $v=0$ is the ground vibrational state of $^2\Sigma_g^+$. The arbitrary choice of the first Brillouin zone $n=0$ corresponds to taking a phase between the molecular state and the field which is uniformly averaged on $[0,2\pi]$. This choice is appropriate for experimentals results, where many molecules contribute.

The discretization of the molecular continua is obtained by using the optical potential model [22], i.e., by introducing a finite asymptotic complex potential $-iV_{\text{opt}}(r)$ along the radial axis of the two energy surfaces. This is a coarse grained procedure which destroys the exact representation of the continuum; all the scattering states are modified in the interaction region and their spectrum is rotated in the complex plane. Nevertheless, some fundamental features are preserved. This transformation assures the analytical continuation of the Green function through the cut constituted by the real axis and can be used to explore the second Riemann sheet and the complex resonance states; it can thus be used to investigate photoreactive processes which are dominated by the influence of field-matter resonances. These results can be understood by noting that the optical potential model modifies the rigorous energy-based definition of the Green function $\lim_{\epsilon\to 0^+}[E-(H_F-i\epsilon)]^{-1}$ into the new more tractable form $\{E-[H_F-iV_{\text{opt}}(r)]\}^{-1}$.

In the new discretized space $\mathcal{H}\otimes L^2(S^1)$ the wave function which issues from the molecular state $|i\rangle$ can be expanded on the complete basis set of generalized Floquet eigenstates [i.e., the eigenvectors of $H_F(s,\phi)$], giving the expansion [8]

$$|\psi(t)\rangle=\sum_j e^{-iE_{\lambda_{j,0}}t/\hbar}|\lambda_{j,0}(t)\rangle\langle\lambda_{j,0}(t=0)|i\rangle. \tag{27}$$

This equation, which assumes a state-to-state correspondence between the nonperturbed states $|j,n\rangle$ (the eigenstates of H_F

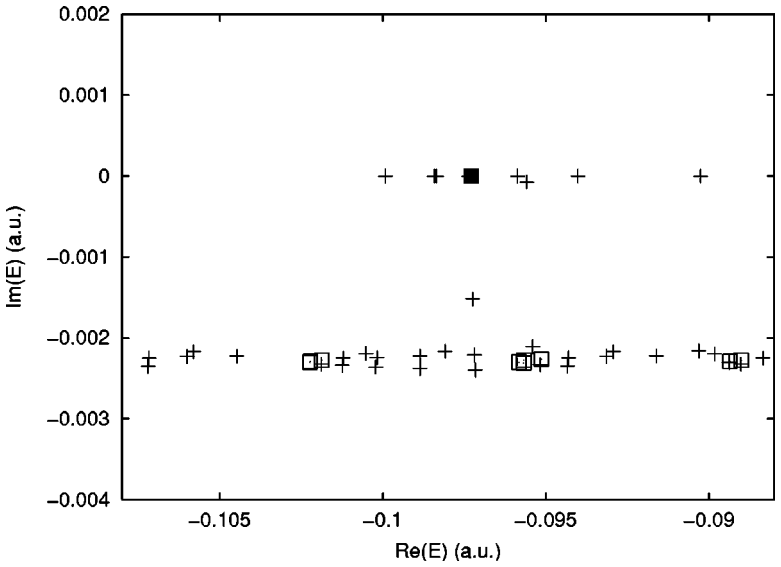

FIG. 2. The unperturbed Floquet spectrum of H_2^+ around the initial state (black square). The ten first states selected by the wave operator sorting algorithm are represented by squares, the other states by the symbol "+."

without the field-matter interaction) and the Floquet eigenstates ($\lambda_{j,n}$) clearly shows that only the Floquet eigenvectors of the first Brillouin zone ($n=0$) contribute. By using the wave operator sorting algorithm of Wyatt and Iung [17], one can easily select a finite group of states $|k,n=0\rangle$ ($k=1-N$) to constitute the active space and limit the sum in Eq. (27) to this group. The dimension N depends directly on the more or less adiabatic character of the dynamics and also, to a certain extent, on the precision which is required. One can then distinguish adiabatic processes when a single state constitutes the active space and nonadiabatic processes when a few states constitute this active space. A similar analysis was made by Barash *et al.* [23], who distinguished "adiabatic ionization" (caused by the presence of complex energies) and "nonadiabatic ionization" (caused by nonadiabatic transitions). However, Barash used a basis set of instantaneous Floquet eigenstates. In such a picture the signature of the nonadiabaticity is the presence of nonadiabatic transitions between the basis states, while the expression of the basis set at $t=0$ (when the field-matter interaction is equal to zero) satisfies in every case the equation $\langle k|\lambda_{j,0}(t=0)\rangle=\delta_{j,k}$. In our generalized Floquet eigenstate picture satisfaction of this equation is, on the contrary, the exclusive signature of an adiabatic process. In the nonadiabatic case the Floquet eigenstates $\lambda_{j,0}(t=0)$ spread out at the initial time over many nonperturbed states $|k,0\rangle$. The size of the active space is then the number of generalized Floquet eigenstates which participate in Eq. (27) and which are necessary to reconstitute at $t=0$ the initial state $|i\rangle$.

A good indicator of the adiabaticity is the complex spectrum of the Floquet Hamitonian near the initial eigenvalue $E_{\lambda_{i,0}}$. As the size of the extended Hilbert space is very large, it is impossible to calculate this spectrum but the picture of the unperturbed part $H_F^o=H_o-i\hbar\partial/\partial t$ (Fig. 2) remains significant insofar as the spectral distortions due to the field-matter interaction are small. The initial state (represented by a black square in Fig. 2) is not perfectly isolated as it should have been in a perfect adiabatic process. Nevertheless, the nearest eigenvalues correspond to bound states of the ground surfaces: $|v=1,n=0\rangle$, $|v=2,n=0\rangle$, which are not selected by the wave operator algorithm because they imply higher perturbation orders. By contrast this algorithm selects continuum states even if they move away from the real axis. One can then expect that the adiabatic character is roughly preserved. This analysis is confirmed by Fig. 3 which presents the transition probabilities.

Figure 3 reveals that the inelastic transition probabilities take small values ($\leqslant 10^{-4}$). The dissociation probability is larger but its value is due to the complex eigenvalue $E_{\lambda_{0,0}}$ and is not produced by nonadiabatic transitions. One can thus conclude that the photodissociation of H_2^+ is not perfectly adiabatic but possesses a strong adiabatic character. A single state $|i,n=0\rangle$ mainly constitutes the model space, so that a single Floquet state $|\lambda_{i,n=0}\rangle$ significantly participates in Eq. (27). The initial conditions require that this single state be characterized by the asymptotic conditions: $\langle k|\lambda_{i,0}(t=0)\rangle=\langle k|\lambda_{i,0}(t=T)\rangle=\delta_{i,k}$ [8], so that this single Floquet state is, at $t=0$, about identical the instantaneous Floquet state $|i,n=0\rangle$. To test the adiabatic theorem corresponding to the two-time wave operator [Eq. (24)] we propose the test described below for this one-dimensional case.

The exact wave operator corresponding to the selected active space is calculated by integrating the equation

$$H_F\Omega_T(\phi,s)=\Omega_T(\phi,s)H_F\Omega_T(\phi,s)=\Omega_T(\phi,s)H_{\text{eff}} \quad (28)$$

on the whole duration [$t=0, t=T=500$ a.u.] of the interaction, using an iterative treatment [24] and a basis consisting of the tensorial product of the free molecular basis set and the Fourier basis $\exp(\imath n\phi)$. Then a local Floquet Hamiltonian $H_F^{s_i}$ is formed by freezing the value of the adiabatic time variable at a grid point value ($s=s_i$) and Eq. (28) is tested locally by using this local Floquet Hamiltonian, namely,

$$[H_F^{s_i}\Omega_T(\phi,s)]_{\phi=s=s_i}\simeq[\Omega_T(\phi,s)H_{\text{eff}}^{s_i}]_{\phi=s=s_i}. \quad (29)$$

In this equation $H_{\text{eff}}^{s_i}$ is a local effective Hamiltonian obtained by taking a narrow Gaussian average centered on the s_i value (different calculations have shown that the test is not affected

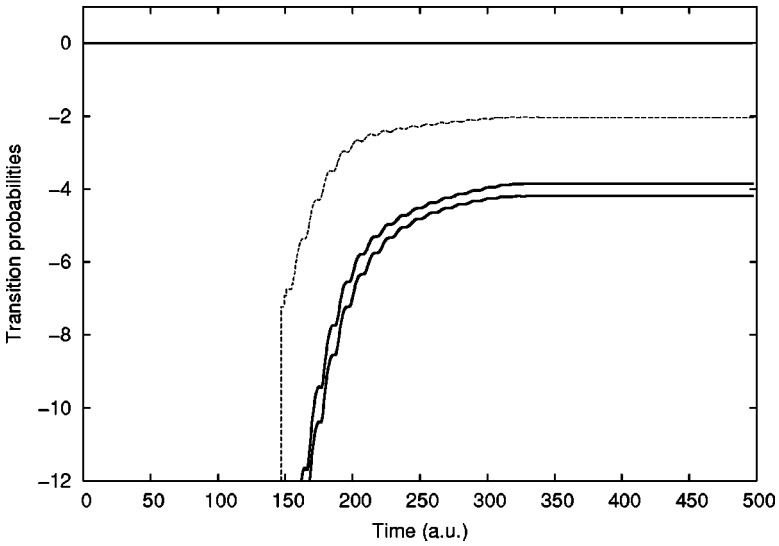

FIG. 3. Transition probabilities on a logarithmic scale. The solid lines represent (from top to bottom) the survival probability $P_{0\to0}$ and the inelastic transition probabilities $P_{0\to1}$ and $P_{0\to2}$. The dashed line represents the dissociation probability.

by the width of this distribution as long as only a few points of the grid contribute to this average).

If the Floquet wave operator is rigorously a succession of instantaneous wave operators then the two members of Eq. (29) are equal and the symbol "=" should take the place of "≃." A first local measure of the nonadiabaticity is thus the modulus of the difference of the right-hand and left-hand sides of Eq. (29),

$$\Xi_1^{s_i} = \sum_i \sum_j |([H_F^{s_i}\Omega - \Omega H_{\text{eff}}^{s_i}]_{s_i})_{i,j}|^2. \tag{30}$$

A more detailed analysis of this equation proves that, in spite of the change $H_F \to H_F^{s_i}$, this measure of the nonadiabaticity tends to zero if the successive effective Hamiltonians $H_{\text{eff}}^{s_i}$ are constant and equal to H_{eff} as defined in Eq. (28). This is because the difference between $H_F\Omega|_{s_i}$ and $H_F^{s_i}\Omega|_{s_i}$ is due to the kinetic part $\iota\partial_s$ solely. The coupling part $\mu f(s)\sin(\phi)$ [Eq. (21)] has a diagonal representation in the DVR basis set $|s_k\rangle$ associated to the FBR basis set $\exp(\iota n 2\pi s)$ so that the matrix product $H_F\Omega|_{s_i}$ does not make use of the values $\Omega(\phi, s_k)$ for $k \neq i$. The kinetic part has a nondiagonal representation but its influence tends to zero at the adiabatic limit. This is a direct consequence of the wave operator adiabatic theorem (Theorem 2): the time-dependent reduced wave operator which is the solution of $\iota\partial_s X_F(\phi,s) = [1 - X_F(\phi,s)]H_F(s,\phi)[1+X_F(\phi,s)]$ [Eq. (23)] tends at the adiabatic limit to the stationary reduced wave operator, a solution of $[1-X_F(\phi,s)]H_F(s,\phi)[1+X_F(\phi,s)]=0$. One can then propose a second measure of the nonadiabaticity, based on the variations of H_{eff}, and given by

$$\Xi_2^{s_i} = \sum_i \sum_j |(H_{\text{eff}})_{i,j} - (H_{\text{eff}}^{s_i})_{i,j}|^2. \tag{31}$$

Figure 4 presents these two measures in the case of H_2^+. For this quite adiabatic system the active space is one dimensional and the reduced wave operator is given by a single column. The amplitude of the field is selected as the single adiabatic parameter. The variations of this parameter are represented in the upper part of this figure.

This figure reveals that the two measures are more or less proportional and that the departures from adiabaticity appear

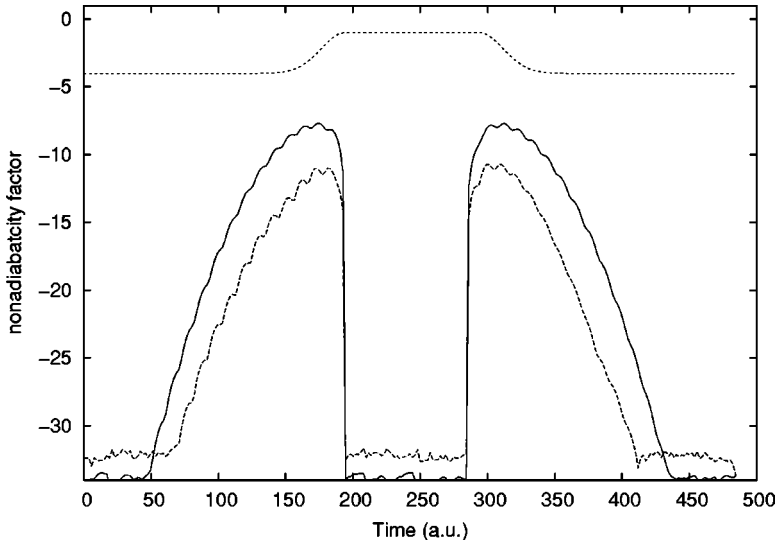

FIG. 4. The two measures of nonadiabaticity in a logarithmic scale in the case of the photodissociation of H_2^+, solid line: Ξ_1; dashed line: Ξ_2. The envelope of the field is represented in the upper part of the figure.

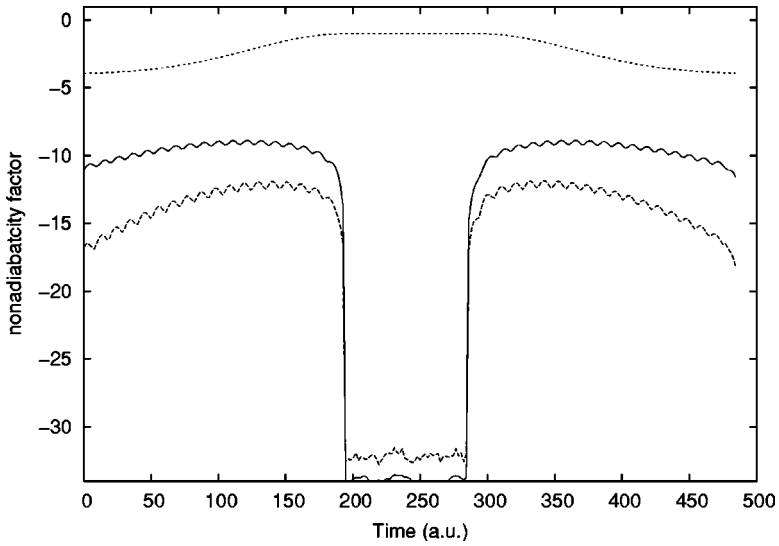

FIG. 5. The same caption as for Fig. 4 but for a more slowly varying field envelope obtained by increasing the rise time from $\tau=25$ a.u. up to $\tau=100$ a.u.

when the adiabatic parameter $f(s)$ [Eq. (21)] does not vary smoothly on the time scale determined by $2\pi/\omega$. It shows both the consistency of the wave operator theorem (which is satisfied with a precision less than 10^{-30} when the adiabatic parameter is constant) and the use of a two-time formalism in the framework of wave operator theory.

The departures from pure adiabaticity mainly come from two photon processes (absorption+emission) which connect the initial state to other bound states of the same ground-state surface. These transitions are favored by strong laser fields and rapid variations of the laser envelope which broaden its spectrum. By increasing the rise time from $\tau=25$ a.u. up to $\tau=100$ a.u. one increases the adiabaticity of the process by making the laser fields more monochromatic. This is confirmed by Fig. 5, which show a signifant decrease of about one order of magnitude of the maxima of the two measures Ξ_1 and Ξ_2.

B. A nonadiabatic case

The second system is a model system similar to the first. The reduced mass and the dipole moment are those of H_2^+. The ground surface is a Morse potential but the upper surface is taken to be the potential of Hulburt and Hirschfelder [25] in place of the structureless surface. These two surfaces are represented in Fig. 6.

Four bound states exist in the well of this upper surface and three shape resonance are clearly identified by a spectral analysis. The field amplitude is characterized by a maximum intensity $I=10^{10}$ W/cm^2 and a Gaussian envelope given by Eq. (26) with $\tau=25$ a.u., $t_1=50$ a.u., and $t_2=450$ a.u. The carrier wave frequency is $\omega_o=0.544$ a.u. with a chirping amplitude $\delta\omega=0.002$ a.u., namely,

$$\omega(t)=\begin{cases}\omega_o & \text{for } t\leqslant t_3\\ \omega_o+\delta\omega(t-t_3)/(t_4-t_3) & \text{for } t_3\leqslant t\leqslant t_4\\ \omega_o+\delta\omega & \text{for } t_4\leqslant t\leqslant t_5\\ \omega_o+\delta\omega(t_6-t)/(t_6-t_5) & \text{for } t_5\leqslant t\leqslant t_6\\ \omega_o & \text{for } t\geqslant t_6\end{cases} \tag{32}$$

with $t_3=130$ a.u., $t_4=230$ a.u., $t_5=350$ a.u., and $t_6=450$ a.u. Linear variations of ω have been chosen so as to obtain analytical relationships between t and ϕ [Eq. (20)].

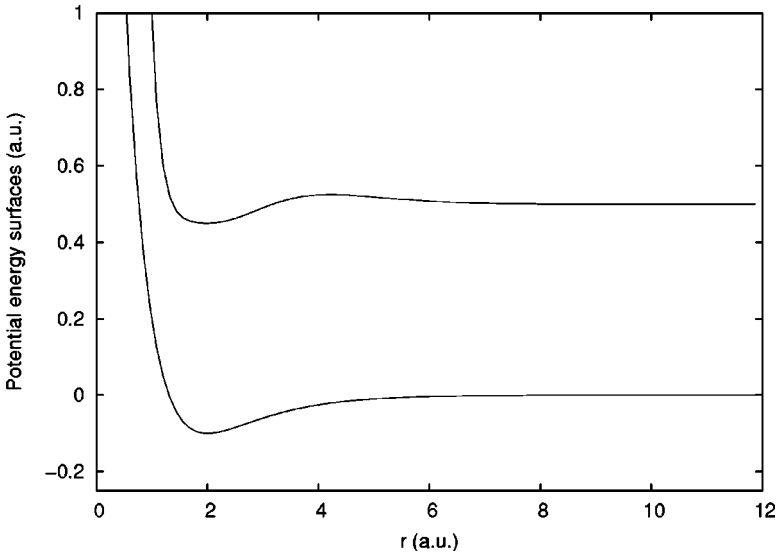

FIG. 6. Representation of the two electronic potential surfaces for our second model system.

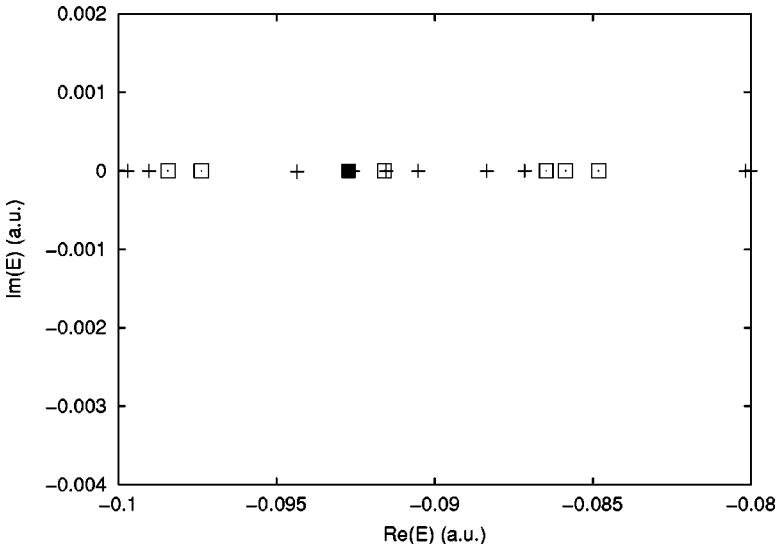

FIG. 7. The unperturbed Floquet spectrum of our second system around the initial state (black square). The ten first states selected by the wave operator sorting algorithm are represented by squares, the other states by the symbol "+."

Because of the modulation of the frequency, the laser is, at certain instants, tuned to the bound-state–bound-state transition ($v=0 \rightarrow v'=0$). This produces a nonadiabatic picture in which the target space incorporates the Floquet state issuing from the bound state $|v'=0\rangle$ of the upper surface. Figure 7 presents the spectrum of the unperturbed Floquet Hamiltonian near the initial eigenvalue $E_{v=0,n=0}$ and confirms this analysis by revealing (near $E_{v=0,n=0}$) a subgroup of eigenvalues situated far from the rest of the spectrum. More precisely the wave operator sorting algorithm selects on the real axis the Floquet states issuing from the first vibrational states of the two surfaces: $|v=i\rangle$, $i=0,1,2$ and $|v'=j\rangle$, $j=0,1,2$.

Figure 8 presents the biggest inelastic transition probabilities and confirms the selection made by the sorting algorithm, for example the probability $P_{v=0\rightarrow v'=0}$ has much larger values than the other inelastic transition probabilities.

Figure 9 presents the measure Ξ_1 for our second system. In this case the frequency is chirped. The envelope of the field $f(s)$ and the frequency $\omega(s)$ are represented in the upper part of the figure.

As in the previous case the departures from adiabaticity increase when one of the two adiabatic parameters varies too rapidly. The effect is particularly important at the times for which $d\phi/dt$ is discontinuous. As the intensity of the field is a hundred times smaller than for H_2^+, the defects corresponding to the use of a one-dimensional active space are comparatively larger in this second system. The most important point is that one can reduce these defects by selecting a convenient degenerate active space. One can, for example, make an improvement of about four order of magnitude by going from $N=1$ to $N=5$. This result confirms that the wave operator formulation can increase the domain of variation of the adiabatic parameters in which the adiabatic limit [Eq. (24)] can be used, by using a finite target space to describe the strong nonadiabatic effects. In this sense the time-dependent wave operator is an ideal tool to generalize the quantum adiabatic theorem in multidimensional spaces. It should be noted that the discretization of the two continua by the introduction of asymptotic absorbing potentials is necessary to work with finite representations and to reduce the size of the active spaces; this optical potential approach is common to the majority of works which use a DVR approach to describe dynamical processes [26,27].

Figure 10 presents the measure Ξ_2, and confirms the proportionality of the two measures of adiabaticity.

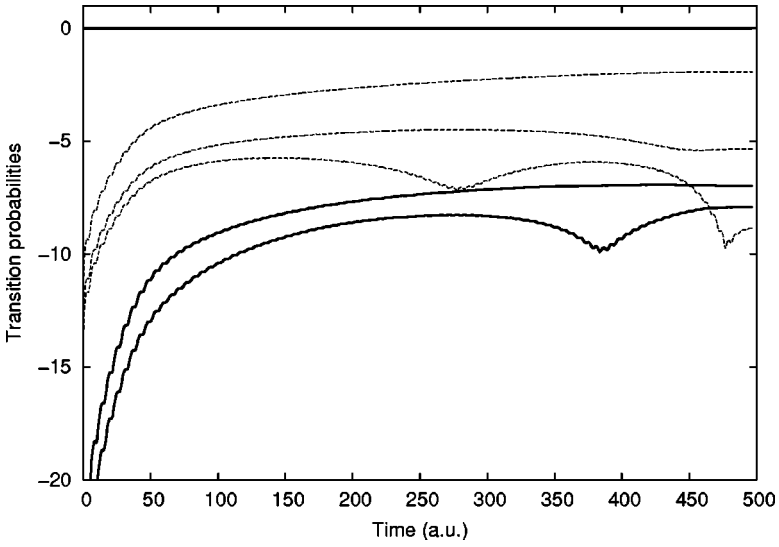

FIG. 8. Transition probabilities on a logarithmic scale. The solid lines represent (from top to bottom), the survival probability $P_{v=0\rightarrow v=0}$ and the inelastic transition probabilities $P_{v=0\rightarrow v=1}$ and $P_{v=0\rightarrow v=2}$. The dashed line represents (from top to bottom) $P_{v=0\rightarrow v'=0}$, $P_{v=0\rightarrow v'=1}$, and $P_{v=0\rightarrow v'=2}$.

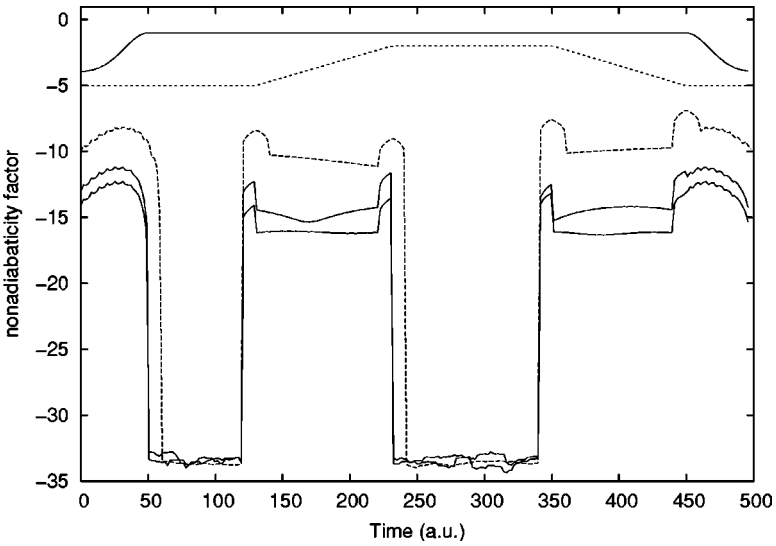

FIG. 9. The measure Ξ_1 of nonadiabaticity in a logarithmic scale for our second system. The envelope $f(s)$ (solid line) and the frequency variations $\omega(s)$ (dotted line) are represented in the upper part of the figure. Three cases are represented: a one-dimensional active space (dashed line) and two degenerate active space of increasing dimensions $N=5$ and $N=10$ (solid lines).

IV. CONCLUSION

In this work the standard quantum-mechanical adiabatic theorem, which applies to the wave function of a single state, is generalized so as to apply to the time-dependent wave operator associated with a multidimensional active space [Eq. (18)]. It is also shown that the two-time formalisms which have sometimes been used to describe the time evolution of periodic systems can be adapted for use with the wave operator approach [Eqs. (22) and (23)]. The value of our adiabatic theorem and of the two-time wave operator formalism are demonstrated by numerical studies of two specimen problems involving laser-molecule interaction. The calculations show that within this formalism it is possible to enhance the effective adiabaticity of the dynamical processes involved by choosing an appropriate degenerate active space and capturing the nonadiabatic effects within corresponding target spaces.

The formalism developed here appears to provide an effective approach to the study of the inelastic and reactive processes caused by the interaction of a molecule with a laser pulse, since the nonadiabatic effects associated with short laser pulses can be dealt with by using an effective Hamiltonian approach together with an appropriate target space. The effective Hamiltonian can take into account the dynamical effects usually associated with level crossings and avoided crossings; the multidimensional target space manages to capture the fast dynamical processes internally while itself evolving in a more adiabatic manner with respect to the other disjoint subspaces within the overall Hilbert space (as described by the generalized adiabatic theorem [Eq. (18)].

A further study of the use of this formalism to describe photoreactive processes is currently in progress, with the aim of adapting it to produce an adiabatic transport theory which uses a discrete lattice within the manifold of control parameters which is needed to describe control processes. The main problem of control theory is not to solve the mathematical inverse problem, because its solution is generally nonrealistic from an experimental point of view and is sometimes unstable. The central problem is rather to select and to understand the few basic processes which influence a full photoreactive experiment. This understanding gives the possibility of modifying some of these basic processes by monitoring some adiabatic parameters and also by introducing

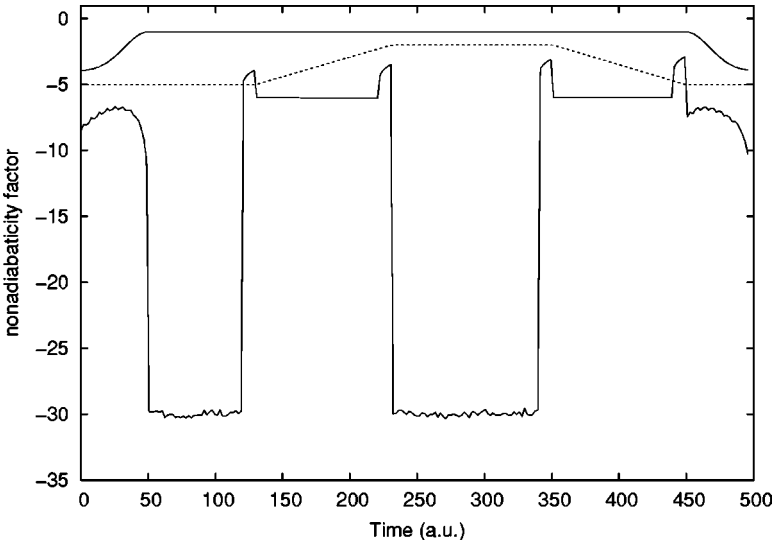

FIG. 10. The measure Ξ_2 of nonadiabaticity in a logarithmic scale for our second system. The envelope $f(s)$ (solid line) and the frequency variations $\omega(s)$ (dotted line) are represented in the upper part of the figure. The case represented corresponds to a degenerate active space of dimension $N=5$.

quantum interference effects between them. Two fundamental concepts involved in the basic theory are those of the adiabatic evolution on the Floquet eigentrajectories and the nonadiabatic transitions between individual levels. For instance, the study of Guérin and Jauslin connects the efficiency of the population transfer between the initial and the target states to the topology of the dressed state energy surfaces, which varies as a function of the time-dependent external field parameters. The adiabatic transport appears in their study as a global adiabatic passage along one eigenstate trajectory, combined with the local diabatic evolution near conical intersections. The present study and the two original theorems that it proposes offers a natural generalization to the degenerate case of the adiabatic conjecture for single Floquet states, leading to an approach which involves driving simultaneously interfering adiabatic trajectories on the dressed state energy surfaces while concentrating the adiabatic transition inside the evolving target space. In our picture the nonadiabatic coupling processes can overlap and interfere during the same time intervals.

The present work is thus a first step forward for molecular control theory. The complete plan of this original approach necessitates two supplementary studies which are currently in progress: a discretization within the manifold of control parameters to make the numerical treatment possible and a more precise analysis of the consistency of the geometric phase with the wave operator formalism.

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