

# Photoabsorption probability for a system governed by a time-dependent Hamiltonian through the $(t, t')$ formalism

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Heller's expression for the absorption cross-section in the weak field limit is extended to cases where the total Hamiltonian contains a strong time-dependent component, supplemented by a weak field. A very similar expression to the original case then results when the  $(t, t')$  formalism is used; one only needs to construct a correlation function for the system without the weak field, and use it to extract the absorption probability for any value of the weak-field frequency (or pulse shape). In addition, a numerical approach for extracting Floquet states without full-matrix diagonalization is demonstrated, by filtering (or filter-diagonalization) a single wave function (or the correlation function) propagated under the  $(t, t')$  Hamiltonian. © 1997 American Institute of Physics. [S0021-9606(97)04717-X]

## INTRODUCTION

In the time-dependent approach for photodissociation, as championed by Heller,<sup>1</sup> the absorption cross-section is proportional, in the weak-field limit, to the Fourier-transform of the overlap between a time-dependent wave packet on a field-free potential surface, and the same wave packet at  $t=0$ . In this article we extend this approach to cases where the total Hamiltonian contains a strong time-dependent component, supplemented by a weak field

$$H = H_0(x, t) + V(x, t),$$

where  $x$  is the multi-dimensional coordinate, and  $V$  is the weak-field perturbation,

$$V(x, t) = \lambda(x) \cos(\omega t).$$

This general case occurs, e.g., for molecules in condensed phase probed by weak light sources, or for molecules acted upon by two laser sources: a strong fixed one, and a probing weak pulse. (The classes of system which are subjected to strong time-dependent Hamiltonians is not limited to molecules in a monochromatic field, and includes also molecules in strong chirped-pulse fields, or subsystems of molecules interacting with a strong bond.)

An example of a possible experimental realization of such a weak-field–strong-field combination is as follows. Recently very extensive studies of the non-linear dynamics in strong fields were carried out. Many studies are associated with the above-threshold-ionization spectra and with the probability to get very high harmonics when the atom is exposed to strong electromagnetic field.<sup>2</sup> In that case when the strong field is turned on sufficiently slowly and supports more than 10–15 oscillations before the field is turned off, one may assume that the field is periodic. Then for high fields (more than  $10^{13}$  W/cm<sup>2</sup>) there are indications that the system is prepared in a single resonance quasi-energy

state.<sup>3,4</sup> After a sufficiently long time since the strong field is turned on, the system is trapped into the longest-lived resonance state.

As long as the strong time-dependent field is on the system would find itself in the quasi-energy states rather than in the field-free eigenstates. A natural question is how and whether it is possible to observe these Floquet states. It is natural to suggest that by probing with a second weak laser pulse ( $V$ ) one may measure the probabilities of the transitions from one quasi-energy state to another. So far such an experiment has not been carried out.

The fact that formally (or even physically) we can view the molecules as lying in discrete or continuous Floquet states, which are analogous to bound-states, motivates examination of whether the same theoretical techniques used for studying weak-field transitions in the absence of a strong underlying field can be used to examine the weak-field-induced transitions in the presence of a strong field. In this work we show that with the appropriate modification, the usual expressions – involving an integral over a correlation-function which is evaluated independently of the probing weak field, and then filtered at any desired weak-field frequency – are also recovered here (in a very compact form).

We comment that there are studies in the literature of numerical techniques and methodologies for studying mixed systems, typically for two color lasers.<sup>5,6</sup> Our goal here is to suggest an alternate approach which automatically extracts the absorption cross-section spectrum for all weak-field frequencies from a single propagation – just like the time-dependent formula for the absorption cross-section complements basis-set based approaches.

Briefly, the development here is as follows. We first assume, as mentioned, that  $H_0$  has a periodic dependence on time with period  $T$ . (For some problems,  $T$  is naturally defined – e.g., the periodicity of the strong source in a two-pulse problem.) We then obtain a very simple expression for

the absorption-probability per unit time (Eq. (1.28)), reformulate this expression using the  $(t, t')$  approach, in which time-dependent Hamiltonians are formally converted into time-independent ones, and get an expression (Eq. (2.14)) which generalizes the formula for a time-independent  $H_0$ .

Our more detailed strategy is as follows. First we shall derive an expression for the survival probability in the presence of time-dependent perturbation. The initial state, however, is not an eigenstate of the field-free Hamiltonian but a quasi-energy Floquet state. (For the initial derivation, we assume that the Floquet quasi-energy is real-valued, but at the end of the paper we generalize our study, and account for the fact that under a strong-field the atomic/molecular system has a finite lifetime due to the presence of the strong electromagnetic field.) After some algebraic manipulations the expression for the absorption probability per unit time,  $J(\omega)$ , would be obtained. This expression is reminiscent of the Heller formula, except for an additional average over time. In the second step of the derivation the final compact expression for the photoabsorption probability (Eqs. (2.10) and (3.4)) will be obtained by using the  $(t, t')$  formulation.<sup>7</sup> By the  $(t, t')$  formalism the time evolution operator for a general time-dependent Hamiltonian has an exponential form similar to the time evolution operator when the Hamiltonian is time independent. The  $(t, t')$  formalism is based on the solution of differential equation where  $t'$  acts as additional coordinate. A simple proof for it has been given by Peskin and Moiseyev in Ref. 7 (see our Appendix which emphasize the fact that several time-dependent wave functions can be propagated simultaneously), another older proof is of Howland.<sup>8</sup> In the  $(t, t')$  formalism the generalization of the definition of the Hilbert space as proposed by Howland is used. For a study of the properties of this generalized inner product see the work of Pfeifer and Levine.<sup>9</sup>

In Section 4 we outline the usefulness of the expression. We show how the absorption cross section can be obtained by a repeated application of the generalized Hamiltonian, without a need to determine any Floquet state (beyond the initial state in which the system is placed). Further, we show how the result of the correlation-function integration yields (smeared) peaks at frequencies associated with a difference in energies between the eigenstates.

In Section 5 we present numerical results for a model continuously driven harmonic oscillator. The absorption spectrum has then discrete peaks, and is dominated by a few of those peaks. By either a long-time filtering or through filter-diagonalization we extract all peaks, i.e., all Floquet eigenvalues (without large-matrix diagonalization). The method is suitable for extracting similarly Floquet eigenstates.

## I. PHOTOABSORPTION PROBABILITY WITH TIME-DEPENDENT HAMILTONIANS

The first stage in our study is the derivation of an expression for the time-dependent absorption probability due to the weak laser-light, in the presence of the underlying time-dependent zeroth-order Hamiltonian. For this purpose we

pick  $|\phi(t=0)\rangle$ , an initial wave function, and define  $|\phi(t)\rangle$  and  $|\psi(t)\rangle$ , respectively, as the evolution of  $|\phi(t=0)\rangle$  under the periodic time-dependent field  $H_0(t)$  and the full Hamiltonian  $H(t)$

$$i \frac{d\phi}{dt} = H_0(t)\phi, \quad i \frac{d\psi}{dt} = H(t)\psi, \quad \psi(t=0) = \phi(t=0), \quad (1.1)$$

and the zeroth-order Hamiltonian, while time-dependent, has a periodicity  $T$ ,

$$H_0(t) = H_0(t+T), \quad (1.2)$$

an important feature in the derivations below. In contrast to  $|\phi(t)\rangle$  the wave function  $|\psi(t)\rangle$ , evolved under the influence of the total Hamiltonian  $H$  (including the weak field), is not periodic.

We now define the propagator  $U_0$  associated with  $H_0$ :

$$|\phi(t)\rangle = U_0(t \leftarrow 0) |\phi(t=0)\rangle, \quad (1.3)$$

which, while not translationally invariant, is invariant under shifts by  $T$ :

$$U_0(t+jT \leftarrow t'+jT) = U_0(t \leftarrow t'), \quad (1.4)$$

for all integers  $j$ .

We now turn to the definition of the absorption probabilities. First, note that the survival probability, i.e., the probability that under the action of the weak field  $\psi(t)$  would remain in its original time-dependent state  $|\phi(t)\rangle$ , is simply  $|a(t)|^2$  where

$$a(t) = \langle \phi(t) | \psi(t) \rangle. \quad (1.5)$$

The absorption probability per unit time has the form

$$J \equiv \lim_{t \text{ large}} \frac{1 - |a(t)|^2}{t}. \quad (1.6)$$

(As usual, the limit in Eq. (1.6) is really taken under the condition that the weak field is so weak that, at time  $t$ , it has not yet pumped appreciable magnitude away from the initial state—so a perturbative treatment is justified. Below we also assume, with no loss of generality, that  $t$  is an integer product of  $T$ .) The absorption probability can then be calculated by noting the following exact relation on  $\psi(t)$ :

$$\psi(t) = \phi(t) - i \int_0^t U_0(t \leftarrow t') V(t') \psi(t') dt'. \quad (1.7)$$

Indeed, this function fulfills  $i(\partial\psi/\partial t) = H\psi$ . For our purposes (evaluating  $a(t)$ ) a second-order perturbative iteration of Eq. (1.7) is required, yielding

$$\begin{aligned} \psi(t) = & \phi(t) - i \int_0^t U_0(t \leftarrow t') V(t') \phi(t') dt' - \int_0^t U_0(t \leftarrow t') \\ & \times V(t') \int_0^{t'} U_0(t' \leftarrow t'') V(t'') \phi(t'') dt' dt'' + O(V^3). \end{aligned} \quad (1.8)$$

When Eq. (1.8) is substituted into Eq. (1.3), it follows that

$$a(t) \equiv \langle \phi(t) | \psi(t) \rangle = 1 - iA - B + O(V^3), \quad (1.9)$$

where

$$A = \int_0^t \langle \phi(t') | V(t') | \phi(t') \rangle dt', \quad (1.10)$$

$$B = \int_0^t \int_0^{t'} \langle \phi(t') | V(t') U_0(t' \leftarrow t'') V(t'') | \phi(t'') \rangle dt' dt'',$$

so that

$$|a(t)|^2 = |(1 - iA - B)|^2 = 1 + A^2 - 2 \operatorname{Re} B - 2A \operatorname{Im} (B), \quad (1.11)$$

where we ignore  $O(V^3)$  terms. Thus we arrive at

$$J = \frac{1 - |a(t)|^2}{t} \cong \frac{-A^2}{t} + \frac{2 \operatorname{Re} B}{t} - \frac{(\int_0^t \langle \phi(t') | V(t') | \phi(t') \rangle dt')^2}{t} + 2 \operatorname{Re} \frac{1}{t} \int_0^t \int_0^{t'} \langle \phi(t') | V(t') U_0(t' \leftarrow t'') \times V(t'') \phi(t'') \rangle dt' dt''. \quad (1.12)$$

We will treat first the  $2 \operatorname{Re} B/t$  term (the  $-A^2/t$  term can be generally ignored, as proved in Appendix A). Our treatment would be based on the explicit form of  $V$  for weak fields:

$$V(x, t) = \lambda(x) \cos wt. \quad (1.13)$$

### A. Initial Floquet states

For a time-independent zeroth-order Hamiltonian  $H_0$ , a choice of a stationary initial state (with  $H\phi = \epsilon\phi$ ) yields very directly the celebrated formula for the absorption probability as a function of time,

$$J \propto \int \langle \lambda \phi | e^{-iH_0 t} | \lambda \phi \rangle e^{i\omega t} dt. \quad (1.14)$$

In the present case, where the Hamiltonian is time-dependent ( $H_0(t)$ ), we will employ in analogy the equivalent of a stationary initial state, i.e., a Floquet eigenstate (see below for details). As explained below, this would lead to a formula which is reminiscent of the Heller–Lax formula (and will be brought to an even more similar form in the next section). First recall the basic properties of Floquet eigenstates. A periodic Hamiltonian  $H_0$  possesses time-dependent solutions  $\phi_n(x, t)$ , which, while non-periodic, are made of a time-dependent phase times a periodic part,  $f_n$ :

$$\phi_n(x, t) = f_n(x, t) e^{-i\epsilon_n t}.$$

Formally, one labels  $\epsilon_n$  as quasi-energies, and  $f_n$  as quasi-stationary states, fulfilling

$$\left( -i \frac{\partial}{\partial t} + H_0(x, t) \right) f_n(x, t) = \epsilon_n f_n(x, t), \quad (1.15)$$

where  $f_n$  is a periodic function, with the same periodicity of  $H_0$

$$f_n(x, t+T) = f_n(x, t). \quad (1.16)$$

We then assume that the initial wave function is a specific Floquet state:  $\phi(x, t=0) = f_n(x, t=0)$ . (For a justification of this assumption, see below.) Using Eqs. (1.13)–(1.15) in Eq. (1.12), and the decomposition

$$2 \cos wt' \cos wt'' = \cos w(t' - t'') + \cos w(t' + t''), \quad (1.17)$$

yields

$$\frac{2 \operatorname{Re} B}{t} = \frac{2}{t} \operatorname{Re} \int_0^t dt' \int_0^{t'} dt'' \langle g(t') | U_0(t' \leftarrow t'') | g(t'') \rangle \times \frac{1}{2} (\cos w(t' - t'') + \cos w(t' + t'')) e^{-i\epsilon_n(t'' - t')}, \quad (1.18)$$

where

$$g(x, t) = \lambda(x) f_n(x, t).$$

We now further simplify the integral in Eq. (1.18). First, we define the term in the integrand as a correlation function (analogous to  $\langle \lambda \phi | e^{-iHt} | \lambda \phi \rangle$  for stationary states)

$$C(t', t'') = \langle g(t') | U_0(t' \leftarrow t'') | g(t'') \rangle, \quad (1.19)$$

and assume that it vanishes for large differences in time:

$$C(t', t'') \rightarrow 0 \text{ as } t' - t'' \rightarrow \infty. \quad (1.20)$$

(This assumption is similar to the assumption

$$\langle \lambda \psi(t) | \lambda \psi(0) \rangle \rightarrow 0 \text{ for } t \rightarrow \infty$$

in the usual derivation of the time-dependent photoabsorption formula, for a case in which the underlying Hamiltonian  $H_0$  is time-independent.)

At this stage, the derivation is almost complete, except that we need to convert the double time-integral to a single-integral. This is achieved here by employing the periodicity of  $H_0$ , as outlined in the remainder of this subsection.

In Eq. (1.18) the  $1/t$  term guarantees that only global contributions from large times need to be included. We can therefore assume  $t' \gg y$  (where  $y \equiv t' - t''$ ) and, using property (1.20), extend the second integration to  $\int_{-\infty}^{t'} dt''$  (rather than  $\int_0^{t'} dt''$ ). By changing variables to  $t'$  and  $y$ , it follows that

$$\frac{2 \operatorname{Re} B}{t} = \frac{1}{t} \operatorname{Re} \int_0^t dt' \int_0^\infty dy C(t', t' - y) e^{i\epsilon_n y} \times \{ \cos wy + \cos[w(2t' - y)] \}. \quad (1.21)$$

We now assume (as mentioned) with no loss of generality that  $t$  is an integer multiple of  $T$ ,

$$t = NT, \quad (1.22)$$

and replace the integration variable  $t'$  by  $m, \tau$  where

$$t' = \tau + mT, \quad (1.23)$$

with

$$0 < \tau < T, \quad (1.24)$$

and

$$m = 0, \dots, N-1, \quad (1.25)$$

so that using the periodicity properties of  $U_0$ , it follows that:

$$\frac{2 \operatorname{Re} B}{NT} = \frac{1}{NT} \int_0^T d\tau \sum_{m=0}^{N-1} \int_0^\infty dy \langle g(\tau) | U_0(T \leftarrow T-y) | g(\tau-y) \rangle \times e^{i\varepsilon_n y} \left[ \frac{1}{2} \cos wy + \frac{1}{2} \cos(w(2\tau-y+2mT)) \right]. \quad (1.26)$$

We now switch the order of  $\int dy$  and  $\sum_m$ , and note that the second term in Eq. (1.26) vanishes then in general for any  $w \neq (i/2)w_0$  (where  $w_0 = 2\pi/T$  and  $j$  is an integer)

$$\frac{1}{N} \sum_{m=0}^{N-1} \cos((2\tau-y)w + 2m\omega T) = \frac{\sin N\tau w}{N \sin T w} \cos(w(2\tau-y) + wNT) \rightarrow 0$$

for  $Tw \neq \pi j$  as  $N \rightarrow \infty$ . (1.27)

[Note that the  $w \neq jw_0/2$  condition has a physical interpretation: perturbation theory breaks down then since two ( $\omega$ ) photons will mix two Floquet states of the unperturbed system.] Equation (1.26) results then at

$$J = \frac{1}{T} \operatorname{Re} \int_0^T d\tau \int_0^\infty dy C(\tau, \tau-y) \cos \omega y e^{i\varepsilon_n y}. \quad (1.28)$$

This simple expression for the absorption probability is reminiscent of the Heller–Lax formulae, except for an additional average over time ( $1/T \int_0^T d\tau$ ). We will now reformulate expression (1.28) to look even more closely associated with the former formula, by using the  $(t, t')$  formalism.

## II. ABSORPTION PROBABILITY WITH THE $(T, T')$ FORMALISM

The  $(t, t')$  formalism is a simple approach to reformulate time-dependent Hamiltonians to have a time-independent-like form. It allows expansion of the powerful numerical algorithms employed in time-dependent formalisms for time-dependent cases, at a price of introducing an extra degree of freedom, which is added to the spatial degrees of freedom  $x$ . (Here, however, it turns out that an extra time-degree of freedom ( $y$ ) is required even in the direct approach—see Eq. (1.28)—so that no additional effort is required when we use the  $(t, t')$  formalism.)

In our case, the generalization proceeds as follows. Define an extra time-coordinate  $t'$  (not directly associated with  $t$  in Section I) and define

$$\mathcal{H}_0(x, t') = H_0(x, t') - i \frac{\partial}{\partial t'}. \quad (2.1)$$

The spatial grid is then replaced by a grid for the generalized coordinate  $(x, t')$ , and the wavefunction is replaced by a generalized function  $\Phi(x, t', t)$  such that<sup>7-9</sup>

$$i \frac{\partial}{\partial t} \Phi(x, t', t) = \mathcal{H}_0(x, t') \Phi(x, t', t). \quad (2.2)$$

As shown by Peskin and Moiseyev<sup>7</sup> it is easy to prove that the function  $\phi(x, t)$  defined by

$$\phi(x, t) = \Phi(x, t' = t, t) \quad (2.3)$$

fulfills the Schrödinger equation

$$i \frac{\partial}{\partial t} \phi(x, t) = H(x, t) \phi(x, t). \quad (2.4)$$

Thus, the solution of the time-dependent wave function can be found using efficient methods suitable for time-independent Hamiltonians, at the cost of the extra coordinate.

Usually, the initial condition on  $\Phi$  is taken to be constant in  $t'$ :

$$\Phi_0(x, t', t=0) = \phi(x), \quad (2.5)$$

where  $\phi$  is a desired initial function. This solution is sufficient when one is interested only in a single initial condition. For our purposes, however, the underlying Floquet function (in the presence of  $H_0$  alone) is  $t'$  dependent. This is not a difficulty, since any “ray”  $t' = t + \text{const.}$  (not only the ray  $t = t'$ ) corresponds to a solution of the Schrödinger equation. For a proof, see Appendix B.

In our case we therefore chose as an initial function  $\Phi$ :

$$\Phi(x, t', t=0) = g(x, t') = \lambda(x) f_n(x, t'). \quad (2.6)$$

Note that we include only the periodic part of the full Floquet wave function. We can formally write Eq. (2.2) as (see Appendix C)

$$\Phi(x, t', t) = g(x, t') = \langle \langle x, t' | e^{-i\mathcal{H}_0 t} | \Phi_0 \rangle \rangle = \langle x | U_0(t' \leftarrow t' - t) | g(t' - t) \rangle. \quad (2.7)$$

Note that the double-bracket in the left-hand side of this equation refers to a generalized  $x, t'$  space (we define  $\langle \langle \dots \rangle \rangle \equiv (1/T) \int_0^T dt' \int dx \dots$ ) and that the single bracket refers to  $x$  alone. By substituting Eq. (2.7) into Eq. (1.19) it follows that

$$C(t', t' - t) = \int g^*(x, t') \Phi(x, t', t) dx. \quad (2.8)$$

Thus, using Eq. (1.28) (and replacing  $\tau \rightarrow t', y \rightarrow t$ ) it follows that the absorption rate equation becomes

$$J = \frac{1}{T} \operatorname{Re} \int_0^T dt' \int_0^\infty dt e^{i\varepsilon_n t} \cos wt \int g(x, t') \Phi(x, t', t) dx = \operatorname{Re} \int_0^\infty dt e^{i\varepsilon_n t} \cos wt \times \left[ \frac{1}{T} \int_0^T \int \Phi^*(x, t', 0) \Phi(x, t', t) dx dt' \right], \quad (2.9)$$

which, using the definition of the inner product in the generalized Hilbert space,<sup>7,8</sup> leads to

$$J = \text{Re} \int_0^\infty dt e^{i\epsilon_n t} \cos \omega t \langle \langle \Phi(0) | \Phi(t) \rangle \rangle. \quad (2.10)$$

This is the desired equation, which shows that to calculate the full absorption probability it is only necessary to propagate  $\Phi$  under the generalized space Hamiltonian  $\mathcal{H}_0$ , calculate the generalized correlation function  $\langle \langle \Phi(0) | \Phi(t) \rangle \rangle$ , and then filter it at any desired frequency. Even more importantly than the calculational prescription, the formula is conceptually attractive as it casts the absorption formula developed for time-independent Hamiltonians as a general approach valid also for time-dependent Hamiltonians.

### III. PHOTOABSORPTION FOR DISSOCIATING SYSTEMS

So far our proof assumed that the Floquet quasi-eigenstate of  $H_0$  that we start from is a true bound state, so that the associated Floquet eigenvalue  $\epsilon_n$  is a real quantity. In practice, however,  $\epsilon_n$  is most often complex (corresponding to leakage, i.e., dissociation), and the associated ‘‘eigenstate’’ is really a resonance state. For narrow resonances ( $\text{Im}(\epsilon_n) \sim 0$ ) Eq. (2.10) would still converge (since  $\langle \langle \Phi(0) | \Phi(t) \rangle \rangle$  would be small long before the exponential increase of  $e^{i\epsilon_n t}$ ). For broader resonances Eq. (2.10) needs to be modified, but the extension is straightforward, as shown below.

The tools generally used to incorporate the possibility of dissociation in a finite-basis calculations are either the complex scaling approach (see, e.g., Refs. 10 and specifically for quasi-energy complex-scaled states see, e.g., Ref. 11), or negative imaginary potentials (Ref. 12) (for resonance applications see, e.g., Ref. 13). With either method<sup>14</sup> almost all eigenvalues (in the presence of the field) are complex, and the field-free bound-states become resonant states with complex eigenvalues,  $\epsilon_n = \epsilon_{nR} - i\Gamma_n/2$ . The resonance quasi-energies, regardless of their lifetime (i.e., narrow, broad, or overlapping resonances) are associated with square-integrable quasi-energy solutions.

The derivations done so far for real  $\epsilon_n$  (bound-states) automatically extend to the complex  $\epsilon_n$  case (resonances), provided one uses the c-product (see Ref. 15 for detailed discussion) rather than the conventional scalar product. In practice, this simply means here that we associate with the state  $\phi(x, t)$  a left-bra state,  $\phi^L(x, t)$ , defined as

$$i \frac{d}{dt} \phi^L = -H_0 \phi^L. \quad (3.1)$$

(Note that if  $H_0$  would have been time-independent, then  $H^0$  would be  $\phi^L = \exp(+iHt)\phi$ .)

Even though the Hamiltonian is now complex (accounting for dissociation), it still remains true that

$$\langle \phi^L(t) | \phi(t) \rangle \equiv \int \phi^L(x, t) \phi(x, t) dx = 1,$$

where we assumed that at  $t=0$ ,  $\phi$  is taken to fulfill

$$\phi^L(t=0) = \phi(t=0)$$

and

$$(\phi(t=0) | \phi(t=0)) = 1. \quad (3.2)$$

The introduction of  $\phi^L$  allows a generalized definition of an absorption amplitude, which is now

$$a(t) = (\phi^L(t) | \psi(t)). \quad (3.3)$$

In general,  $a(t)$  measures the probability-amplitude for a (decaying)  $\psi$  to still contain the (decaying)  $\phi$ . (The states decay, but not necessarily their coefficients  $a$ .) In the absence of the weak field, the survival probability defined in this way is still equal to 1 (in spite of the decay of  $\phi(t)$ ). Therefore, the absorption probability per unit time, as defined in Eq. (1.6), is equal to 0 (as it should) in the absence of the external weak field, while with the weak field it is still equal to  $(1 - |a_n(t)|^2)/t$  for large  $t$ . The remainder of the proof goes as before, with particular care in the ‘‘bra’’ terms.<sup>16</sup> It thus follows that the final equation for the absorption probability, Eq. (2.10), becomes here

$$J(\omega) = \text{Re} \int_0^\infty dt e^{+(\Gamma_n/2)t} e^{+i\epsilon_n t} \cos \omega t \langle \langle \Phi(0) | \Phi(t) \rangle \rangle. \quad (3.4)$$

The exponential increase in the expression for  $J$  can be compensated by the inherent decaying of  $|\Phi\rangle$  (and further, as in the real  $\epsilon_n$  case, by the damping of the generalized correlation function).

### IV. THE ABSORPTION CROSS SECTION

In this section we derive several expressions for formal and numerical analysis of the frequency-dependent absorption probability, Eq. (3.4). These expressions are entirely analogous to well-known expressions derived when  $H_0$  is time-independent.

First, we note that a very efficient approach for propagating  $|\Phi(t)\rangle$  forward in time is through a polynomial expansion of the evolution operator,

$$e^{-i\mathcal{H}_0 t} |\Phi\rangle = \sum_l a_l(t) R_l(\mathcal{H}_0) |\Phi\rangle,$$

where  $R_l$  are polynomials in  $\mathcal{H}_0$  (e.g., Lancosz,<sup>17</sup> Chebyshev,<sup>18</sup> Newton,<sup>19</sup> Favre,<sup>20</sup> or modified Chebyshev polynomials<sup>21</sup>), and  $a_l$  are associated numerical coefficients. (For an application of Chebyshev polynomials with the  $(t, t')$  formalism, see Ref. 18b.) Denoting by  $T_{\max}$  a time for which the correlation function in Eq. (3.4) vanishes, it follows that

$$J = \sum_l (b_l(\epsilon_n - w) + b_l(\epsilon_n + w)) \langle \langle \Phi | R_l(\mathcal{H}_0) | \Phi \rangle \rangle, \quad (4.1)$$

where

$$b_l(E) = \int_0^{T_{\max}} a_l(t) e^{iEt} dt.$$

(Note that due to the fact that the argument of  $b_l$  is here complex (since  $\epsilon_n$  is) there will be a difficulty in applying expressions<sup>18,20,21</sup> geared for the case that  $T_{\max} = \infty$ .)

Next we note that a formally equivalent way to rewrite Eq. (3.4) is

$$\begin{aligned}
J &= \text{Re} \left\langle \left\langle \Phi \left| \int_0^\infty \cos wte^{i\varepsilon_n t} \right| \Phi(t) \right\rangle \right\rangle dt \\
&= \text{Im} \left( \left\langle \left\langle \Phi \left| \frac{1}{\varepsilon_n + w - \mathcal{H}_0} \right| \Phi \right\rangle \right\rangle \right. \\
&\quad \left. + \left\langle \left\langle \Phi \left| \frac{1}{\varepsilon_n - w - \mathcal{H}_0} \right| \Phi \right\rangle \right\rangle \right). \quad (4.2)
\end{aligned}$$

In the derivation of Eq. (4.2) we assume that the integral (3.4) converges with time, which is equivalent to requiring that no resonance is narrower than  $\varepsilon_n$ . (Physically, this is due to the fact that even if we were to start the system in a wide resonance, the magnitude of the coefficient  $a$  in Eq. (3.3) would be larger than 1 due to transitions to narrower resonances.)

Finally, we show how the peaks in  $J(\omega)$  correspond to transitions between different Floquet states. We note that the eigenstates  $f_m(x, t')$  of  $\mathcal{H}_0$ , fulfilling

$$\left( H_0(x, t') - i \frac{\partial}{\partial t'} \right) f_m = \varepsilon_m f_m$$

and

$$f_m(x, T) = f_m(x, 0),$$

are simply the periodic parts of the Floquet eigenstate of  $H_0$ . (Each Floquet state is associated with other Floquet states with frequencies equispaced by  $w_0 = 2\pi/T$ ; the number of such states depends on the grid-discretization of  $t'$ .)

The operator  $\mathcal{H}_0$  can be resolved in terms of these eigenstates, so the spectral representation of the Green's operator is

$$\frac{1}{\varepsilon_n + w - \mathcal{H}_0} = \sum_n |f_m\rangle \frac{1}{\varepsilon_n + w - \varepsilon_m} \langle\langle f_m|$$

and therefore the absorption probability becomes

$$\begin{aligned}
J(w) &= \text{Re} \sum_n \langle\langle f_n | \lambda | f_m \rangle \rangle^2 \left( \frac{1}{\varepsilon_n + w - \varepsilon_m} \right. \\
&\quad \left. + \frac{1}{\varepsilon_n - w - \varepsilon_m} \right), \quad (4.3)
\end{aligned}$$

showing that a peak in  $J$  would result whenever  $w = \pm \text{Re}(\varepsilon_n - \varepsilon_m)$ , as expected, with the peak magnitude proportional to the overlap between the two states over the difference in the resonance widths.

At this point we need to clarify the use of Floquet states in Eq. (4.3). Just like the usual time-dependent formula (1.14) (or the equivalent of Eq. (4.1)), Eq. (3.4) refers to direct propagation in time, not using Floquet states. Thus, Eqs. (3.4) and (4.1) can be used even in the case where a very large number of Floquet states exists for the system (so that extraction of all these eigenstates would be impractical). The only Floquet state that needs to be an input to expression (3.4) or (4.1) is the initial state,  $f_n$ , but this state is easily extracted by repetitive application of  $\exp(-i\mathcal{H}_0 t)$  (similarly,

in Eq. (1.14) the initial  $\phi_0(x)$  state needs to be given). The position of any other Floquet eigenvalues *need not be determined here a priori*.

## V. APPLICATIONS

The formalism studied here can be applied in two ways. First, to obtain a physical measure of absorption from one Floquet state to another (or, in the case of absorption probabilities, to all other Floquet states) due to the weak laser. This suggests naturally that such transitions can be studied experimentally.

A second way in which the results of the paper are useful is numerical, in that they show that a single  $(t, t')$  propagation of  $\Phi$  can lead to extraction of multiple time-dependent Floquet eigenstates, from a Fourier-transform of  $\Phi$  (or of the correlation function).<sup>22</sup>

We illustrate here the two applications on a model problem of a continuously driven harmonic oscillator, with linear polarization:

$$H_0 = \frac{\mathbf{J}^2}{2I} + D \cos \Omega t \cos \theta,$$

where  $D$  is the product of the field strength and the dipole moment.

The calculations are done in an  $m=0$  spherical basis:

$$|j\rangle \equiv |y_{j0}(\theta, \phi)\rangle.$$

For this study, we used the following model parameters:  $D=5.466, I=24, \Omega=1$  (all in a.u.) and a limited basis,  $j=0, \dots, 9$ , was employed. (The lower Floquet states are converged with this choice.) Thus, the zeroth-order Hamiltonian we study is a  $10 \times 10$  time-dependent matrix

$$(H_0)_{j,j'}(t) = \frac{j(j+1)}{2I} \delta_{j,j'} + D \cos \Omega t \langle j | \cos \theta | j' \rangle,$$

For calculating the absorption cross-section in the presence of the field we obtain first a Floquet eigenstate  $\phi_n(j, t)$  of  $H_0$  (either by traditional approaches or by filtering — see below for more details). With a traditional floquet state extraction, a total of 4096 grid points in time are used to minimize the error in the final  $\phi_n(j, t)$ . The initial wave function for the  $t, t'$  propagation is then obtained by storing the Floquet state, at *different* times, on the  $t'$  grid

$$\Phi(j, t', t=0) = e^{i\varepsilon_n t'} \langle j | \cos \theta | \phi_n(\theta, t) \rangle$$

(where the exponential is used, as explained above, to extract the periodic part of the Floquet state).

We then simply propagate  $\Phi$  under the  $t$ -independent Hamiltonian  $\mathcal{H}_0 (= H_0 - i\partial/\partial t')$  on the  $j, t'$  grid at all times  $t$ , and use it to construct

$$C(t) = \frac{1}{T} \sum_j \int \Phi^*(j, t', t=0) \Phi(j, t', t) dt'$$

(with  $T=2\pi/\Omega$ ). In computing  $\Phi(j, t', t)$ , we do not use all 4096 grid points in  $t'$ . Instead, we only sample 32 points out

of the 4096 points which are enough for convergence. Thus, the  $(t, t')$  calculation converges with a much larger time step.

From the correlation function we obtain the absorption spectrum using Eq. (3.4). Specifically, a relatively large time step was taken ( $dt=1$ ) and the  $(t, t')$  wave function  $|\Phi(t)\rangle$  was propagated with a Chebychev algorithm<sup>18a,18b</sup> using 70 terms for each time step. Here,  $J(\omega)$  would be a series of isolated peaks since all Floquet eigenvalues are real (there is no amplitude damping mechanism). The content of the spectrum is then both the strength of the peaks, and their locations.

Two methods were then used to analyze the signal. First, a numerical construction of  $J(\omega)$  with a total time of up to 6000 a.u. A related approach would be to simply calculate the regular half-Fourier spectrum of  $C(t)$

$$C(\omega) = \text{Re} \int_0^{\infty} e^{i\omega t} C(t) dt. \quad (5.1)$$

Alternately, we use a short-time segment of the signal to extract the Floquet state by filter-diagonalization.<sup>23</sup> This approach ‘‘circumvents’’ the Heisenberg principle by combining a short-time filter of  $C(t)$  at any desired spectral range, which is then used to construct a *small* matrix whose eigenvalues are the desired energies at the desired range. For details of the method see Refs. 23.

The two approaches give, upon their convergence, identical results for the spectrum, as explicitly verified for this model system. First, using either the explicit absorption spectrum formula (2.10) or the related (5.1), Figure 1 shows that upon starting with a Floquet eigenstate with the eigenvalue  $-0.4056529$  (the initial state is labeled arbitrarily here at  $\epsilon_0$ ; the energy levels do not reflect the order of the zero-field states) the most intense absorption is to two neighboring states at energies  $-0.210546$  and  $-\hbar\Omega + 0.422976$ . Similarly, the absorption spectrum peaks at the difference between these eigenvalues and the initial Floquet energy. This is reminiscent of the  $j \pm 1$  absorption peaks for a usual rigid rotor (without the strong field component).

Next, we used filter-diagonalization to pick Floquet energies from the Fourier spectrum (or the absorption spectrum). This approach requires a much shorter time and resolves all these states with little error (see Table I), within a short time (100–200 a.u. here, i.e., no more than 32 optical cycles, and a factor of 30 smaller than the time (6000 a.u.) required to extract the eigenfrequencies by filtering alone).

## VI. CONCLUSIONS

Heller’s expression for the absorption cross-section in the weak field limit is extended here (Eqs. (2.10), (3.4), (4.1), (4.2)) to cases where the total Hamiltonian contains a strong time-periodic component, supplemented by a weak field which is not in resonance with the strong original component. Like the situation for time-independent Hamiltonians, the system must initially be an eigenstate of the field – except that here the eigenstate is a Floquet state.

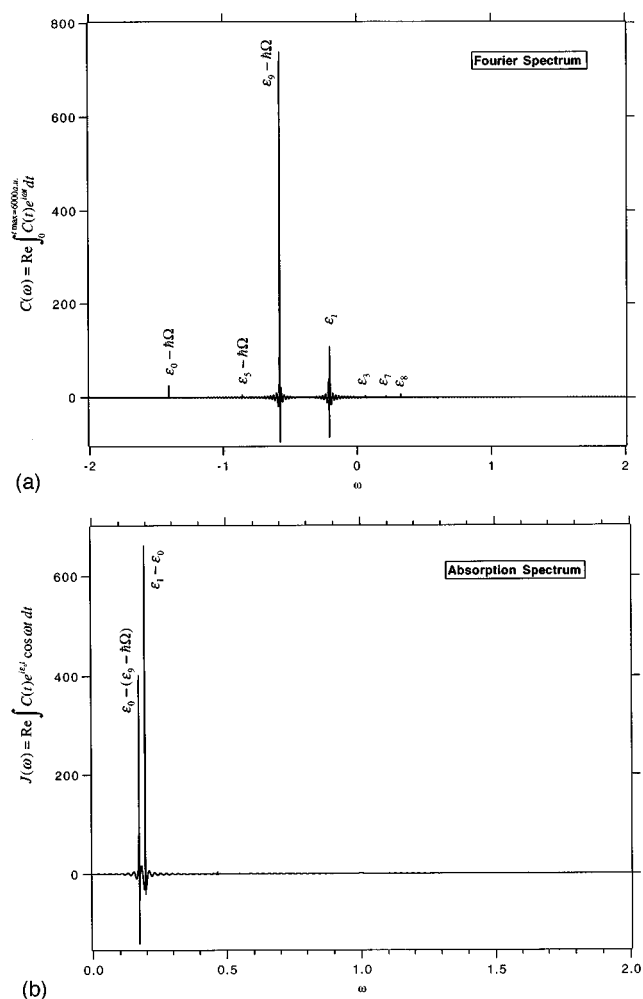


FIG. 1. Shown are (a) the Fourier-transformed correlation function (Eq. (5.1)) and (b) the absorption spectrum (Eq. (2.10) or (3.4)) for the model of the continuously driven harmonic oscillator (driven with  $\Omega=1$ ), started in a specific Floquet state ( $\epsilon_n = -0.4056529$ ), and probed by the weak laser, as a function of the latter’s frequency ( $\omega$ ). The peaks in (a) correspond to neighboring eigenvalues (difference eigenvalues in (b)) that are strongly absorbing, like a  $j \pm 1$  absorption rule in the usual rigid rotor. Also note an  $\epsilon_n - \hbar\Omega$  peak in (a), and several small peaks associated with other Floquet states. Finally, note that the energy labeling is arbitrary; we label the energies by their order in Table I. Thus, the peaks in the absorption spectrum at  $\epsilon_0 - (\epsilon_0 - \hbar\Omega)$  and  $\epsilon_1 - \epsilon_0$  simply signals that the states ( $\epsilon_0$  and  $\epsilon_1$ ) are close in energy, modulus  $\hbar\Omega$  (Ref. 26).

The derivation naturally separates the effects of a strong time-dependent perturbation and the weak probing field. For example, the strong time-dependent component can be a fluctuating field changing the vibrational environment of a molecule (e.g., in a cage) but not inducing electronic-transitions. Then, expressions (2.10) and (3.4) show that, if the system is in an initial ‘‘eigenstate-like’’ state (i.e., Floquet state) then we can think of its evolution in time after excitation as proceeding as a new wave packet (in time and position) which evolves on the electronically excited state. One other very useful case where the system is in a Floquet state is adiabatic evolution<sup>24</sup> (e.g., due to a slow time-dependence of an external field).

Other useful examples are pulsed-excitations, or mixing

TABLE I. Floquet states obtained from  $C(t)$  by filter-diagonalization, as a function of the length of the time segment used for the extraction. Shown are the true eigenvalues (obtained by traditional approaches) and the eigenvalues obtained with segments of length  $T=100$  a.u. (16 strong-field optical cycles), 200 a.u., and 600 a.u. Also shown are an internal error-measure of the filter-diagonalization approach and the absolute error (relative to the true eigenvalues).

True Floquet eigenvalues with field	Filter-diagonalization		
	$t=100.0$ a.u.	$t=200.0$ a.u.	$t=600.0$ a.u.
0.422976	0.4229976	0.4229976	0.4229976
Intrinsic error	0.00	0.00	0.00
Absolute error	0.00	0.00	0.00
0.3251242	0.3250923 0.0000074 0.0000319	0.3251263 0.00 0.0000021	0.3251242 0.00 0.00
0.2170691	0.2168519 0.0000913 0.0002172	0.2170691 0.00 0.00	0.2170691 0.00 0.00
0.2152128	0.2152119 0.0000007 0.0000009	0.2152128 0.00 0.00	0.2152128 0.00 0.00
0.1444449	0.1444453 0.00 0.0000004	0.1444449 0.00 0.00	0.1444449 0.00 0.00
0.1407065	0.1407126 0.0000355 0.0000061	0.1407059 0.00 0.0000006	0.1407065 0.00 0.00
0.0606168	0.0606178 0.0000011 0.0000010	0.0606174 0.00 0.0000006	0.0606168 0.00 0.00
-0.0349729	-0.0349819 0.0000071 0.0000090	-0.0349742 0.00 0.0000013	-0.0349729 0.00 0.00
-0.2105464	-0.2105463 0.00 0.0000001	-0.2105464 0.00 0.00	-0.2105464 0.00 0.00
-0.4056529	-0.4056527 0.00 0.0000002	-0.4056529 0.00 0.00	-0.4056528 0.00 0.0000001

of a strong-laser and weak laser pulses.<sup>5,6</sup> Even for non-periodic initial Hamiltonian, provided the duration of the laser pulse is sufficiently long to support more than  $\approx 15$  oscillations of the field, the approach can still be applied. Further, if the strong component is due to a laser-pulse, it need not even have a “sin” structure but can be an arbitrary mixture of harmonics (e.g., a periodic chirp). Thus, if the system can be experimentally prepared in a specific Floquet state (or, if sufficient time is allowed, winds in the one with the smallest resonance width) then this Floquet state can be “probed” by excitations by a weak pulse – just like a bound-state can, and with the same paradigm of wave packet

“motion away from the excitation region,” as usually associated with time-independent Hamiltonian-evolution.

## ACKNOWLEDGMENTS

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## APPENDIX A: PROOF THAT THE $A^2$ TERM CAN BE IGNORED

Here we prove that the contribution of the  $A^2/t$  term to Eq. (1.12) vanishes for the “cos” potential (see Eq. (1.13)), also when the initial state is the time-periodic Floquet state,  $f_n(x, t') = f_n(x, t' + T)$ . Specifically

$$\begin{aligned} \frac{A^2}{t} &= \frac{1}{t} \left( \int_0^t \langle \phi(t') | V(t') | \phi(t') \rangle dt' \right)^2 \\ &= \frac{1}{t} \left( \int_0^t \langle f_n(t') | \lambda(x) \cos(\omega t') | f_n(t') \rangle dt' \right)^2 \end{aligned}$$

and the transformation

$$t' \rightarrow t' + mT; \quad m = 0, \dots, N-1$$

is carried out then ( $0 \leq t' \leq T$ )

$$\begin{aligned} \frac{A^2}{t} &= \left( \frac{1}{\sqrt{NT}} \int_0^T \langle f_n(t') | \lambda(x) \right. \\ &\quad \left. \times \sum_{m=0}^{N-1} \cos \omega(t' + mT) | f_n(t') \rangle dt' \right)^2. \end{aligned}$$

However, for  $\omega \neq 2\pi/T$ , it is clear that

$$\frac{1}{\sqrt{N}} \sum_{m=0}^{N-1} \cos \omega(t' + mT) \rightarrow 0 \quad \text{as } N \rightarrow \infty,$$

and therefore

$$\frac{A^2}{t} \rightarrow 0$$

for large  $t$ . The proof is formally valid when  $\epsilon_n$  is real, but would also be useful when it has an imaginary part that is not too large.

## APPENDIX B: MULTIPLE TIME-DEPENDENT WAVE FUNCTIONS FROM A SINGLE $t, t'$ EVOLUTION

Usually, one picks an initially  $t'$ -independent functions in the  $(t, t')$  formalism, i.e.,  $\Phi$  is taken to be constant in  $t'$  at  $t=0$ . Here however we note that there is no formal reason to choose only the  $t=t'$  ray, and useful information can be obtained from any ray  $t=t'+\text{const}$ . Indeed, we see that for any constant  $r$ , the function

$$\eta_r(x, t+r) \equiv \Phi(x, t+r, t)$$

fulfills the original Schrödinger equation

$$i \frac{\partial \eta_r}{\partial t} = H(x, t+r) \eta_r(x, t+r).$$

Proof (using Eq. (2.2)):

$$\begin{aligned} i \frac{\partial \eta_r}{\partial t} &= i \frac{d\Phi(x, t+r, t)}{dt} \\ &= i \frac{\partial \Phi(x, t+r, t)}{\partial t} \Big|_{t=t'+r} + i \frac{\partial \Phi(x, t+r, t)}{\partial t} \Big|_{t=t'+r} \\ &= H(x, t+r) \Phi(x, t+r, t) = H(x, t+r) \eta_r(x, t+r). \end{aligned}$$

This leads here naturally to a choice of an initial function  $\Phi(x, t', t=0)$  which is  $t'$ -dependent.

The proof above implies that by a single propagation of  $\Phi$  from 0 to  $t$ , we obtain a set of physical wave functions  $\eta_r$ , each propagated from a time  $t$  to a later time  $t+r$ . The true Hamiltonian underlying the propagation of each function  $\eta_r$  is of course time-dependent: At the beginning of the propagation it is  $H(x, r)$ , and with the  $t, t'$  evolution of the  $\Phi$  function from 0 to  $t$  this physical Hamiltonian evolves (it is  $H(x, t+r)$ ).

### APPENDIX C: PROOF OF (2.7)

Using Appendix B it is clear that

$$U_0(t+r \leftarrow r)g(r) = [e^{-i\mathcal{H}_0 t} \Phi_0]_{t'=t+r}$$

where the initial state for the  $t, t'$  propagation is

$$\Phi(x, t'=r, 0) = g(x, r).$$

The wave function  $\Phi(x, t', t)$  is obtained first, and then the set of “cuts”  $t'=t+r$  is taken. Then

$$U_0(t+r \leftarrow r)g(r) = \Phi(x, t', t) \Big|_{t'=t+r} = \Phi(x, t+r, t).$$

Let us substitute

$$r = t' - t$$

and we get that

$$U_0(t' \leftarrow t' - t)g(t' - t) = \Phi(x, t', t) \Big|_{t'=t+r} = \Phi(x, t+r, t)$$

as required.<sup>25</sup>

<sup>1</sup>E. J. Heller, *Act. Chem. Res.* **14**, 368 (1981). For earlier developments, see R. G. Gordon, *Adv. Magn. Reson.* **3**, 1 (1968).

<sup>2</sup>See, for example, Proceedings of the Annual Meeting of the American Optical Society, Quebec, Canada, 1995. Also see: *Atoms in Intense Laser Fields*, edited by Mihai Gavrilă (Academic, Boston, 1992).

<sup>3</sup>N. Ben-Tal, N. Moiseyev, R. Kosloff, and C. Cerjan, *J. Phys. B* **26**, 1445 (1993).

<sup>4</sup>One indication is that there seem to be no interference peaks in the ATI spectrum, which is equispaced – pointing at a single initial Floquet state.

<sup>5</sup>T. S. Ho, S. I. Chu, and J. U. Tietz, *Chem. Phys. Lett.* **96**, 464 (1983).

<sup>6</sup>M. Dorr, R. M. Potvliege, D. Proulx, and R. Shakeshaft, *Phys. Rev. A* **44**, 574 (1991).

<sup>7</sup>U. Peskin and N. Moiseyev, *J. Chem. Phys.* **99**, 4590 (1993).

<sup>8</sup>J. S. Howland, *Math. Ann.* **207**, 315 (1974); *Indiana University Math. J.* **28**, 471 (1979).

<sup>9</sup>P. Pfieler and R. D. Levine, *J. Chem. Phys.* **79**, 5512 (1983).

<sup>10</sup>W. P. Reinhardt, *Ann. Rev. Phys. Chem.* **33**, 223 (1982); B. R. Junker, *Adv. At. Mol. Phys.* **18**, 207 (1982); N. Moiseyev, *Isr. J. Chem.* **31**, 311 (1991).

<sup>11</sup>H. J. Korsch and N. Moiseyev, *Phys. Rev. A* **42**, 4045 (1990); *Isr. J. Chem.* **30**, 107 (1990).

<sup>12</sup>D. Neuhauser and M. Baer, *J. Chem. Phys.* **90**, 4351 (1989).

<sup>13</sup>G. Jolicard and E. J. Austin, *Chem. Phys. Lett.* **121**, 106 (1985); D. Neuhauser, *J. Chem. Phys.* **95**, 4927 (1991).

<sup>14</sup>In complex scaling, the transformation is  $f_{n_{\text{res}}}(x, t) \rightarrow 0$  as  $|x| \rightarrow \infty$ , where  $x = x' e^{i\theta}$  is the rotational angle, and  $x'$  is a real variable, ranging throughout  $(-\infty, \infty)$  (see the reviews in Ref. 10). When negative imaginary potentials,  $-iV_I$ , are used,  $H$  is supplemented by  $-iV_I$ ; for proper forms of  $V_I$ , see, e.g., Ref. 12.

<sup>15</sup>N. Moiseyev, in *Lecture Notes in Physics*, edited by E. Brandas and N. Elander (Springer, New York, 1984), Vol. 211; N. Moiseyev, P. R. Certain, and F. Weinhold, *Mol. Phys.* **36**, 1613 (1978).

<sup>16</sup>In particular, the expression for the second-order term  $B$  in (1.10) is still valid, since  $(\phi^L(t)|U_0(t \leftarrow t') = (\phi^L(t')|$ .

<sup>17</sup>E. Haller, L. S. Cederbaum, and W. Domke, *Mol. Phys.* **41**, 1291 (1980); G. Moro and J. H. Freed, *J. Phys. Chem.* **84**, 2837 (1980); R. A. Friesner, J. P. Brunet, R. E. Wyatt, and C. Leforestier, *J. Supercomp. Appl.* **1**, 1 (1987); O. Kollin, C. Leforestier, and N. Moiseyev, *J. Chem. Phys.* **89**, 6836 (1988).

<sup>18</sup>(a) R. Kosloff, *J. Phys. Chem.* **92**, 2087 (1988); (b) U. Peskin, R. Kosloff, and N. Moiseyev, *J. Chem. Phys.* **100**, 8849 (1994); (c) D. Neuhauser, *ibid.* **93**, 2611 (1990).

<sup>19</sup>H. Tal-Ezer, R. Kosloff, and C. Cerjan, *J. Comp. Phys.* **100**, 179 (1992); S. M. Auerbach and C. Leforestier, *Comp. Phys. Commun.* **78**, 55 (1993).

<sup>20</sup>D. K. Hoffman, M. Arnold, W. Zhu, and D. J. Kouri, *J. Chem. Phys.* **99**, 1124 (1993).

<sup>21</sup>V. A. Mandelshtam and H. S. Taylor, *J. Chem. Phys.* **103**, 2903 (1995).

<sup>22</sup>The extraction of Floquet states by filtering the  $(t, t')$  wave function is independently pursued by J. Wells — we thank him for correspondence on this fact.

<sup>23</sup>D. Neuhauser, *J. Chem. Phys.* **100**, 5076 (1994); M. R. Wall and D. Neuhauser, *ibid.* **102**, 8011 (1995); J. W. Pang and D. Neuhauser, *Chem. Phys. Lett.* **252**, 173 (1996); see also Ref. 18c.

<sup>24</sup>For example, most recently Jungwirth and Gerber have demonstrated that the dynamics of very large weakly bound systems is often described by set of coupled one dimensional time-dependent Hamiltonian (P. Jungwirth and R. B. Gerber, *J. Chem. Phys.* **102**, 8855 (1995)). The absorption cross-section expression we derived enables one to calculate the absorption spectra when a large cluster, as described by the Jungwirth–Gerber time dependent Hamiltonian, is subjected to weak electromagnetic field — for an eigenstate which changes “adiabatically” with time.

<sup>25</sup>As an additional check on the  $t, t'$  approach, we have also done the following check (due to a suggestion by S. H. Patil). We define a modified the initial wave function as simply  $X(j, t, t'=0) = \Phi(j, t', t=0) \sin(\Omega t')$ , where the purpose of the  $\sin(\Omega t')$  is to modify the wave function so that it would vanish at  $t=t'=0$  and at  $t' - \pi/\Omega = t=0$ . Throughout the  $t, t'$  propagation of  $X$  it should still be true then that  $X(j, t=t', t) = X(j, t=t' + \pi/\Omega) = 0$ , since in principle every ray  $t'=t + \text{const}$  corresponds to a different solution of the time-dependent Schrödinger equation, and the solution at the two rays [associated with  $t=t'$  and  $t=t' + \pi/\Omega$ ] is explicitly made to have a vanishing amplitude at the start of the rays (at  $t=0$ ). Indeed, a numerical propagation of  $X$  under  $\mathcal{H}_0$  was found to fulfill this property to better than  $10^{-15}$ .

<sup>26</sup>The energy spectrum in the Floquet problem is infinitely large (and periodic) so that the choice of the energy levels by their order in the region  $[-0.5, 0.5]$  is arbitrary (and not necessarily related to the zero-field order). Thus, energy levels “0” and “9” are really neighboring in energies, which leads to the corresponding peak in Figure 1. The peaks in the graph are similar when 14 basis functions are used.