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Time-independent scattering theory for time-periodic Hamiltonians: Formulation and complex-scaling calculations of above-threshold-ionization spectra

Uri Peskin and Nimrod Moiseyev
Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

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A time-independent scattering theory is introduced for time-periodic Hamiltonians. The theory is applicable in cases where at infinite time ($t=\pm\infty$) the relative motion between the colliders is free, and therefore the asymptotic kinetic energy can be defined experimentally. This asymptotic condition and the time periodicity of the Hamiltonian lead to time-independent expressions for the distribution of the kinetic energy in the relative motion of the fragments for a half-collision and for a full-collision experiment. These expressions are combined with the complex-coordinate method to give an efficient numerical algorithm for the calculation of multiphoton ionization-dissociation probabilities within the framework of the finite-range-potential approximations. The theory is applied to a model Hamiltonian of an atom in a strong ac field. The obtained above-threshold-ionization spectra are in excellent agreement with theoretical results previously obtained from time-dependent calculations.

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I. INTRODUCTION

Time-periodic Hamiltonians play an important role in understanding matter-radiation interactions [1(a)]. Consider, for example, a molecular (or an atomic) system, subjected to a high-intensity laser pulse. If the pulse duration is much longer than the optical period [1(b)], the interaction between the system and the electromagnetic field can be well described semiclassically as time periodic. This description also holds for an experiment in which the laser induces dissociation, and the photofragments leave the focal region of the beam before the pulse intensity vanishes.

The dynamics of systems that are described by time-periodic Hamiltonians can be studied by the Floquet theory [2]. By regarding the time as a dynamic variable, Sambe [3] and Howland [4] have shown that the eigenvectors of the Floquet Hamiltonian matrix (the quasienergy states) span a Hilbert space in analogy to the stationary states of a time-independent Hamiltonian. This analogy inspired the use of theoretical approaches that were originally developed for time-independent Hamiltonians for the study of time-periodic ones. For example, Millack [5] has shown that the language of scattering theory can be used in order to obtain a "Lippman Schwinger" equation for the quasienergy states. In recent years, the combination of Floquet theory with the complex-coordinate method has been used extensively for the study of quasienergy resonance states and the decay rates in photoionization and photodissociation processes [6-24]. In these processes the bound states of the field-free Hamiltonian become metastable resonance states due to the interaction of the atomic (molecular) system with the electromagnetic field. The resonance states are associated with square-integrable eigenfunctions of the complex-scaled Floquet Hamiltonian operator. Knowledge of the resonance quasienergies and quasienergy states gives a sufficient description of the dynamics as long as they are isolated and narrow (Breit-Wigner) [25] resonances. Indeed, recently, a full description of the above-threshold-ionization (ATI) spectrum (ionization probability versus kinetic energy of the photoelectron) was obtained for a model system, based solely on the resonance quasienergy state analysis [19]. The multiphoton-ionization experiment has been associated with a single complex-scaled resonance state which gave a maximal overlap integral with the initial bound state of the field-free Hamiltonian. The real part of the resonance energy provided the location of the peaks in the ATI spectrum, while the total width of the peaks was subtracted from the imaginary part [19]. By carrying out an asymptotic analysis of the complex-scaled resonance state [17,22,26,27], the partial widths were obtained and provided the relative heights of the ATI peaks [19]. In the general case, however, there is additional information about the process which cannot be obtained by the resonances state analysis alone (the latter is especially true for full-collision processes). In order to obtain all the dynamical information, a time-dependent wave-packet simulation is usually carried out [12,28-30]. The time-dependent approach seems necessary for the treatment of very short laser pulses. It has a disadvantage, however, when the laser pulse is long and long-time propagation calculations are required. In such cases the extraction of *time-independent* dynamical quantities such as photoionization-photodissociation probabilities from time-dependent calculations is often a hard and nonrigorous task.

The purpose of this article is to derive rigorous expressions for *time-independent* state-to-state transition probabilities for *time-periodic* Hamiltonians. The key point in our derivation is the analytical evaluation of the time evolution of the system up to infinite times ($t=+\infty$ and/or $t=-\infty$) based on Shirley's formalism [31], combined with analytical continuation of the photofragment energy into the lower half of the complex energy plane.

Like any other time-independent scattering theory, our theory is limited in its application to potentials for which a free particle is obtained as $t \to \infty$. To satisfy this condition, the following two limitations should be imposed on the field-free ("bare") potential and on the atom-field interaction potential.

(1) The atomic or molecular potential should be a non-Coulombic type (as in any other scattering theory which is based on the asymptotic condition). It can be a finite-, short-, or long-range potential. For example, due to the screening effect of the inner-shell electrons, the interaction of an ionizing electron with the ion is often described by an effective short-range potential. (See, for example, [13,21,24].) For hydrogeniclike atoms, our approach can be used only within the framework of the cutoff Coulomb potentials where we assume that $V(r>r_0)=0$.

(2) The atom-field interaction potential should vanish as $x \to \infty$. This is not the case when the length gauge is used and the atom-field interaction potential is often taken as $\epsilon_0 x \cos(wt)$. However, the time-dependent Hamiltonian can be transformed from the length gauge to the acceleration gauge [24] for which

$$V(x,t)=V(x+(\epsilon_0/w^2)\cos(wt)) \ ,$$

and $V \to 0$ as $x \to \infty$ at any given time and for any value of the field intensity. Therefore, our time-independent scattering theory is applicable when the acceleration gauge is used to describe the multiphoton ionization-dissociation process.

For the sake of clarity, in Sec. II we present an overview of the Floquet theory for time-periodic Hamiltonians. The Floquet Hamiltonian and the time-evolution operator are presented in the generalized Hilbert space introduced by Sambe [3]. The time-independent expression for the state-to-state ionization (dissociation) probabilities is derived in Sec. III. The half-collision formulation is extended to account for full-collision experiments with a finite-range time-periodic interaction. In Sec. IV the complex-coordinate method is introduced into the theory and the computational procedure for calculating multiphoton-ionization (dissociation) probabilities is given. An application of the theory to the calculation of the ATI spectrum for a one-dimensional time-periodic model Hamiltonian is given in Sec. V and the results are compared to time-dependent calculations [29]. An alternative derivation of the theoretical time-independent probabilities expressions in the generalized Hilbert space is given in the Appendix.

II. A BRIEF REVIEW OF THE FLOQUET THEORY

A. The Floquet Hamiltonian

We shall discuss the case of a one-dimensional time-periodic Hamiltonian. The generalization for higher dimensions is straightforward. The time-dependent Schrödinger equation is

$$i\hbar\frac{\partial}{\partial t}\psi(x,t)=\hat{H}(x,t)\psi(x,t) \ , \tag{2.1}$$

where

$$\hat{H}(x,t)=\hat{H}(x,t+T) \ . \tag{2.2}$$

T is the time period, and the corresponding angular frequency is $w=2\pi/T$. According to the Floquet theory [2], a solution to the time-dependent Schrödinger equation is given by

$$\psi_\lambda(x,t)=e^{-i\lambda t/\hbar}\phi_\lambda(x,t) \ , \tag{2.3}$$

where $\phi_\lambda(x,t)$ is time periodic with the period T:

$$\phi_\lambda(x,t+T)=\phi_\lambda(x,t)=\sum_{n=-\infty}^{\infty} e^{inwt}\phi_\lambda^n(x) \ , \tag{2.4}$$

λ is a quasienergy of the system, and $\psi_\lambda(x,t)$ is the corresponding quasienergy state. Substitution of the solution [Eq. (2.3)] into the Schrödinger equation [Eq. (2.1)] leads to a time-dependent eigenvalue equation:

$$\hat{\mathcal{H}}_f(x,t)\phi_\lambda(x,t)=\lambda\phi_\lambda(x,t) \ , \tag{2.5}$$

where the Floquet Hamiltonian $\hat{\mathcal{H}}_f(x,t)$ is defined as

$$\hat{\mathcal{H}}_f(x,t)=\hat{H}(x,t)-i\hbar\frac{\partial}{\partial t} \ . \tag{2.6}$$

The quasienergy spectrum is uniquely defined modulo $\hbar w$. That is, if λ is a quasienergy, so is $\lambda+\hbar wq$, for any integer q. This fact can be proved by defining a function

$$\phi_{\lambda,q}(x,t)=e^{iwqt}\phi_\lambda(x,t) \ . \tag{2.7}$$

Substituting this function in Eq. (2.5), we obtain

$$\hat{\mathcal{H}}_f(x,t)\phi_{\lambda,q}(x,t)=(\lambda+\hbar wq)\phi_{\lambda,q}(x,t) \ . \tag{2.8}$$

Therefore, $\phi_{\lambda,q}(x,t)$ is an eigenfunction of the Floquet Hamiltonian with the eigenvalue $\lambda+\hbar wq$. From the comparison of Eq. (2.5) with Eq. (2.8), one obtains

$$\phi_{\lambda+\hbar wq}(x,t)=\phi_{\lambda,q}(x,t)=e^{iwqt}\phi_\lambda(x,t) \ . \tag{2.9}$$

A useful relation between the Fourier components of $\phi_\lambda(x,t)$ and $\phi_{\lambda+\hbar wq}(x,t)$ is derived from Eqs. (2.4) and (2.9):

$$\phi_\lambda^n(x)=\phi_{\lambda+\hbar wq}^{n+q}(x) \ . \tag{2.10}$$

[Note that although $\phi_\lambda(x,t)$ and $\phi_{\lambda+\hbar wq}(x,t)$ are different, the corresponding solutions to the Schrödinger equation, $\psi_\lambda(x,t)$ and $\psi_{\lambda+\hbar wq}(x,t)$, are identical, and describe the same physical situation. This can be confirmed by substituting the two solutions into Eq. (2.3).]

Each Fourier component of $\phi_\lambda(x,t)$ for any n can be expanded in a complete set of orthonormal square-integrable basis functions (using "box normalization"):

$$\{\chi_\alpha(x)\} \ , \quad \alpha=1,2,\ldots,\infty \ .$$

Therefore,

$$\phi_\lambda(x,t)=\sum_{n,\alpha} C_{\lambda,\alpha}^{(n)}\chi_\alpha(x)e^{inwt} \ , \tag{2.11}$$

where

$$C_{\lambda,\alpha}^{(n)}=\frac{1}{T}\int_0^T dt\int_{-\infty}^{\infty} dx\, e^{-inwt}\chi_\alpha^*(x)\phi_\lambda(x,t) \ . \tag{2.12}$$

As was shown by Sambe [3], the function $\phi_\lambda(x,t)$ is a representation of a state vector in a generalized Hilbert space which consists of all possible time-periodic square-integrable functions. The inner product between two functions $f(x,t)$ and $g(x,t)$ in this linear space is defined as

$$(f,g)=\int_{-\infty}^{\infty} dx \frac{1}{T}\int_0^T dt\, f^*(x,t)g(x,t) \ , \tag{2.13}$$

or in Dirac notation,

$$\langle\langle f|g\rangle\rangle=\int_{-\infty}^{\infty} dx \frac{1}{T}\int_0^T dt \langle f(t)|x\rangle\langle x|g(t)\rangle \ . \tag{2.14}$$

An orthonormal basis in the generalized space is given by

$$\langle\langle x,t|\alpha,n\rangle\rangle=\chi_\alpha(x)e^{inwt} \tag{2.15}$$

for $n=-\infty,\ldots,\infty$ and $\alpha=1,2,\ldots,\infty$. In Dirac notation, Eq. (2.11) can be rewritten

$$\begin{aligned}\phi_\lambda(x,t)\equiv\langle\langle x,t|\lambda\rangle\rangle&=\sum_{n,\alpha}\langle\langle x,t|\alpha,n\rangle\rangle\langle\langle\alpha,n|\lambda\rangle\rangle\\&=\sum_{n,\alpha}\langle\langle x,t|\alpha,n\rangle\rangle C_{\lambda,\alpha}^{(n)} \ .\end{aligned} \tag{2.16}$$

The unity operator can be identified as

$$\hat{I}=\sum_{n,\alpha}|\alpha,n\rangle\rangle\langle\langle\alpha,n| \ . \tag{2.17}$$

The Schrödinger equation (Eq. 2.5) can be rewritten in the generalized Hilbert space:

$$\hat{\mathcal{H}}_f|\lambda\rangle\rangle=\lambda|\lambda\rangle\rangle \ . \tag{2.18}$$

Inserting the unity operator $\hat{I}$ into Eq. (2.18) and multiplying from the left by $\langle\langle\beta,m|$, for $m=-\infty,\ldots,\infty$, $\beta=1,2,\ldots,\infty$, we obtain a time-independent equation for the quasienergy state components, $\langle\langle\beta,m|\lambda\rangle\rangle$:

$$\sum_{n,\alpha}\langle\langle\beta,m|\hat{\mathcal{H}}_f|\alpha,n\rangle\rangle\langle\langle\alpha,n|\lambda\rangle\rangle=\lambda\langle\langle\beta,m|\lambda\rangle\rangle \ . \tag{2.19}$$

The Schrödinger equation can therefore be solved as a time-independent matricial eigenvalue equation:

$$\mathbf{H}_f\boldsymbol{\lambda}=\lambda\boldsymbol{\lambda} \ , \tag{2.20}$$

where $\mathbf{H}_f$ is the matrix representation of $\hat{\mathcal{H}}_f$ in the basis set $\{|\alpha,n\rangle\rangle\}$ defined in Eq. (2.15) and $\boldsymbol{\lambda}$ is the vector representation of $|\lambda\rangle\rangle$ in this basis, whose components are $C_{\lambda,\alpha}^{(n)}=\langle\langle\alpha,n|\lambda\rangle\rangle$.

B. The time-evolution operator

The time-evolution operator $\hat{U}(t,t_0)$ is defined by the equation

$$\hat{U}(t,t_0)|\psi(t_0)\rangle=|\psi(t)\rangle \ , \tag{2.21}$$

where $|\psi(t)\rangle$ is the time-dependent state vector of the system. A Schrödinger equation for $\hat{U}(t,t_0)$ is obtained by substituting Eq. (2.21) into Eq. (2.1):

$$i\hbar\frac{\partial}{\partial t}\hat{U}(t,t_0)=\hat{H}(t)\hat{U}(t,t_0) \ . \tag{2.22}$$

In the general case of a time-dependent Hamiltonian, the formal solution for $\hat{U}(t,t_0)$ is given by an infinite Dyson series [32]. Therefore, time integration is carried out numerically for consistent (small-) time intervals [33]. In the case of a time-periodic Hamiltonian, however, $\hat{U}(t,t_0)$ is given by an exact and simple expression, derived by Shirley [31]:

$$\begin{aligned}&\langle\beta|\hat{U}(t,t_0)|\alpha\rangle\\&\quad=\sum_{\lambda,n}e^{inwt}e^{-i\lambda(t-t_0)/\hbar}\langle\langle\beta,n|\lambda\rangle\rangle\langle\langle\lambda|\alpha,0\rangle\rangle \ ,\end{aligned} \tag{2.23}$$

where $|\alpha\rangle$ and $|\beta\rangle$ are two time-independent basis vectors and the inner product $\langle\ |\ \rangle$ is defined as usual:

$$\langle\beta|\alpha\rangle=\int_{-\infty}^{\infty}dx\langle\beta|x\rangle\langle x|\alpha\rangle=\int_{-\infty}^{\infty}dx\,\chi_\beta^*(x)\chi_\alpha(x) \ . \tag{2.24}$$

The validity of Eq. (2.23) can be confirmed by substituting $\langle\beta|\hat{U}(t,t_0)|\alpha\rangle$ into the Schrödinger equation for $\hat{U}(t,t_0)$ [Eq. (2.22)]:

$$\begin{aligned}\langle\beta|\hat{H}(t)\hat{U}(t,t_0)|\alpha\rangle&=\sum_{\gamma}\langle\beta|\hat{H}(t)|\gamma\rangle\langle\gamma|\hat{U}(t,t_0)|\alpha\rangle\\&=\sum_{\gamma,m,\lambda,n}e^{imwt}\langle\langle\beta,m|\hat{H}|\gamma,0\rangle\rangle e^{inwt}e^{-i\lambda(t-t_0)/\hbar}\langle\langle\gamma,n|\lambda\rangle\rangle\langle\langle\lambda|\alpha,0\rangle\rangle\\&=\sum_{\lambda,m'}e^{im'wt}e^{-i\lambda(t-t_0)/\hbar}\langle\langle\beta,m'|\hat{H}|\lambda\rangle\rangle\langle\langle\lambda|\alpha,0\rangle\rangle\\&=\sum_{\lambda,m'}e^{im'wt}e^{-i\lambda(t-t_0)/\hbar}(\lambda-\hbar wm')\langle\langle\beta,m'|\lambda\rangle\rangle\langle\langle\lambda|\alpha,0\rangle\rangle\\&=i\hbar\frac{\partial}{\partial t}\langle\beta|\hat{U}(t,t_0)|\alpha\rangle \ ,\end{aligned} \tag{2.25}$$

where we have used the following identities:

$$\langle\beta|\hat{H}(t)|\gamma\rangle=\sum_m e^{imwt}\langle\langle\beta,m|\hat{H}|\gamma,0\rangle\rangle \ , \tag{2.26a}$$

$$\langle\langle\beta,m|\hat{H}|\gamma,0\rangle\rangle=\langle\langle\beta,m+n|\hat{H}|\gamma,n\rangle\rangle \ , \tag{2.26b}$$

$$m'=m+n \ , \tag{2.26c}$$

$$\langle\langle\beta,m'|\hat{H}|\lambda\rangle\rangle=\langle\langle\beta,m'|(\lambda-\hbar wm')|\lambda\rangle\rangle \ . \tag{2.26d}$$

III. TIME-INDEPENDENT SCATTERING PROBABILITIES FOR TIME-PERIODIC HAMILTONIANS

In several photoionization or photodissociation experiments, the kinetic energy of the photofragments has been measured [34–36]. In this section we derive expressions for the ionization-dissociation probability as a function of the relative kinetic energy between the fragments of the system.

A. The asymptotic condition

We assume that at infinite time the exact time-dependent wave function is a freely evolving wave packet along the reaction coordinate which is the coordinate of the relative motion between the fragments. Note that although the Hamiltonian we consider is time periodic, a free motion is obtained as $t \rightarrow \infty$. This is the case in an experiment in which the interaction between a system and a time-periodic field vanishes as the fragments of the system move apart. Therefore, we refer to a motion described by a nonCoulombic (finite-, short-, or long-range) time-periodic potential, $\hat{V}(x,t)$. We adopt the asymptotic condition of time-independent scattering theory [37]: Each freely moving wave packet $|\varphi_f(t)\rangle$ is the asymptote of an exact solution $|\psi_f(t)\rangle$ of the time-dependent Schrödinger equation. This reads

$$\lim_{t\rightarrow\infty} \hat{U}_0(t,0)|\varphi_f(0)\rangle = \lim_{t\rightarrow\infty} \hat{U}(t,0)|\psi_f(0)\rangle \ , \tag{3.1}$$

where $\hat{U}_0(t,0)$ is the time-evolution operator for a free motion:

$$\hat{U}_0(t,0)=e^{-i\hat{H}_0 t/\hbar} \ , \quad \hat{H}_0=\frac{\hat{p}^2}{2m} \tag{3.2}$$

and $\hat{U}(t,0)$ is the exact time-evolution operator of the system.

B. The exact outgoing wave function

Our first concern is the exact solution of the time-dependent Schrödinger equation at $t=0$, $|\psi_f(0)\rangle$, which is associated with the final asymptotic wave packet $|\varphi_f(\infty)\rangle$. From the asymptotic condition we obtain

$$|\psi_f(0)\rangle = \lim_{t\rightarrow\infty} \hat{U}^\dagger(t,0)\hat{U}_0(t,0)|\varphi_f(0)\rangle \ , \tag{3.3}$$

where we use the unitarity of the time-evolution operator:

$$\hat{U}^\dagger(t,0)=\hat{U}^{-1}(t,0)=\hat{U}(0,t) \ . \tag{3.4}$$

Using the Schrödinger equation for $\hat{U}(t,0)$ [Eq. (2.22)], the time derivative of $\hat{U}^\dagger(t,0)$ is obtained

$$-i\hbar\frac{\partial}{\partial t}\hat{U}^\dagger(t,0)=\hat{U}^\dagger(t,0)\hat{H}(t) \ . \tag{3.5}$$

The expression for $|\psi_f(0)\rangle$ in the limit $t\rightarrow\infty$ can be evaluated as an integral from $t=0$ to $t=+\infty$:

$$\begin{aligned} |\psi_f(0)\rangle &= |\varphi_f(0)\rangle + \int_0^\infty dt \frac{\partial}{\partial t}\hat{U}^\dagger(t,0)e^{-i\hat{H}_0 t/\hbar}|\varphi_f(0)\rangle \\ &= |\varphi_f(0)\rangle + \int_0^\infty dt \left[\left[\frac{\partial}{\partial t}\hat{U}^\dagger(t,0) \right] - \frac{i}{\hbar}\hat{U}^\dagger(t,0)\hat{H}_0 \right] e^{-i\hat{H}_0 t/\hbar}|\varphi_f(0)\rangle \\ &= |\varphi_f(0)\rangle + \frac{i}{\hbar}\int_0^\infty dt\, \hat{U}(0,t)\hat{V}(t)e^{-i\hat{H}_0 t/\hbar}|\varphi_f(0)\rangle \ , \end{aligned} \tag{3.6}$$

where in the last step we used Eqs. (3.2), (3.4), and (3.5) and the time-dependent potential $\hat{V}(t)$ was introduced:

$$\hat{V}(t)=\hat{H}(t)-\hat{H}_0 \ . \tag{3.7}$$

The evaluation of the integral in Eq. (3.6) is simplified by taking two steps. First, we note that the integral is convergent due to the asymptotic condition assumption [37]. Therefore, the integrand can be multiplied by an exponential damping factor $\exp(-\varepsilon t)$, where $\varepsilon\rightarrow+0$.

$$|\psi_f(0)\rangle = |\varphi_f(0)\rangle + \frac{i}{\hbar}\lim_{\varepsilon\rightarrow+0}\int_0^\infty dt\, e^{-\varepsilon t}\hat{U}(0,t)\hat{V}(t) \times e^{-i\hat{H}_0 t/\hbar}|\varphi_f(0)\rangle \ . \tag{3.8}$$

(From now on we shall omit the limit notation.) Second, we use the fact that the wave packet $|\varphi_f(0)\rangle$ can be expanded as a linear combination of plane waves $|p\rangle$:

$$|\varphi_f(0)\rangle = \int_{-\infty}^{\infty} dp|p\rangle\langle p|\varphi_f(0)\rangle \ . \tag{3.9}$$

By substituting the plane-wave expansion in the equation for $|\psi_f(0)\rangle$ [Eq. (3.8)], we obtain

$$|\psi_f(0)\rangle = \int_{-\infty}^{\infty} dp|\psi_p(0)\rangle\langle p|\varphi_f(0)\rangle \ , \tag{3.10}$$

where $|\psi_p(0)\rangle$ is given by

$$|\psi_p(0)\rangle = |p\rangle + \frac{i}{\hbar}\int_0^\infty dt\, e^{-\varepsilon t}\hat{U}(0,t)\hat{V}(t)e^{-iE_p t/\hbar}|p\rangle \ , \tag{3.11}$$

using the fact that

$$\hat{H}_0|p\rangle=E_p|p\rangle \ , \quad E_p=\frac{p^2}{2m} \ . \tag{3.12}$$

The state $|\psi_p(0)\rangle$ can be regarded as the state of the system at $t=0$ which has the asymptotic behavior of a plane wave $|p\rangle$ at $t=\infty$. However, it is only $|\psi_f(0)\rangle$ and not $|\psi_p(0)\rangle$ which satisfies the asymptotic condition assumption [Eq. (3.1)]. We rewrite Eq. (3.11) for the projection of the state $|\psi_p(0)\rangle$ on a basis state $\langle\alpha|$ using the conventional inner product [Eq. 2.24)]:

$$\begin{aligned}\langle\alpha|\psi_p(0)\rangle=\langle\alpha|p\rangle+\frac{i}{\hbar}\int_0^\infty dt\sum_{\beta,\gamma}\langle\alpha|\hat{U}(0,t)|\beta\rangle\\ \times\langle\beta|\hat{V}(t)|\gamma\rangle\\ \times\langle\gamma|e^{-i(E_p-i\varepsilon)t}|p\rangle\ .\end{aligned}\tag{3.13}$$

So far, our treatment concerns any time dependence of the Hamiltonian $\hat{H}(t)$. We now restrict the discussion to systems with a time-periodic potential $\hat{V}(t)$. In this case, the potential can be expanded in a Fourier series:

$$\langle\beta|\hat{V}(t)|\gamma\rangle=\sum_m e^{im\omega t}\langle\langle\beta,m|\hat{V}|\gamma,0\rangle\rangle\ ,\tag{3.14}$$

and the time-evolution operator $\hat{U}(0,t)$ is given by Eq. (2.23). In Eqs. (2.23) and (3.14), the notation $\langle\langle\ |\ \rangle\rangle$ stands for the generalized inner product introduced in Eqs. (2.13) and (2.14). The usual inner product can also be expressed as a generalized one:

$$\langle\alpha|p\rangle=\langle\langle\alpha,n|p,n\rangle\rangle\tag{3.15}$$

for any value of n (we shall choose $n=0$). Substituting Eq. (2.23) (replacing t by 0 and t_0 by t) and Eqs. (3.14) and (3.15) into Eq. (3.13), we obtain

$$\begin{aligned}\langle\alpha|\psi_p(0)\rangle=\langle\langle\alpha,0|p,0\rangle\rangle+\frac{i}{\hbar}\int_0^\infty dt\sum_{\beta,m,\gamma,n,\lambda}e^{-i(E_p-i\varepsilon)t/\hbar}e^{i\lambda t/\hbar}\langle\langle\alpha,n|\lambda\rangle\rangle\langle\langle\lambda|\beta,0\rangle\rangle e^{im\omega t}\\ \times\langle\langle\beta,m|\hat{V}|\gamma,0\rangle\rangle\langle\langle\gamma,0|p,0\rangle\rangle\ .\end{aligned}\tag{3.16}$$

At this stage, the time integral can be evaluated analytically:

$$\begin{aligned}\frac{i}{\hbar}\int_0^\infty dt\, e^{-i[(E_p-i\varepsilon)-(\lambda+\hbar\omega m)]t/\hbar}\\ =[E_p-i\varepsilon-(\lambda+\hbar\omega m)]^{-1}\ .\end{aligned}\tag{3.17}$$

The number of summations in Eq. (3.16) can be reduced, taking into consideration the properties of the eigenvectors of the Floquet Hamiltonian (the set $\{|\lambda\rangle\rangle\}$). First, from Eq. (2.10), we obtain

$$\begin{aligned}\langle\langle\alpha,n|\lambda\rangle\rangle=\langle\langle\alpha,n+m|\lambda+\hbar\omega m\rangle\rangle\ ,\\ \langle\langle\lambda|\beta,0\rangle\rangle=\langle\langle\lambda+\hbar\omega m|\beta,m\rangle\rangle\ .\end{aligned}\tag{3.18}$$

Second, we recall that the Floquet Hamiltonian is Hermitian in the generalized Hilbert space [3,31], and therefore its eigenvectors are a complete set:

$$\sum_\lambda|\lambda\rangle\rangle\langle\langle\lambda|=\hat{I}\ .\tag{3.19}$$

Using Eqs. (2.17), (2.18), and (3.16)–(3.19) and changing indices in Eq. (3.16), we obtain

$$\begin{aligned}\langle\alpha|\psi_p(0)\rangle=\langle\langle\alpha,0|p,0\rangle\rangle\\ +\sum_n\langle\langle\alpha,n|[(E_p-i\varepsilon)\hat{I}-\hat{\mathcal{H}}_f]^{-1}\hat{V}|p0\rangle\rangle\ .\end{aligned}\tag{3.20}$$

Let us introduce the generalized Green operator, operating in the generalized Hilbert space:

$$\hat{G}(z)=[z\hat{I}-\hat{\mathcal{H}}_f]^{-1}\ .\tag{3.21}$$

Equation (3.20) can be rewritten as

$$\langle\alpha|\psi_p(0)\rangle=\sum_n\langle\langle\alpha,n|\hat{I}+\hat{G}(E_p-i\varepsilon)\hat{V}|p,0\rangle\rangle\ .\tag{3.22}$$

The importance of Eq. (3.22) is in the fact that the state $|\psi_p(0)\rangle$ [and therefore the actual state of the system $|\psi_f(0)\rangle$, through Eq. (3.10)] is given by a time-independent expression, which recalls the well-known Lippman-Schwinger equation [37] of stationary scattering theory. The main difference from the stationary scattering theory is the change of the definition of the inner product, such that the time is regarded as a dynamic variable. By using the time-evolution operator for time-periodic Hamiltonians [Ref. [31] or Eq. (2.23)], the generalized Lippman-Schwinger equation [Eq. (3.22)] is obtained for $|\psi_p(0)\rangle$, where $|\psi_p(0)\rangle$ stands for *any* time-dependent solution of the Schrödinger equation, with the asymptotic behavior $|p\rangle$. Note in passing that in Ref. [5] a similar Lippman-Schwinger equation was introduced by using the language of scattering theory, but only for the quasienergy states (the eigenstates of the Floquet Hamiltonian).

C. Ionization-dissociation probabilities for a half-collision experiment

Consider an experiment in which at $t\le 0$, the system is in a well-defined bound state of a field-free Hamiltonian. At $t=0$, an interaction with a time-periodic field is switched on and the system is ionized or dissociated due to the interaction with the field. If the time needed for the interaction to reach its maximum intensity amplitude is much smaller than the time period of the field, the switch can be well described as instantaneous. We argue that in such a case the "history" of the system at times $t<0$ is irrelevant to the dynamics of the ionization-dissociation process. Therefore, the process can be well described by a Hamiltonian which is time periodic for all times, as long as at $t=0$ the wave packet representing the system is the bound state of the field-free Hamiltonian. This allows the use of Floquet theory in the calculation of the ionization-dissociation probabilities. Our concern is the probability to obtain a freely moving wave packet at $t=\infty$, $|\varphi_f(\infty)\rangle$, provided that at $t=0$, the system is in a state $|\varphi_b(0)\rangle$. According to the initial condition in the experiment, $|\varphi_b(0)\rangle$ is a bound state of the field-free Hamiltonian. Since the full Hamiltonian is time periodic, we can use Eqs. (3.10) and (3.22) to obtain a wave packet at $t=0$, $|\psi_f(0)\rangle$, which will evolve in time to $|\varphi_f(\infty)\rangle$. The probability for the transition from $|\varphi_b(0)\rangle$ to $|\varphi_f(\infty)\rangle$ is therefore given by the absolute square of the overlaps between the two states at $t=0$:

$$Pf\leftarrow b=|\langle\psi_f(0)|\varphi_b(0)\rangle|^2\ , \tag{3.23}$$

where, according to Eq. (3.10),

$$\langle\psi_f(0)|\varphi_b(0)\rangle=\int_{-\infty}^{\infty}dp\,\langle\varphi_f(0)|p\rangle\langle\psi_p(0)|\varphi_b(0)\rangle\ . \tag{3.24}$$

Using Eq. (3.22) for $|\psi_p(0)\rangle$ we obtain

$$\begin{aligned}\langle\psi_p(0)|\varphi_b(0)\rangle&=\sum_{\alpha,n}\langle\langle p,0|\hat{V}\hat{G}(E_p+i\varepsilon)+\hat{I}|\alpha,n\rangle\rangle\langle\alpha|\varphi_b(0)\rangle\\&=\sum_{n}\langle\langle p,0|\hat{I}+\hat{V}\hat{G}(E_p+i\varepsilon)|\varphi_b(0),n\rangle\rangle\ .\end{aligned} \tag{3.25}$$

The last equation can be physically interpreted for ionization or dissociation of a system in an electromagnetic field. The values of n represent the different field states which can be obtained during the process. The total ionization-dissociation probability amplitude for the final wave packet, $|\varphi_f(\infty)\rangle$, is obtained as a sum over these states, and the calculation of the amplitude itself [Eq. (3.23)] takes into account the interferences between the different possible interaction paths during the ionization-dissociation process.

The scattering asymptotic state represents the final measurements in the experiment. For example, the measurement of the averaged relative momentum between the collision fragments, and the uncertainty in its determination, define the center and the width of a Gaussian wave packet which represent the asymptotic state of the system, $|\varphi_f(\infty)\rangle$. If the momentum in the relative motion of the fragments is measured exactly, a final state can be represented as a plane wave with a well-defined momentum p':

$$|\varphi_f(0)\rangle=|p'\rangle\ . \tag{3.26}$$

Substituting Eq. (3.26) into Eqs. (3.23) and (3.24), we obtain

$$Pf\leftarrow b\equiv P_b(p')=|\langle\psi_{p'}(0)|\varphi_b(0)\rangle|^2\ . \tag{3.27}$$

$P_b(p')$ is the probability density to obtain the fragments of the system in a well-defined relative moment p'. The normalization condition for the probability density is satisfied when

$$\int_{-\infty}^{\infty}dp'P_b(p')=1\ . \tag{3.28}$$

The probability density $P_b(E_{p'})$ to obtain the fragments in a well-defined kinetic energy, $E_{p'}=p'^2/2m$, is defined by the equation

$$P_b(p')dp'=P_b(Ep')dE_{p'}\ . \tag{3.29}$$

From Eqs. (3.29) and (3.27), we obtain

$$P_b(E_{p'})=\frac{m}{|p'|}|\langle\psi_{p'}(0)|\varphi_b(0)\rangle|^2\ . \tag{3.30}$$

By choosing the asymptotic state in Eq. (3.26), $\varphi_f(0)$, as an energy-normalized [38] plane wave:

$$|\varphi_f(0)\rangle=\left[\frac{m}{p'}\right]^{1/2}\left|p'\right\rangle\ , \tag{3.31}$$

$P_b(E_{p'})$ is obtained directly from $P_{f\leftarrow b}$ by Eq. (3.27).

D. Transition probabilities for a full-collision experiment

Consider an experiment in which the interaction between two particles (or fragments) is time periodic, the intensity of the interaction changes as a function of the relative distance coordinate between the particles, and it vanishes as the distance becomes infinite (a finite-range interaction). A collision starts at $t=-\infty$ where the wave packet describing the system evolves in time freely. As the fragments collide, they interact with each other and with the external time-periodic field, and state-to-state transitions may occur. After the collision is over, as $t\rightarrow\infty$, the relative motion is free again. In such a process the Hamiltonian is time periodic for all times. However, the transition probabilities are time independent, provided that the experimental detection is carried out at times that are much larger than the collision time.

In this section we derive expressions for the time-independent probability that a system, described by a free wave packet $|\varphi_i(t)\rangle$ at $t=-\infty$ (initial state), will be found at $t=+\infty$ in a state $|\varphi_f(t)\rangle$ (final state). Both the initial and the final states satisfy an asymptotic condition. Therefore, for each one of them there is a unique state at $t=0$, which will evolve to it, by the time-evolution operator of the interacting system:

$$\begin{aligned}\lim_{t\rightarrow-\infty}\hat{U}(t,0)|\psi_i(0)\rangle&=\lim_{t\rightarrow-\infty}\hat{U}_0(t,0)|\varphi_i(0)\rangle\ ,\\\lim_{t\rightarrow\infty}\hat{U}(t,0)|\psi_f(0)\rangle&=\lim_{t\rightarrow\infty}\hat{U}_0(t,0)|\varphi_f(0)\rangle\ .\end{aligned} \tag{3.32}$$

The transition probability amplitude is given by the overlaps between the exact states at $t=0$, $|\psi_i(0)\rangle$, and $|\psi_f(0)\rangle$:

$$Pf\leftarrow i=|\langle\psi_f(0)|\psi_i(0)\rangle|^2\ , \tag{3.33}$$

$$\begin{aligned}\langle\psi_f(0)|\psi_i(0)\rangle&=\int_{-\infty}^{\infty}dp\int_{-\infty}^{\infty}dp'\langle\varphi_f(0)|p\rangle\\&\quad\times\langle\psi_p(0)|\psi_{p'}(0)\rangle\langle p'|\varphi_i(0)\rangle\end{aligned} \tag{3.34}$$

and we can use Eq. (3.22) for $|\psi_p(0)\rangle$. In order to evaluate the overlap $\langle\psi_p(0)|\psi_{p'}(0)\rangle$ in Eq. (3.34), we should obtain an expression for $|\psi_{p'}(0)\rangle$. This expression is obtained from the asymptotic condition in the limit

$t \to -\infty$:

$$\langle \alpha | \psi_{p'}(0) \rangle = \sum_m \langle\langle \alpha, m | \hat{I} + \hat{G}(E_{p'} + i\varepsilon)\hat{V} | p', 0 \rangle\rangle \; . \tag{3.35}$$

An alternative expression for the transition probability amplitude can be derived by imposing the asymptotic condition directly on the amplitude. From Eq. (3.32) we obtain

$$\begin{aligned} \langle \psi_f(0) | \psi_i(0) \rangle &= \lim_{t \to +\infty} \langle \varphi_f(0) | \hat{U}_0^\dagger(t,0)\hat{U}(t,0)\hat{U}^\dagger(-t,0)\hat{U}_0(-t,0) | \varphi_i(0) \rangle \\ &= \lim_{t \to +\infty} \langle \varphi_f(0) | e^{i\hat{H}_0 t/\hbar}\hat{U}(t,-t)e^{i\hat{H}_0 t/\hbar} | \varphi_i(0) \rangle \; . \end{aligned} \tag{3.36}$$

Using a derivation similar to the one in Sec. III B, the probability amplitude $\langle \psi_f(0) | \psi_i(0) \rangle$ can be obtained as an integral over time. Using Eq. (2.23) for the time-evolution operator of the interacting system $[\hat{U}(t,t_0)]$, this integral can be evaluated. Without going through the details of the derivation, we give the final time-independent expression for the probability amplitude

$$\langle \psi_f(0) | \psi_i(0) \rangle = \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dp' \langle \varphi_f(0) | p \rangle S(p',p) \langle p' | \varphi_i(0) \rangle \; , \tag{3.37}$$

where

$$S(p',p) = \langle p | p' \rangle + \tfrac{1}{2} \sum_{n=-\infty}^{\infty} \left\langle\!\left\langle p,0 \left| \hat{V}\hat{G}\left[\frac{E_p + E_{p'} + \hbar w n}{2} + i\varepsilon \right] + \hat{G}\left[\frac{E_p + E_{p'} + \hbar w n}{2} + i\varepsilon \right]\hat{V} \right| p',n \right\rangle\!\right\rangle \tag{3.38}$$

and $\hat{G}(z)$ is defined in Eq. (3.21). We define two new operators in the generalized Hilbert space:

$$\hat{G}_0(z) = [z\hat{I} - (\hat{\mathcal{H}}_f - \hat{V})]^{-1} \tag{3.39}$$

and

$$\hat{T}(z) = \hat{V} + \hat{V}\hat{G}(z)\hat{V} \; . \tag{3.40}$$

The operators $\hat{V}$, $\hat{G}$, $\hat{G}_0$, and $\hat{T}$ are related by the identity

$$\hat{V}\hat{G}(z) + \hat{G}(z)\hat{V} = \hat{G}_0(z)\hat{T}(z) + \hat{T}(z)\hat{G}_0(z) \; , \tag{3.41}$$

which can be verified, if the operators $[(z\hat{I} - \hat{\mathcal{H}}_f)]$ and $[z\hat{I} - (\hat{\mathcal{H}}_f - \hat{V})]$ are not singular [37]. In our case, z has a nonzero imaginary part (ε) and indeed these operators are regular. Using Eq. (3.41) and the fact that

$$\hat{G}_0(z) | p,n \rangle\rangle = [z - (E_p + \hbar w n)]^{-1} | p,n \rangle\rangle \; , \tag{3.42}$$

Eq. (3.38) can be rewritten

$$S(p',p) = \langle p | p' \rangle + \sum_n \left\langle\!\left\langle p,0 \left| \hat{T}\left[\frac{E_p + E_{p'} + \hbar w n}{2} + i\varepsilon \right] \right| p',n \right\rangle\!\right\rangle \left[\frac{1}{E_p - (E_{p'} + \hbar w n) + i\varepsilon} + \frac{1}{E_{p'} + \hbar w n - E_p + i\varepsilon} \right] . \tag{3.43}$$

Taking the limit $\varepsilon \to 0$ and using the definition of Dirac's δ function, we finally obtain

$$S(p',p) = \delta(p - p') - 2\pi i \sum_n \left\langle\!\left\langle p,0 \left| \hat{T}\left[\frac{E_p + E_{p'} + \hbar w n}{2} + i\varepsilon \right] \right| p',n \right\rangle\!\right\rangle \delta(E_p - (E_{p'} + \hbar w n)) \; . \tag{3.44}$$

Our derivation and the final result are in close analogy to the well-known results of the stationary scattering theory [37]. For example, by recognizing $S(p',p)$ as the scattering matrix and the matrix elements of $\hat{T}$ as the T matrix, Eq. (3.44) is a well-known relation between the S matrix and the T matrix [37]. The main differences from stationary scattering theory arises from the use of the time-evolution operator for time-*periodic* Hamiltonians. The last equation gives physical insight for scattering with a time-periodic interaction. We see that a plane wave with a momentum p gains or loses quantized energy $\hbar w n$, where w is the frequency of the time-periodic field and n can get positive or negative integer values. For an electromagnetic field, the index n can be interpreted as the number of photons which are absorbed or emitted by the system during the process. The infinite summation over n in Eq. (3.44) takes into account all of the possible multiphoton transitions. The interference between the different transitions, as well as the momentum representation of the initial and final wave packets, are taken into account by substituting the probability amplitudes in Eqs. (3.33) and (3.37). Since the Hamiltonian is time dependent, there is no energy-conservation limitation on the process. However, the δ function imposes that for the n photon transition [the nth term in Eq. (3.44)]; the initial and the final momenta are related through the equation $E_p = E_{p'} + \hbar w n$.

Equation (3.37) is an expression for the transition probability amplitude between two states defined by the wave packets $|\varphi_f(0)\rangle$ and $|\varphi_i(0)\rangle$. As in the case of a half-collision experiment, we are interested in the transition probabilities between states in which the relative momentum is asymptotically well defined. By choosing $|\varphi_f(0)\rangle$ as $|p\rangle$ and $|\varphi_i(0)\rangle$ as $|p'\rangle$, we obtain from Eqs. (3.33) and (3.37):

$$Pf \leftarrow i \equiv P(p',p) = |S(p',p)|^2 \ . \tag{3.45}$$

$P(p',p)$ is the transition probability density, which we normalize in the momentum space

$$\int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dp' P(p',p) = 1 \ . \tag{3.46}$$

We denote the transition probability density as a function of the fragments' initial and final kinetic energy as $P(E_{p'},E_p)$, where $E_p = p^2/2m$ and $E_{p'} = p'^2/2m$. $P(E_{p'},E_p)$ is related to $P(p',p)$ by

$$P(E_{p'},E_p)dE_{p'}dE_p = P(p',p)dp'dp \ . \tag{3.47}$$

Therefore

$$P(E_{p'},E_p) = \left[\frac{m}{|p|}\right]\left[\frac{m}{|p'|}\right]|S(p',p)|^2 \ . \tag{3.48}$$

As in Sec. III C, we note that $P(E_{p'},E_p)$ is obtained directly by Eqs. (3.33) and (3.37) if the initial and final wave packets are energy normalized as in Eq. (3.31).

IV. THE COMPLEX-COORDINATE SCATTERING THEORY FOR TIME-PERIODIC HAMILTONIANS

The complex-coordinate scattering theory is by now an established tool for calculations of inelastic transition probabilities. A remarkable agreement between theoretical transition probabilities and experimental scattering intensities was obtained for the cases of He scattering from corrugated Cu surfaces [39–42] and HD scattering from flat metal (Ag, Pt) surfaces [43]. Recently, the theory was found to be efficient for the calculation of the scattering matrix even for long-range (non-Coulombic) time-independent potentials [44]. The potential that was studied in [44] was of the type $-[(1-e^{-r})^n]/r^{n+1}$, $n > 1$. The successful application of the time-independent complex-coordinate scattering theory to such potentials is of physical importance, since these potentials represent the field-free s-wave interaction between an electron and many-electron ions.

The key point in the theory is the rotation of the reaction coordinate (the relative distance between the collision fragments) into the complex-coordinate plane $x \rightarrow x\exp(i\theta)$ [45–50]. The complex-coordinate method has also been applied to the calculation of quasienergy resonance states of atomic and molecular systems interacting with a time-periodic field [7–24]. In the following discussion we make use of the complex-coordinate method in order to obtain state-to-state transition probabilities for these systems. We combine the time-independent scattering theory for time-periodic Hamiltonians with the complex-coordinate scattering theory approach and derive an algorithm for the computational implementations of the equations that were derived in Sec. III.

A. The complex-coordinate Green operator

The main difficulty in the calculation of the transition probability amplitudes $\langle\psi_p(0)|\varphi_b(0)\rangle$ [Eq. (3.25)] or $S(p',p)$ [Eq. (3.44)] is in the evaluation of the matrix element of the generalized Green operator [Eq. (3.21)] in the limit $\varepsilon \rightarrow 0$:

$$\lim_{\varepsilon\rightarrow 0}\langle\langle f|[(E+i\varepsilon)\hat{I}-\hat{\mathcal{H}}_f]^{-1}|g\rangle\rangle = \sum_{\lambda}\frac{\langle\langle f|\lambda\rangle\rangle\langle\langle\lambda|g\rangle\rangle}{E-\lambda} \ . \tag{4.1}$$

In Eq. (3.25), $|f\rangle\rangle$ and $|g\rangle\rangle$ are given by

$$\langle\langle f| = \langle\langle p,0|\hat{V}, \quad |g\rangle\rangle = \sum_n |\varphi_b(0),n\rangle\rangle \ , \tag{4.2}$$

whereas in Eq. (3.44)

$$|g\rangle\rangle = \hat{V}|p',n\rangle\rangle \ , \quad \langle\langle f| = \langle\langle p,0|\hat{V} \ . \tag{4.3}$$

The complete set $(\{|\lambda\rangle\rangle\})$ are the eigenstates of the Floquet Hamiltonian operator:

$$\hat{\mathcal{H}}_f|\lambda\rangle\rangle = \lambda|\lambda\rangle\rangle \ . \tag{4.4}$$

It is seen that for any possible value of the energy E, the denominator vanishes for one of the values of λ, since λ gets real values from $-\infty$ to $+\infty$. This problem can be avoided provided that the interaction potential is an analytic function in the coordinate representation and that $\langle\langle x,t|f\rangle\rangle$ and $\langle\langle x,t|g\rangle\rangle$ are square-integrable functions of the coordinate x. Both conditions are satisfied for an analytic finite-range potential $\hat{V}$ [see Eqs. (4.2) and (4.3)]. In such a case the integration contour in Eq. (4.1) can be rotated into the complex-coordinate plane:

$$x \rightarrow xe^{i\theta} \ . \tag{4.5}$$

By introducing the unity operator in the generalized Hilbert space [Eq. (2.17)] under the inner product defined in Eq. (2.14) into Eq. (4.1), we obtain the complex-scaled matrix element

$$\begin{aligned}\lim_{\varepsilon\rightarrow 0}&\langle\langle f|[(E+i\varepsilon)\hat{I}-\hat{\mathcal{H}}_f]^{-1}|g\rangle\rangle \\ &= \langle\langle f^{-\theta}|\hat{G}^{\theta}(E)|g^{\theta}\rangle\rangle \\ &= \sum_{\alpha,\beta,m,n}\langle\langle f^{-\theta}|\beta,m\rangle\rangle\langle\langle\beta,m|\hat{G}^{\theta}|\alpha,n\rangle\rangle\langle\langle\alpha,n|g^{\theta}\rangle\rangle \ .\end{aligned} \tag{4.6}$$

In (x,t) representation, $\langle\langle f^{-\theta}|\beta,m\rangle\rangle$ and $\langle\langle\alpha,n|g^{\theta}\rangle\rangle$ are given by

$$\begin{aligned}\langle\langle f^{-\theta}|\beta,m\rangle\rangle &\\ &= \int_{-\infty}^{\infty}dx\, e^{i\theta}\frac{1}{T} \\ &\qquad\times\int_0^T dt\frac{1}{\sqrt{e^{i\theta}}}f^*(xe^{-i\theta},t)e^{imwt}\chi_\beta(x) \ , \\ \langle\langle\alpha,n|g^{\theta}\rangle\rangle &\\ &= \int_{-\infty}^{\infty}dx\, e^{i\theta}\frac{1}{T} \\ &\qquad\times\int_0^T dt\, e^{-inwt}\chi_\alpha^*(x)g(xe^{i\theta},t)\frac{1}{\sqrt{e^{i\theta}}} \ ,\end{aligned} \tag{4.7}$$

$f(z,t)$ and $g(z,t)$ are the analytical continuations of $f(x,t)$ and $g(x,t)$ into the complex-coordinate (z) plane, and the factors $1/\sqrt{e^{i\theta}}$ arose from the renormalization of the scattering asymptotic states [in Eqs. (4.2) and (4.3)] on the complex contour $x\exp(i\theta)$. For a more detailed discussion of the generalized complex inner products, see [51,52].

The complex-scaled generalized Green operator $\hat{G}^{\theta}(E)$ is defined in (x,t) representation as the analytical continuation of $\hat{G}(E)$ in Eq. (3.21):

$$\hat{G}^{\theta}(E)=[E\hat{I}-\hat{\mathcal{H}}_f(xe^{i\theta},t)]^{-1}\ . \tag{4.8}$$

As in the nonscaled problem [see Eq. (4.1)], $G^{\theta}(E)$ can be represented using the eigenvectors of the complex-scaled Floquet Hamiltonian $\hat{\mathcal{H}}_f^{\theta}$:

$$\hat{\mathcal{H}}_f^{\theta}=\hat{\mathcal{H}}_f(xe^{i\theta},t)\ . \tag{4.9}$$

To obtain the eigenvectors, we represent $\hat{\mathcal{H}}_f^{\theta}$ as a matrix in the generalized Hilbert space, $\mathbf{H}_f^{\theta}$, where

$$[\mathbf{H}_f^{\theta}]_{(\beta,m),(\alpha,n)}=\langle\langle\beta,m|\hat{\mathcal{H}}_f^{\theta}|\alpha,n\rangle\rangle\ . \tag{4.10}$$

The right and left eigenvectors of the analytically continued matrix are given by

$$\begin{aligned}&\mathbf{H}_f^{\theta}\boldsymbol{\lambda}^R=\lambda^{\theta}\boldsymbol{\lambda}^R\ ,\\&(\boldsymbol{\lambda}^L)^t\mathbf{H}_f^{\theta}=\lambda^{\theta}(\boldsymbol{\lambda}^L)^t\ .\end{aligned} \tag{4.11}$$

Since the complex-scaled Hamiltonian matrix $\mathbf{H}_f^{\theta}$ is non-Hermitian, its left eigenvectors $\boldsymbol{\lambda}^L$ *cannot* be obtained by taking the complex conjugate of the transposed right eigenvector $\boldsymbol{\lambda}^R$. Rather, they are the right eigenvectors of the transposed matrix, $\mathbf{H}_f^{\theta}$ [51,52] as can be verified by transposing the last equation:

$$(\mathbf{H}_f^{\theta})^t\boldsymbol{\lambda}^L=\lambda^{\theta}\boldsymbol{\lambda}^L\ . \tag{4.12}$$

The spectrum $(\{\lambda^{\theta}\})$ of $\mathbf{H}_f^{\theta}$ may be incomplete for specific values of the scaling angle θ [53]. However, even for these values, a complete spectrum is obtained by infinitesimal change of the value of θ [53]. Therefore, it is always possible to normalize the right and left eigenvectors such that

$$(\boldsymbol{\lambda}^L)^t\boldsymbol{\lambda}'^R=\delta_{\lambda,\lambda'}\ . \tag{4.13}$$

Provided that the spectrum of $\mathbf{H}_f^{\theta}$ is complete, we can represent the complex-scaled generalized Green operator as a matrix $\mathbf{G}^{\theta}(E)$ in the generalized Hilbert space using the components of the right and left eigenvectors:

$$\begin{aligned}\langle\langle\beta,m|\hat{G}^{\theta}(E)|\alpha,n\rangle\rangle&=[\mathbf{G}^{\theta}(E)]_{(\beta,m),(\alpha,n)}\\&=\sum_{\lambda^{\theta}}\frac{\lambda^R_{(\beta,m)}\lambda^L_{(\alpha,n)}}{E-\lambda^{\theta}}\ .\end{aligned} \tag{4.14}$$

The eigenvalues of the non-Hermitian complex-scaled Floquet Hamiltonian $\{\lambda^{\theta}\}$ are complex and therefore the denominator in the last equation is nonzero for all values of E (excluding the threshold energies; see, for example, Fig. 2 in Ref. 43). There are two kinds of eigenvalues. One kind are the continuum energies which are rotated into the complex energy plane by the angle 2θ. These eigenvalues are given by the equation

$$\lambda=|\lambda'-\hbar\omega n|\exp(-2i\theta)\ ,$$

for $n=-\infty,\ldots,+\infty$ and $\lambda'\in[0,\infty]$. The eigenvalues of the second kind are the complex resonance energies $\lambda=\lambda_r-i\Gamma/2$, which are independent of the rotation angle θ. The resonances become square integrable in the complex-coordinate representation when θ exceeds a critical value [46–50]. Each resonance represents a metastable state where λ_r is the resonance position and $\hbar/\Gamma$ is the lifetime of the state.

Equation (4.14) provides an explicit expression for the matrix $\mathbf{G}^{\theta}(E)$ for *any* value of the energy E. However, if $\mathbf{G}^{\theta}(E)$ is required for a *specific* value of E, it is possible to reduce the numerical effort in the calculation. First, we introduce the matrices $\mathbf{U}^R$ and $\mathbf{U}^L$, whose columns are the eigenvectors $\boldsymbol{\lambda}^R$ and $\boldsymbol{\lambda}^L$ correspondingly:

$$\begin{aligned}&\mathbf{U}^R=[\boldsymbol{\lambda}_1^R,\boldsymbol{\lambda}_2^R,\ldots]\ ,\\&\mathbf{U}^L=[\boldsymbol{\lambda}_1^L,\boldsymbol{\lambda}_2^L,\ldots]\ .\end{aligned} \tag{4.15}$$

These matrices are related according to Eq. (4.13):

$$(\mathbf{U}^L)^t(\mathbf{U}^R)=\mathbf{I}\ . \tag{4.16}$$

We rewrite Eq. (4.14) for $\mathbf{G}^{\theta}(E)$:

$$\mathbf{G}^{\theta}(E)=\mathbf{U}^R\mathbf{A}^{-1}(\mathbf{U}^L)^t\ , \tag{4.17}$$

where the matrix $\mathbf{A}(E)$ is defined by

$$[\mathbf{A}]_{i,j}=(E-\lambda_i)\delta_{i,j}\ . \tag{4.18}$$

From Eqs. (4.11) and (4.16), it follows that

$$\mathbf{A}=(\mathbf{U}^L)^t[E\mathbf{I}-\mathbf{H}_f^{\theta}]\mathbf{U}^R\ . \tag{4.19}$$

By substituting Eq. (4.19) into Eq. (4.17) using Eq. (4.16), we obtain

$$\mathbf{G}^{\theta}(E)=[E\mathbf{I}-\mathbf{H}_f^{\theta}]^{-1} \tag{4.20}$$

or

$$\begin{aligned}\langle\langle\beta,m|\hat{G}^{\theta}(E)|\alpha,n\rangle\rangle&=[\mathbf{G}^{\theta}(E)]_{(\beta,m),(\alpha,n)}\\&=[E\mathbf{I}-\mathbf{H}_f^{\theta}]^{-1}_{(\beta,m),(\alpha,n)}\ .\end{aligned} \tag{4.21}$$

The matrix elements of $\mathbf{G}^{\theta}(E)$ can therefore by obtained by a matrix inversion (for a specific energy E) instead of a matrix diagonalization (for any E).

By substituting $\langle\langle\beta,m|\hat{G}^{\theta}(E)|\alpha,n\rangle\rangle$ from either Eq. (4.14) or Eq. (4.21), and Eq. (4.7) into Eq. (4.6), an explicit expression for the calculation of the Green-operator matrix element is obtained. In contrast to the nonscaled expression [given in Eq. (4.1)], the scaled one does not suffer from singularity problems.

B. Complex-scaled ionization-dissociation probabilities for a half-collision experiment

In a half-collision experiment the system is initially bounded in a state $|\varphi_b(0)\rangle$ and at $t=0$ it is exposed to a time-periodic interaction (see Sec. III C). The probability density $P_b(E_p)$ to obtain the fragments of the system in a well-defined kinetic energy E_p is given by Eq. (3.30), and the probability density amplitude $\langle \psi_p(0)|\varphi_b(0)\rangle$ is given by Eq. (3.25). We obtain the complex-coordinate scattering theory expression for the amplitude by substituting Eqs. (4.2) and (4.6) into Eq. (3.25):

$$\langle \psi_p(0)|\varphi_b(0)\rangle^\theta = \langle p|\varphi_b(0)\rangle + \sum_n \langle\langle p^{-\theta},0|\hat{V}^\theta \hat{G}^\theta(E_p)|\varphi_b^\theta,(0)n\rangle\rangle \;, \tag{4.22}$$

where

$$\langle\langle p^{-\theta},0|\hat{V}^\theta\hat{G}^\theta(E_p)|\varphi_b^\theta(0),n\rangle\rangle = \sum_{\alpha,\beta,m,k} \langle\langle p^{-\theta},0|\hat{V}^\theta|\beta,m\rangle\rangle \times \langle\langle \beta,m|\hat{G}^\theta(E_p)|\alpha,k\rangle\rangle \langle\langle \alpha,k|\varphi_b^\theta(0),n\rangle\rangle \;. \tag{4.23}$$

$\langle\langle \beta,m|\hat{G}^\theta(E_p)|\alpha,k\rangle\rangle$ is given by Eq. (4.21) [or by Eq. (4.14)]. From Eq. (4.7) we obtain

$$\langle\langle p^{-\theta},0|\hat{V}^\theta|\beta,m\rangle\rangle = \int_{-\infty}^{\infty} dx\, e^{i\theta}\frac{1}{T} \times \int_0^T \frac{dt}{\sqrt{e^{i\theta}}} \frac{e^{-i(pxe^{i\theta})/h}}{\sqrt{2\pi\hbar}} \times V(xe^{i\theta},t)e^{imwt}\chi_\beta(x) \;, \tag{4.24}$$

$$\langle\langle \alpha,k|\varphi_b^\theta(0),n\rangle\rangle = \int_{-\infty}^{\infty} dx\, e^{i\theta}\frac{1}{T} \times \int_0^T \frac{dt}{\sqrt{e^{i\theta}}} e^{-ikwt} \times \chi_\alpha^*(x)\varphi_b(xe^{i\theta},0)e^{inwt} \;.$$

The substitution of Eqs. (4.21), (4.23), and (4.24) into Eq. (4.22) provides the exact expression for the amplitude. However, in numerical applications the summation in Eq. (4.23) is over a finite set of variational basis functions. In any *finite* basis-set representation the amplitude depends on the value of the scaling angle θ. This dependence was studied extensively for time-independent Hamiltonians [44,45,54–58]. It was shown that the variationally optimal scaling angle θ_{opt} satisfies a stationarity condition of the transition amplitude [44]. In our case this condition reads

$$\left.\frac{\partial(\langle \psi_p(0)|\varphi_b(0)\rangle^\theta)}{\partial\theta}\right|_{\theta=\theta_{\text{opt}}} = 0 \;. \tag{4.25}$$

The complex-scaled time-independent variational expression for the probability density to obtain the half-collision fragments in a final kinetic energy E_p is therefore [see Eq. (3.30)]

$$P_b(E_p) = \frac{m}{|p|}|\langle \psi_p(0)|\varphi_b(0)\rangle^{\theta_{\text{opt}}}|^2 \;. \tag{4.26}$$

C. Complex-scaled transition probabilities for a full-collision experiment

Here we consider an experiment in which two fragments collide under the influence of a time-periodic finite-range potential (as discussed in Sec. III D). For initial and final states in which the relative kinetic energy of the fragments is well defined ($E_{p'}$ and E_p, respectively), the transition probability density is given by Eq. (3.48). The probability density amplitude $S(p',p)$ is given by Eq. (3.44). We obtain the complex-coordinate scattering theory expression for the amplitude by substituting Eqs. (4.3), (4.6), and (3.40) into Eq. (3.44):

$$S^\theta(p',p) = \delta(p-p') - 2\pi i \sum_n \left[\langle\langle p,0|\hat{V}|p',n\rangle\rangle + \left\langle\!\!\left\langle p^{-\theta},0 \left| \hat{V}^\theta\hat{G}^\theta\left[\frac{E_p+E_{p'}+\hbar wn}{2}\right]\hat{V}^\theta \right| p'^\theta,n \right\rangle\!\!\right\rangle \right] \times\delta(E_p-(E_{p'}+\hbar wn)) \;, \tag{4.27}$$

where

$$\left\langle\!\!\left\langle p^{-\theta},0 \left| \hat{V}^\theta\hat{G}^\theta\left[\frac{E_p+E_{p'}+\hbar wn}{2}\right]\hat{V}^\theta \right| p'^\theta,n \right\rangle\!\!\right\rangle = \sum_{\beta,m,\alpha,k} \langle\langle p^{-\theta},0|\hat{V}^\theta|\beta,m\rangle\rangle \left\langle\!\!\left\langle \beta,m \left| \hat{G}^\theta\left[\frac{E_p+E_{p'}+\hbar wn}{2}\right] \right| \alpha,k \right\rangle\!\!\right\rangle \langle\langle \alpha,k|\hat{V}^\theta|p'^\theta,n\rangle\rangle \;. \tag{4.28}$$

$\langle\langle \beta,m|\hat{G}^\theta(E)|\alpha,k\rangle\rangle$ is given by Eq. (4.21) [or by Eq. (4.14)]. From Eq. (4.7) we obtain

$$\langle\langle p^{-\theta},0|\hat{V}^\theta|\beta,m\rangle\rangle = \int_{-\infty}^{\infty} dx\, e^{i\theta}\frac{1}{T}\int_0^T \frac{dt\, e^{(-ipxe^{i\theta})/\hbar}}{\sqrt{2\pi\hbar e^{i\theta}}} V(xe^{i\theta},t)e^{imwt}\chi_\beta(x) \;,$$

$$\langle\langle \alpha,k|\hat{V}^\theta|p'^\theta,n\rangle\rangle = \int_{-\infty}^{\infty} dx\, e^{i\theta}\frac{1}{T}\int_0^T dt\, \chi_\alpha^*(x)e^{-ikwt}V(xe^{i\theta},t)\frac{e^{(ip'xe^{i\theta})/\hbar}}{\sqrt{2\pi\hbar e^{i\theta}}}e^{inwt} \;. \tag{4.29}$$

As discussed in Sec. IV B, in numerical applications of the theory the amplitude is θ dependent due to the use of a *finite* basis-set representation. The variationally optimal scaling angle θ_{opt} satisfies the equation [44]

$$\left.\frac{\partial S^{\theta}(p',p)}{\partial\theta}\right|_{\theta=\theta_{\mathrm{opt}}}=0 . \tag{4.30}$$

The complex-scaled time-independent variational expression for the transition probability density is therefore [see Eq. (3.48)]

$$P(E_{p'},E_p)=\frac{m^2}{|p\cdot p'|}|S^{\theta_{\mathrm{opt}}}(p',p)|^2 , \tag{4.31}$$

where $S^{\theta_{\mathrm{opt}}}$ is obtained by substituting Eqs. (4.21), (4.28), and (4.29) into Eq. (4.27).

V. ILLUSTRATIVE NUMERICAL EXAMPLE: THE CALCULATION OF ABOVE-THRESHOLD-IONIZATION SPECTRA

In this section we apply the theory to the study of ionization of an atomic system due to its interaction with a monochromatic electromagnetic field. The Hamiltonian (in a.u.) of the field-free system is $\hat{H}_a(x)$:

$$\hat{H}_a(x)=-\frac{1}{2}\frac{\partial^2}{\partial x^2}+\hat{V}_0(x) , \tag{5.1}$$

where the potential $\hat{V}_0(x)$ supports bound states of the electron-atom system. Within the framework of the semiclassical treatment of a monochromatic electromagnetic field, the full Hamiltonian for the atom interacting with the field is given by

$$\hat{H}(x,t)=\hat{H}_a(x)+A_0\hat{\mu}(x)\cos(wt) . \tag{5.2}$$

$\mu(x)$ is the dipole moment of the system and A_0 is the amplitude of the field intensity. We choose to study the Rosen-Morse [15–17,19,21,22,59] model for the atom-field interaction where

$$\hat{\mu}(x)=\hat{V}_0(x)=-\frac{V_0}{\cosh^2(\alpha x)} , \tag{5.3}$$

with the parameters $V_0=2$, $\alpha=1/\sqrt{3}$. The initial state of the system is a bound state of the field-free Hamiltonian. This wave function is obtained by diagonalization of $\hat{H}_a(x)$ in a linear variational space. As a basis set we choose N_x particle-in-a-box basis functions, with a box length L. The initial bound state is obtained as

$$\begin{aligned}\langle x|\varphi_b(0)\rangle&=\varphi_b(x,0)\\ &=\sum_{\alpha=1}^{N_x}C_\alpha\left[\frac{2}{L}\right]^{1/2}\sin\left[\frac{\alpha\pi(x+L/2)}{L}\right] .\end{aligned} \tag{5.4}$$

The coefficient vector $\mathbf{C}$ is the solution to the eigenvalue problem

$$\mathbf{H}_a\mathbf{C}=E_b\mathbf{C} , \tag{5.5}$$

where the matrix elements of $\mathbf{H}_a$ are given by

$$\begin{aligned}\mathbf{H}_{a_{\alpha,\beta}}=\frac{2}{L}\int_{-L/2}^{L/2}&\sin\left[\frac{\alpha\pi(x+L/2)}{L}\right]\\ &\times\left[-\frac{1}{2}\frac{\partial^2}{\partial x^2}+V_0(x)\right]\\ &\times\sin\left[\frac{\beta\pi(x+L/2)}{L}\right]dx\end{aligned} \tag{5.6}$$

and E_b is the bound state energy.

The above-threshold ionization spectrum is the ionization probability versus the final kinetic energy of the emitted electrons, $P_b(E_p)$. In order to obtain the spectrum, we use the complex-coordinate time-independent expression given by Eqs. (4.21)–(4.26).

In the first step of the calculation we represent the complex-scaled operators and asymptotical states in a set of variational basis functions. The Fourier basis functions are used for the time-variable representation and the particle-in-a-box functions (that were used to obtain $\varphi_b(x,0)$ [Eq. (5.4)]) are used for the x-coordinate representation. The matrix elements of the complex-scaled Floquet Hamiltonian

$$\hat{\mathcal{H}}_f^{\theta}=-i\hbar(\partial/\partial t)+\hat{H}(xe^{i\theta},t)$$

are therefore given by

$$\begin{aligned}&[\mathbf{H}_f^{\theta}]_{(\beta,m),(\alpha,n)}\\ &=\frac{2}{L}\int_{-L/2}^{L/2}dx\frac{1}{T}\int_0^T dt\, e^{-imwt}\sin\left[\frac{\beta\pi\left[x+\frac{L}{2}\right]}{L}\right]\\ &\qquad\times\left[-i\hbar\frac{\partial}{\partial t}-\frac{\hbar^2}{2m_e e^{2i\theta}}\frac{\partial^2}{\partial x^2}+V_0(xe^{i\theta})+A_0\mu(xe^{i\theta})\cos(wt)\right]e^{inwt}\sin\left[\frac{\alpha\pi\left[x+\frac{L}{2}\right]}{L}\right] ,\end{aligned} \tag{5.7}$$

where $\beta=1,2,\ldots,N_x$; $\alpha=1,2,\ldots,N_x$; and $n=-N_t/2,\ldots,+N_t/2$; $m=-N_t/2,\ldots,+N_t/2$. (In the present calculations $N_x=100$ and $N_t=8$ were found sufficient for convergence.) The final asymptotic state with the kinetic energy E_p and the interaction potential are complex scaled and represented in the basis set according to Eq. (4.24):

$$\langle\langle p^{-\theta},0|\hat{V}^{\theta}|\beta,m\rangle\rangle=\frac{1}{T}\int_0^T dt\int_{-L/2}^{L/2}dx\, e^{i\theta}\frac{e^{-i[(pxe^{i\theta})/\hbar]}}{\sqrt{2\pi\hbar e^{i\theta}}}[V_0(xe^{i\theta})+A_0\mu(xe^{i\theta})\cos(wt)]$$
$$\times\left[\frac{2}{L}\right]^{1/2}\sin\left[\frac{\beta\pi\left[x+\frac{L}{2}\right]}{L}\right]e^{imwt}\ . \tag{5.8}$$

The complex-scaled initial bound state is similarly obtained from Eq. (4.24):

$$\langle\langle\beta,m|\varphi_b^{\theta}(0),n\rangle\rangle=\int_{-L/2}^{L/2}dx\, e^{i\theta}\left[\frac{2}{L}\right]^{1/2}\sin\left[\frac{\beta\pi\left[x+\frac{L}{2}\right]}{L}\right]\frac{1}{\sqrt{e^{i\theta}}}\varphi_b(xe^{i\theta},0)\delta_{n,m}\ . \tag{5.9}$$

In the second step of the calculations the complex-scaled generalized Green matrix [Eq. (4.20)] is obtained for a given final kinetic energy E_p by a matrix inversion according to Eq. (4.21):

$$\mathbf{G}^{\theta}(E_p)=[E_p\mathbf{I}-\mathbf{H}_f^{\theta}]^{-1}\ . \tag{5.10}$$

The complex-scaled ionization probability density amplitude is obtained from Eqs. (4.22) and (4.23):

$$\langle\psi_p(0)|\varphi_b(0)\rangle^{\theta}=\langle p|\varphi_b(0)\rangle+(\mathbf{p}^{\theta})^t\mathbf{G}^{\theta}(E_p)(\mathbf{b}^{\theta})\ , \tag{5.11}$$

where

$$\begin{aligned}[\mathbf{p}^{\theta}]_{\beta,m}&=\langle\langle p^{-\theta},0|\hat{V}^{\theta}|\beta,m\rangle\rangle\ ,\\ [\mathbf{b}^{\theta}]_{\beta,m}&=\sum_n\langle\langle\beta,m|\varphi_b^{\theta}(0),n\rangle\rangle\ .\end{aligned} \tag{5.12}$$

According to Eq. (4.26), the probability density for ionization with a well-defined relative kinetic energy E_p is given by

$$P_b(E_p)=\frac{m}{|p|}|\langle p|\varphi_b(0)\rangle+(\mathbf{p}^{\theta_{\rm opt}})^t\mathbf{G}^{\theta_{\rm opt}}(E_p)(\mathbf{b}^{\theta_{\rm opt}})|^2\ , \tag{5.13}$$

where $p=\sqrt{2mE_p}$ and the variationally optimized sealing angle $\theta_{\rm opt}$ is determined from the stationarity condition:

$$\left.\frac{\partial\langle\psi_p(0)|\varphi_b(0)\rangle^{\theta}}{\partial\theta}\right|_{\theta_{\rm opt}}=0\ . \tag{5.14}$$

In Fig. 1 the results for $P_b(E_p)$ are presented. The field intensity parameter is $A_0=0.8$ a.u. and the initial state was chosen as the first excited eigenstate of $\hat{H}_a$. The dots represent the results obtained by the complex-coordinate time-independent scattering theory [Eq. (5.13)], while the solid line represents results of time-dependent wave-packet calculations that were carried out by Bench, Korsch, and Moiseyev [29] for the same model Hamiltonian. The agreement between the results is remarkable. The present time-independent calculation, however, has the advantage of using a much smaller grid space ($\frac{1}{16}$) and number of basis functions for the coordinate representation (100 particle-in-a-box functions rather than 10 000 grid points). This is due to the absorbing boundary conditions which are imposed by the complex coordinate and which result in a decay of the resonance wave functions at large values of x. Another important advantage of the present calculation is that the time integration of the Schrödinger equation is carried out analytically to $t=\infty$ and therefore no time-averaging procedures are needed in order to obtain a time-independent spectrum. This advantage of the time-independent scattering theory is especially pronounced when narrow (long-lived) resonances are studied and long propagation times are required in order to obtain the time-independent ATI spectrum. Therefore, it is expected that it will be difficult to obtain the narrow peaks in the ATI spectra from time-dependent calculations. The truncation of the time prop-

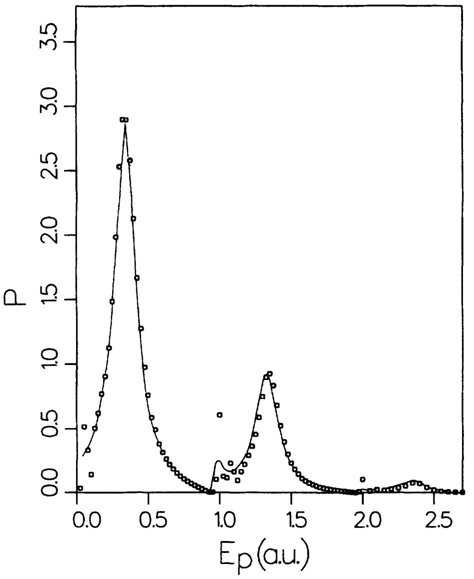

FIG. 1. Time-independent photoionization probability density vs. the final kinetic energy of the electron. The initial bound-state energy is $-\frac{2}{3}$ a.u. and the field intensity parameter is $A_0=0.8$ a.u. The dots represent the results obtained by the time-independent complex-coordinate scattering theory. The solid line is borrowed from Ref. [29]. It represents the results of a time-dependent calculation. The spectra are normalized such that the total-ionization probability is unity.

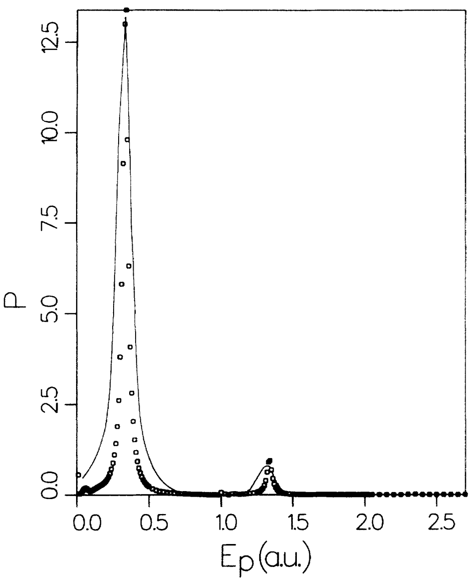

FIG. 2. The same as Fig. 1, with $A_0=0.4$ a.u. The normalized results of Ref. [29] were multiplied by a factor of 2.33 in order to fit the maxima of the two spectra.

agation at a finite time results in broadening the peaks in the ATI spectrum. Indeed, as one can see from the results presented in Fig. 2, when the field intensity parameter is reduced to $A_0=0.4$ (and the resonance lifetime is almost doubled), the peaks in the ATI spectrum obtained from the time-dependent calculation are broader than the peaks obtained from the "$t=\infty$" ATI spectrum. The ATI spectra presented in Figs. 1 and 2 clearly show peaks which correspond to the absorption of an integer number of photons by the emitted electron. The sharp structure of the ATI spectrum can be explained by analyzing a single complex-scaled square-integrable resonance wave function that had maximal overlap with the bound state of the field-free Hamiltonian [19]. The width of the peaks in the ATI spectrum is the total width of the resonance state, whereas the relative heights of the peaks are proportional to the partial widths obtained by asymptotical analysis of the resonance wave function [17,22,26,27]. The present calculation is also based on the complex-coordinate method. The complex-scaled quasienergy resonance states are used with all other quasienergy states in order to obtain the ionization probability [see Eq. (4.14)]. Therefore, we believe that the theory presented here should also have a pronounced advantage in the study of photoionization or photodissociation processes which cannot be explained by analyzing a single resonance state. This may be the case in systems where overlapping resonances or avoided crossing of resonances occurs, for high field intensities.

VI. CONCLUDING REMARKS

A time-independent scattering theory for time-periodic Hamiltonians was developed. Expressions for state-to-state transition probabilities were obtained for half-collision experiments [Eqs. (4.22)–(4.26) or Eq. (A14)] and for full-collision experiments [Eqs. (4.27)–(4.31) or Eq. (A22)]. In the text an *ab initio* scattering theory was introduced, which is based on the asymptotic condition assumption. In the Appendix the derivation is based on the representation of the asymptotic states as vector functions. We postulated that the initial vector function describes the noninteracting system of an atom or molecule and a field, while the final vector function represents free motion in the absence of the field. The latter assumption is justified only by the fact that it yielded the same expressions as the *ab initio* theory for the transition probabilities. However, we argue that the vector function representation of the asymptotic states provides insight for the understanding of multiphoton ionization-dissociation processes.

The key point in our derivation is the analytical evaluation of the time evolution of the system up to $t=\pm\infty$. This is enabled by using Shirley's expression for the time-evolution operator and by carrying out analytical continuation of the photofragment energy into the lower half of the complex energy plane. In our numerical application to the calculation of ATI spectra, the analytical continuation was carried out by the complex-coordinate method (known also as complex scaling or the complex rotation method). We should stress here that any other kind of analytical continuation could be used as well. For example, one could use "optical" potentials [60–62] or the exterior complex scaling [20,63–65] in order to impose absorbing boundary conditions.

The ATI spectra for a model system which were calculated by the time-independent method presented here were found to be in remarkable agreement with spectra that were previously obtained from time-dependent calculations. The possibility to avoid long propagation times and large grid space looks promising for the future applications of the method using three-dimensional realistic model Hamiltonians. This however is beyond the scope of the present article.

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APPENDIX: AN ALTERNATIVE DERIVATION OF THE COMPLEX-SCALED TIME-INDEPENDENT TRANSITION PROBABILITIES

Using the matrix representation of the Floquet Hamiltonian combined with the complex-coordinate method, the time-independent transition probability amplitudes for half-collision and for full-collision processes in the presence of time-periodic potentials are obtained. In the present derivation we use the fact that all the eigenvalues of the complex-scaled Floquet Hamiltonian are complex with negative imaginary parts and the generalized inner product for non-Hermitian operators (also known as the *c* product [51,52]).

The time-independent Floquet Hamiltonian matrix which describes the interaction of an atom (or a molecule) with an external time-periodic field is given by

$$[\hat{\mathbf{H}}_f(x)]_{n',n} = \frac{1}{T}\int_0^T \hat{H}(x,t)e^{iw(n'-n)t}dt + \hbar w n \delta_{n',n} , \qquad \text{(A1)}$$

where

$$\hat{H}(x,t) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \hat{V}(x,t) ,$$

$$\hat{V}(x,t) = \hat{V}(x,t+T) , \qquad \text{(A2)}$$

$$T = 2\pi/w .$$

As in solid-state theory, the indices n and n' refer to the nth and n'th Brillouin zones, respectively. In the case of an electromagnetic field, $m = (n - n')$ can be regarded as the number of photons which are absorbed ($m < 0$) or emitted ($m > 0$) as a result of the interaction between the atom (molecule) and the field.

The coordinates are scaled by a complex factor such that

$$x = x'e^{i\theta} , \qquad \text{(A3)}$$

where x' gets real values only. Following the c-product definition, we will not take the complex conjugate of $\exp(i\theta)$ whenever matrix elements with complex-scaled functions are evaluated. [This definition is equivalent to the introduction of the complex integration contour in Eq. (4.7).] $\hat{\mathbf{H}}_f(x)$ is a time-independent matricial operator which is represented as a matrix in the Fourier basis by an integration over the time t [Eq. (A1)]. The states which describe the atom-field system are therefore vector functions. The components of the vector functions are the x-dependent coefficients in the Fourier basis-set expansion of the states. The representation of the initial and the final scattering asymptotes as vector functions is the key point in the following derivation.

1. Half-collision processes

At $t < 0$ the atom or molecule is in an eigenstate of the field-free Hamiltonian, $\varphi_b(x)$. At $t = 0$ the atom or molecule is suddenly exposed to a time-periodic field. Our definition of the vector function that describes the atom or molecule and the field at $t = 0$ is

$$\boldsymbol{\phi}_b(x,0) = (\ldots, \varphi_b(x), \varphi_b(x), \varphi_b(x), \ldots) . \qquad \text{(A4)}$$

That is, at $t = 0$ the initial state is a vector whose components at any Brillouin zone $n = -\infty, \ldots, \infty$ are given by $\varphi_b(x)$. $\boldsymbol{\phi}_b(x,0)$ is developed in time under the influence of the time-independent Floquet matrix operator. Therefore,

$$\boldsymbol{\phi}_b(x,t) = e^{-i\hat{\mathbf{H}}_f(x)t/\hbar}\boldsymbol{\phi}_b(x,0) . \qquad \text{(A5)}$$

The final state is determined by the detector which is located far from the focal region of the electromagnetic field. Therefore,

$$\psi_f(x,t) = e^{-iE_p t/\hbar}\left[\frac{m}{2\pi\hbar p e^{i\theta}}\right]^{1/2} e^{ipx/\hbar} \qquad \text{(A6)}$$

describes the free particles (electrons or ions) with the kinetic energy $E_p = p^2/2m$ which are trapped by the detector. The final state can be represented as a vector function:

$$\boldsymbol{\phi}_p(x,t) = e^{-iE_p t/\hbar}\boldsymbol{\phi}_p(x,0) = e^{-i\hat{\mathbf{H}}_f^0 t/\hbar}\boldsymbol{\phi}_p(x,0) , \qquad \text{(A7)}$$

where the diagonal block Floquet Hamiltonian matrix $\hat{\mathbf{H}}_f^0$ is given by

$$\hat{\mathbf{H}}_f^0(x) = \hat{\mathbf{H}}_f(x) - \hat{\mathbf{V}}(x) , \qquad \text{(A8)}$$

$$[\hat{\mathbf{V}}(x)]_{n',n} = \frac{1}{T}\int_0^T \hat{\mathbf{V}}(x,t)e^{iw(n'-n)t}dt \qquad \text{(A9)}$$

and $\boldsymbol{\phi}_p(x,0)$ is given by

$$\boldsymbol{\phi}_p(x,0) = \left[\ldots, 0, 0, \left[\frac{m}{2\pi\hbar p e^{i\theta}}\right]^{1/2} e^{ipx/\hbar}, 0, 0, \ldots\right] , \qquad \text{(A10)}$$

where the only nonzero component is for $n = 0$.

At $t \to \infty$ the state vector of the system $\boldsymbol{\phi}_b(x,t)$ is spanned by the set of all possible final states. The complex-scaled probability to detect a final kinetic energy E_p is therefore given by

$$P_b^\theta(E_p) = |\lim_{t\to\infty}\langle \boldsymbol{\phi}_p(t)|\boldsymbol{\phi}_b(t)\rangle|^2 . \qquad \text{(A11)}$$

$\boldsymbol{\phi}_p(t)$ stands for the transposed vector $[\boldsymbol{\phi}_p(t)]^t$, and $\langle\ |\ \rangle$ stands for the c product [51,52] (an integration on the complex-coordinate contour, $x'e^{i\theta}$). The probability amplitude is obtained by using Eqs. (A5) and (A7):

$$\begin{aligned}
\lim_{t\to\infty}\langle \boldsymbol{\phi}_p(t)|\boldsymbol{\phi}_b(t)\rangle &= \langle \boldsymbol{\phi}_p(0)|\boldsymbol{\phi}_b(0)\rangle + \int_0^\infty dt \frac{\partial}{\partial t}\langle \boldsymbol{\phi}_p(t)|\boldsymbol{\phi}_b(t)\rangle \\
&= \langle \boldsymbol{\phi}_p(0)|\boldsymbol{\phi}_b(0)\rangle + \int_0^\infty dt \frac{\partial}{\partial t}\langle \boldsymbol{\phi}_p(0)|e^{i\hat{\mathbf{H}}_f^0 t/\hbar}e^{-i\hat{\mathbf{H}}_f t/\hbar}|\boldsymbol{\phi}_b(0)\rangle \\
&= \langle \boldsymbol{\phi}_p(0)|\boldsymbol{\phi}_b(0)\rangle - \frac{i}{\hbar}\int_0^\infty dt \langle \boldsymbol{\phi}_p(0)|\hat{\mathbf{V}}e^{-i(\hat{\mathbf{H}}_f - E_p\hat{\mathbf{I}})t/\hbar}|\boldsymbol{\phi}_b(0)\rangle . \qquad \text{(A12)}
\end{aligned}$$

Using the spectral representation of the Green operator and bearing in mind the fact that all eigenvalues of the complex-scaled Floquet Hamiltonian matrix are complex with negative imaginary parts, we immediately get the result that

$$-\frac{i}{\hbar}\int_0^\infty e^{-i(\hat{\mathbf{H}}_f - E_p\hat{\mathbf{I}})t/\hbar}dt = [E_p\hat{\mathbf{I}} - \hat{\mathbf{H}}_f]^{-1} \equiv \hat{\mathbf{G}}(E_p) . \qquad \text{(A13)}$$

By substituting Eqs. (A12) and (A13) into Eq. (A11), one gets that

$$P_b^\theta(E_p)=|\langle \boldsymbol{\phi}_p(0)|\hat{\mathbf{I}}+\hat{\mathbf{V}}\hat{\mathbf{G}}(E_p)|\boldsymbol{\phi}_b(0)\rangle|^2 , \qquad \text{(A14)}$$

where all components of $|\boldsymbol{\phi}_b(0)\rangle$ are identical and equal to the bound eigenstate of the field-free Hamiltonian, whereas the only nonzero component in $|\boldsymbol{\phi}_p(0)\rangle$ is the $n=0$ component as described above. Note that Eq. (A14) is equivalent to Eqs. (4.22), (4.23), and (4.26) in the text. The difference is that in the present representation the operators and the states are represented as functions of x, whereas in the text they are presented in a basis set $\{|\alpha\rangle\}$. As discussed in the text, the numerical advantage of this formula is in the fact that only one inversion of the complex-scaled Floquet Hamiltonian matrix (constructed from square-integrable basis functions) is required in order to obtain the transition probability amplitude for a given value of the kinetic energy E_p of the detected free particle.

2. Full-collision processes

Here we describe a situation where, for example, a positive ion and an electron (or a negative ion) with a relative kinetic energy $E_{p'}$ collide inside an ac field. As a result, an electron and an ion with a relative kinetic energy E_p are obtained. Let us define the vector state of the system at $t=0$ as $\boldsymbol{\psi}(x,0)$. The initial and final asymptotical vector states are represented by the vectors $\boldsymbol{\phi}_{p'}(x,-\infty)$ and $\boldsymbol{\phi}_p(x,\infty)$, respectively, where at $t=0$,

$$\begin{aligned}\boldsymbol{\phi}_{p'}(x,0)&=(\ldots,\varphi_{p'}(x),\varphi_{p'}(x),\varphi_{p'}(x),\ldots) ,\\ \boldsymbol{\phi}_p(x,0)&=(\ldots,0,\varphi_p(x),0,\ldots) ,\end{aligned} \qquad \text{(A15)}$$

and

$$\varphi_p(x)=\left[\frac{m}{2\pi\hbar p e^{i\theta}}\right]^{1/2} e^{ipx/\hbar} . \qquad \text{(A16)}$$

As $t\rightarrow\infty$, the actual vector state of the system $\boldsymbol{\psi}(x,t)$ is spanned by all possible final states. By introducing the time-evolution operators from Eqs. (A5) and (A7), we obtain

$$e^{-i\hat{\mathbf{H}}_f(x)t/\hbar}\boldsymbol{\psi}(x,0)\xrightarrow[t\rightarrow\infty]{}a_p e^{-i\hat{\mathbf{H}}_f^0(x)t/\hbar}\boldsymbol{\phi}_p(x,0) , \qquad \text{(A17)}$$

where $|a_p|^2$ is the probability to find the system at $\boldsymbol{\phi}_p(x,t)$ as $t\rightarrow\infty$. As $t\rightarrow-\infty$, the initial vector state of the system is $\boldsymbol{\phi}_{p'}(x,0)$. Therefore,

$$e^{-i\hat{\mathbf{H}}_f(x)t/\hbar}\boldsymbol{\psi}(x,0)\xrightarrow[t\rightarrow-\infty]{}e^{-i\hat{\mathbf{H}}_f^0(x)t/\hbar}\boldsymbol{\phi}_{p'}(x,0) \qquad \text{(A18)}$$

or (by replacing t by $-t$)

$$e^{i\hat{\mathbf{H}}_f(x)t/\hbar}\boldsymbol{\psi}(x,0)\xrightarrow[t\rightarrow\infty]{}e^{i\hat{\mathbf{H}}_f^0(x)t/\hbar}\boldsymbol{\phi}_{p'}(x,0) . \qquad \text{(A19)}$$

From Eq. (A19) one can get that as $t\rightarrow\infty$,

$$\boldsymbol{\psi}(x,0)\xrightarrow[t\rightarrow\infty]{}e^{-i\hat{\mathbf{H}}_f(x)t/\hbar}e^{i\hat{\mathbf{H}}_f^0(x)t/\hbar}\boldsymbol{\phi}_{p'}(x,0) . \qquad \text{(A20)}$$

By substituting Eq. (A20) into Eq. (A17), we obtain

$$\begin{aligned}a_p\boldsymbol{\phi}_p(x,0)=\lim_{t\rightarrow\infty} & e^{i\hat{\mathbf{H}}_f^0(x)t/\hbar}e^{-2i\hat{\mathbf{H}}_f(x)t/\hbar}\\ & \times e^{i\hat{\mathbf{H}}_f^0(x)t/\hbar}\boldsymbol{\phi}_{p'}(x,0) .\end{aligned} \qquad \text{(A21)}$$

Therefore,

$$P^\theta(E_{p'},E_p)=|a_p|^2=|\lim_{t\rightarrow\infty}\langle\boldsymbol{\phi}_p(0)|e^{i\hat{\mathbf{H}}_f^0 t/\hbar}e^{-2i\hat{\mathbf{H}}_f t/\hbar}e^{i\hat{\mathbf{H}}_f^0 t/\hbar}|\boldsymbol{\phi}_{p'}(0)\rangle|^2 . \qquad \text{(A22)}$$

As for the case of a half collision, we can replace the limit $t\rightarrow\infty$ by time integration from 0 to ∞. Thus, we obtain

$$P^\theta(E_{p'},E_p)=\left|\langle\boldsymbol{\phi}_p(0)|\boldsymbol{\phi}_{p'}(0)\rangle+\tfrac{1}{2}\sum_{n=-\infty}^{\infty}\left\langle\boldsymbol{\phi}_p(0)\left|\hat{\mathbf{V}}\hat{\mathbf{G}}\left[\frac{E_p+E_{p'}+\hbar\omega n}{2}\right]+\hat{\mathbf{G}}\left[\frac{E_p+E_{p'}+\hbar\omega n}{2}\right]\hat{\mathbf{V}}\right|\boldsymbol{\phi}_{p'}^n(0)\right\rangle\right|^2 . \qquad \text{(A23)}$$

$|\boldsymbol{\phi}_{p'}^n(0)\rangle$ is a vector function in which the only nonzero component is the nth component of $|\boldsymbol{\phi}_{p'}(x,0)\rangle$ defined by Eq. (A16). We now replace $\hat{\mathbf{V}}\hat{\mathbf{G}}$ by $\hat{\mathbf{G}}^0\hat{\mathbf{T}}$ and $\hat{\mathbf{G}}\hat{\mathbf{V}}$ by $\hat{\mathbf{T}}\hat{\mathbf{G}}^0$, where [37]

$$\hat{\mathbf{T}}=\hat{\mathbf{V}}+\hat{\mathbf{V}}\hat{\mathbf{G}}\hat{\mathbf{V}} \qquad \text{(A24)}$$

and

$$\hat{\mathbf{G}}^0(E)=[E\hat{\mathbf{I}}-\hat{\mathbf{H}}_f^0]^{-1} . \qquad \text{(A25)}$$

Note that the complex-scaled operator $\hat{\mathbf{G}}^0(E)$ cannot be computed directly by Eq. (A25) if the Hamiltonian supports bound states. In such a case the bound-state energies are real even upon complex scaling and the operator $[E\hat{\mathbf{I}}-\hat{\mathbf{H}}_f^0]$ is singular. The formal solution to this problem is the introduction of a factor $\exp(-\varepsilon t)$ into the time integration leading from Eq. (A22) to Eq. (A23) and taking the limit $\varepsilon\rightarrow 0$. Therefore, by operating with $\hat{\mathbf{G}}^0(E)$ on the asymptotic vector functions, the time-independent complex-scaled transition probability is obtained:

$$\begin{aligned}P^\theta(E_{p'},E_p)=\Big|&\langle\varphi_p|\varphi_{p'}\rangle\\ &-2\pi i\sum_n\langle\boldsymbol{\phi}_p(0)|\hat{T}(E_{p'})|\boldsymbol{\phi}_{p'}^n(0)\rangle\Big|^2 ,\end{aligned} \qquad \text{(A26)}$$

where E_p and $E_{p'}$ are related by the equation

$$E_p = E_{p'} + \hbar\omega n > 0 \ , \quad n = 0 \ , \pm 1, \pm 2, \pm 3 \ . \qquad \text{(A27)}$$

The last equation is identical to Eqs. (4.27), (4.28), and (4.31) in the text, if a basis set is used to represent the coordinates. We note in passing that unlike in the half-collision experiment, the kinetic energy of the detected electron is quantized and that it may happen that $E_p < E_{p'}$.

[1] (a) F. H. M. Faisal, *Theory of Multiphoton Processes* (Plenum, New York, 1987). (b) Numerical studies have shown that the Floquet theory is applicable when the field is applied over ≈100 optical cycles. For example, see Fig. 7 in Ref. [23].

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