Reactive scattering theory for molecular transitions in time-dependent fields

Uri Peskin and William H. Miller
Department of Chemistry, University of California, Lawrence Berkeley Laboratory, Berkeley, California 94720 and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

I. INTRODUCTION

Explicitly time-dependent Hamiltonians are commonly used in studies of field-induced processes in atomic and molecular systems.1 Until recently, however, the numerical methods for solving the time-dependent Schrödinger equation with explicitly time-dependent Hamiltonians failed to reach the degree of accuracy which was obtained in the case of time-independent Hamiltonians. Moreover, there was no rigorous expression for time-independent state-to-state transition probabilities for explicitly time-dependent Hamiltonians, mainly due to the “time ordering” problem associated with Dyson’s series.2

Recently, Peskin and Moiseyev3 have shown that computational approaches which were originally developed for the study of time-independent Hamiltonians can be applied also in the study of explicitly time-dependent ones, where the time-dependent Schrödinger equation is represented in an extended Hilbert space with an additional time-coordinate, t’.4–7 New computational algorithms were introduced for the solution of the time-dependent Schrödinger equation, which include the use of variational basis sets,8,9 as well as grid methods10 such as the pseudospectral or the discrete variable representations for the time coordinate. By using global polynomial propagators (such as the Chebychev expansion9,10) it was illustrated that the Schrödinger equation with time-dependent Hamiltonians can be solved to machine accuracy.

In the case of time-periodic Hamiltonians, or when time-periodic boundary conditions are artificially imposed,3 the (t,t’), approach reproduces the well known result of the Floquet theorem for the time evolution operator.11 By using the analytical form of the propagator U(t,t0), a stationary scattering theory (a Kohn-type variational method) was introduced in Ref. 12 for calculating state-specific transition probabilities for time-periodic Hamiltonians (Ref. 12) or time-dependent Hamiltonians with time-periodic boundary conditions (Ref. 3). It was assumed that the final states of the system are associated with a free motion along a spatial reaction coordinate and “outgoing wave” boundary conditions were imposed along that coordinate by means of complex scaling.12

The main purpose of the present paper is to generalize the stationary treatment of field induced transitions (i.e., of time-dependent Hamiltonians) to cases in which the field is localized in time (such as short laser pulses). In this case the vanishing of the field at infinite times implies that any eigenstate of the field-free molecular system, including bound states, can be obtained asymptotically (in contrast to the case of time-periodic Hamiltonians with a finite time period). In Sec. II (and in the Appendix) scattering theory in the extended Hilbert space is developed. It is shown that transition probabilities (bound-to-bound, bound-to-continuum, or continuum-to-continuum) in the “usual” (i.e., coordinate) Hilbert space are rigorously associated with scattering matrix elements in the extended space (i.e., including the time coordinate, t’). For a given initial state of the molecular system, a single operation of the Green’s operator in the extended space provides all the state-specific transition probabilities in the “usual” space. The new formulation is also shown to reproduce exactly infinite-order time-dependent perturbation theory. In Sec. III a computational method is introduced, based on the discrete variable representation (DVR) with an absorbing boundary conditions (ABC) Green’s function as introduced by Seideman and Miller for calculations of cumulative13 and state-specific14 reaction probabilities. In the present application ABC are applied for the time coordinate (t’) as well as for any other coordinates which are associated with asymptotic free motion.

In Sec. IV the method is applied to a bound model system (the pulsed driven harmonic oscillator), where t’ is the (only) scattering coordinate. In a more realistic case, however, the field-free system has a finite number of bound states and a continuum of scattering states. This case is discussed in Sec. V, and bound-to-continuum state-specific ionization probabilities (ATI spectra) are calculated for a modified version of the Rosen–Morse model Hamiltonian (with a finite
pulse). In some practical applications state-specific transition probabilities may be too detailed to be measured, or to be of interest, and the ABC-DVR approach enables a direct calculation of partial-state-resolved transition probabilities, avoiding the need to sum (or integrate) over all possible final states, as illustrated in Sec. VI. Concluding remarks are given in Sec. VII.

II. “REACTIVE” SCATTERING MATRIX FOR TIME-DEPENDENT HAMILTONIANS

The present study is limited to interactions which are local in time and vanish for positive and negative infinite times. (For a complimentary study of interactions with time-periodic boundary condition see Ref. 12.) For simplicity, the molecular system is represented by a one-dimensional Hamiltonian, \( \hat{H}_M(x) \), and the time-dependent interaction by a potential operator, \( \hat{V}(x,t) \). In the more general case \( x \) may stand for a multidimensional vector representing all the molecular degrees of freedom. The dynamics induced by the time-dependent field is described by the time-dependent Schrödinger equation

\[
[\hat{H}_M(x) + \hat{V}(x,t)] \Phi(x,t) = \hat{H}(x,t) \Phi(x,t)
\]

\[
= i \hbar \frac{\partial}{\partial t} \Phi(x,t).
\]

According to the \((t,t')\) formalism, the solution \( \Phi(x,t) \) is obtained by representing the equation in an extended Hilbert space with an additional time coordinate \( t' \)

\[
\hat{\mathcal{H}}(x,t') \chi(x,t',t) = i \hbar \frac{\partial}{\partial t} \chi(x,t',t),
\]

where

\[
\hat{\mathcal{H}}(x,t') = \hat{H}(x,t') - i \hbar \frac{\partial}{\partial t'},
\]

such that

\[
\Phi(x,t) = \chi(x,t',t)|_{t'=t} = [e^{-i\hat{\mathcal{H}}(x,t')/\hbar} \Phi(x,0)]|_{t'=t},
\]

where \( \Phi(x,0) \) is an initial condition.

Assuming that the physical initial and the final states are eigenstates of the molecular system in the “usual” Hilbert space, i.e.,

\[
\hat{H}_M \phi_M(x) = E_M \phi_M(x)
\]

and

\[
\hat{H}_M \phi_F(x) = E_F \phi_F(x),
\]

and according to Eq. (4), the evolution from the initial state to all possible final states is given by a solution of the Schrödinger equation in the extended space, \( \chi(x,t',t) \), which satisfies the following asymptotic conditions:

\[
\lim_{t' \to -\infty} \chi(x,t',t)|_{t'=t} = C \times e^{-iE_M t/\hbar} \phi_M(x),
\]

and

\[
\lim_{t' \to +\infty} \chi(x,t',t)|_{t'=t} = C \times \sum_f S_{f,i} e^{-iE_f t/\hbar} \phi_f(x),
\]

where \( C \) is a normalization constant. The time-independent transition probability from \( \phi_M(x) \) to \( \phi_f(x) \) is given by

\[
P_{i-f} = |S_{f,i}|^2,
\]

where \( S_{f,i} \) is the scattering probability amplitude (the S matrix). As in the conventional scattering theory, an explicit expression for the S matrix can be derived either from the asymptotic behavior of the stationary solutions of Eq. (2), or by directly evaluating the overlap of asymptotic wave packets. Here we follow the stationary formulation, and the alternative derivation, which is similar to the one in Ref. 12, is given in the Appendix. The stationary solutions (with respect to \( t \)) of Eq. (2) are given by

\[
\chi(x,t',t) = e^{-iE t/\hbar} \psi_E(x,t'),
\]

where \( E \) is the total “energy” in the extended Hilbert space and \( \psi_E(x,t') \) is an energy normalized eigenfunction of \( \hat{\mathcal{H}}(x,t') \), such that

\[
\hat{\mathcal{H}}(x,t') \psi_E(x,t') = E \psi_E(x,t'),
\]

and

\[
\langle \langle \psi_E | \psi_E' \rangle \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dt' \psi_E^*(x,t') \psi_{E'}(x,t')
\]

\[
= \delta(E - E').
\]

The double brackets, \( \langle \langle ... \rangle \rangle \), stand for the inner product in the extended Hilbert space. Equation (9) can be converted into an integral (Lippmann Schwinger) equation

\[
\psi_E(x,t') = \psi_E(x,t') + \int_{-\infty}^{\infty} dx'' \int_{-\infty}^{\infty} dt'' G_E^0(x,t''',x',t'')
\]

\[
\times V(x',t'') \psi_E(x'',t''),
\]

where \( \psi_E \) is an eigenfunction of the free evolution Hamiltonian in the extended space, i.e.,

\[
\hat{\mathcal{H}}_0(x,t') \phi_E(x,t') = E \phi_E(x,t'),
\]

where

\[
\hat{\mathcal{H}}_0(x,t') = \hat{\mathcal{H}}(x,t') - \hat{\mathcal{V}}(x,t') = \hat{H}_M(x) - i \hbar \frac{\partial}{\partial t'},
\]

\[
G_E^0(x,t''',x',t'') = \langle \langle x,t'' | [E - \hat{\mathcal{H}}_0 + i \epsilon]^{-1} | x',t'' \rangle \rangle.
\]

Using a complete set of energy normalized [see Eq. (10)] eigenfunctions of \( \hat{\mathcal{H}}_0(x,t') \), i.e.,

\[
\langle \langle x,t' | \phi_m, E' \rangle \rangle = \phi_m(x) e^{iE't'/\hbar} \sqrt{\frac{2}{\pi \hbar}},
\]

one obtains from Eq. (14)
where the energy normalization \( \sum \) is unity for positive arguments and zero otherwise. Substituting Eq. (16) into Eq. (11), one has

\[
\psi_E(x,t') = \phi_E(x,t') + \frac{-i}{\hbar} \sum_m \phi_m(x) e^{i(E-E_m)(t'-t)/\hbar} \int_{t'}^{\infty} dt'' \times e^{-i(E-E_m) t''/\hbar} \phi^*_m(x') V(x',t'') \psi_E(x',t''),
\]

where the full Green’s operator is defined as

\[
\hat{G}(E) = (E - \hat{\mathcal{H}} + i\epsilon)^{-1}.
\]

Making use of Eqs. (21) and (22) and of the fact that \( |\phi_i,E-E_i\rangle \) and \( \langle \phi_f,E-E_f| \) are eigenstates of \( \hat{\mathcal{H}}_0 \) with the eigenvalue \( E \), Eq. (20) can be written as

\[
S_{f,i} = \delta_{f,i} - 2 \pi i \langle \phi_f,E-E_f| \hat{\mathcal{H}} - E \rangle + \langle \hat{\mathcal{H}} - E \hat{G}(E)(\hat{\mathcal{H}} - E)|\phi_i,E-E_i\rangle).
\]

Another computationally useful, and formally exact expression for the probability amplitude can be derived by replacing the asymptotic states by any distorted waves, which are free time-waves in the asymptotic region (i.e., as \( t' \rightarrow \pm \infty \)). In this case,

\[
S_{f,i} = S^0_{f,i} - 2 \pi i \langle \phi_f,E-E_f| \hat{\mathcal{H}} - E \rangle + \langle \hat{\mathcal{H}} - E \hat{G}(E)(\hat{\mathcal{H}} - E)|\phi_i\rangle,
\]

where \( S^0_{f,i} \) is the transition amplitude from the initial to the final state, contained in the asymptotic form of the distorted waves. By choosing the initial and final “distorted waves” \( \phi_i(x,t') \) and \( \phi_f(x,t') \), as “nonreactive”, such that they are “switched on” only for asymptotic negative or positive times respectively, \( S^0_{f,i} \) vanishes.

### III. ABC-DVR FOR THE TIME COORDINATE

The exact transition probability amplitudes are associated with the limit \( \epsilon \rightarrow 0 \) in the Green’s operator [Eq. (22)]. The existence of that limit for the amplitude is assured by the assumption that the time-dependent interaction vanishes asymptotically. From a computational point of view, however, it has been shown that a well behaved representation of the Green’s operator, and thus correct scattering amplitudes, can be obtained by introducing a coordinate dependent positive operator, \( \hat{\epsilon} \), which vanishes in the interaction region but increases asymptotically along the reaction coordinate. Such optical potentials absorb outgoing flux which exits the interaction region and avoid unphysical reflections due to finite basis (or grid) representations.

In the present work we explicitly impose absorbing boundary conditions for the time coordinate \( t' \). For this purpose we introduce a time \( (t') \) dependent operator

\[
\hat{\epsilon}(t',x) = \hat{\epsilon}_i(t'') + \hat{\epsilon}_f(t',x),
\]

where
where \( \hat{e} \) and \( \hat{e}_f \) correspond to the absorbing potentials for negative and positive times, respectively. The \( x \)-dependent part in \( e_f \) is introduced for cases where the molecular system dissociates and bound-to-continuum transitions occur. In these cases the optical potential absorbs flux for asymptotic values of \( x \), regardless of time. As shown by Seideman and Miller,\(^{13}\) and by Thompson and Miller\(^ {14}\) the reactive scattering probability amplitude can be rewritten by making use of the following operator identities:

\[
(\hat{\mathcal{H}} - E) + (\hat{\mathcal{H}} - E) \hat{G}(E)(\hat{\mathcal{H}} - E) = (\hat{\mathcal{H}} - E) \hat{G}(E)i \hat{e} = -[i \hat{e} + \hat{e}\hat{G}(E)\hat{e}]. \tag{26}
\]

Substituting Eq. (26) into Eq. (24), one has

\[
S_{f,t} = S^0_{f,t} + 2 \pi i \langle \varphi_f | i \hat{e} + \hat{e}\hat{G}(E)\hat{e} | \varphi_i \rangle,
\]

which is the ABC version of the transition probability amplitude.

It is especially convenient to apply Eq. (27) within a discrete variable representation\(^ {19,19}\) in which the optical potential is diagonal. For an equally spaced symmetric DVR, \( x \) (in the multidimensional case) and \( t' \) are discretized as

\[
x_{i} = -X/2 + (i_x - 1) \Delta x,
\]

\[
t'_j = -T/2 + (i_t - 1) \Delta t',
\]

where \( T = (N_t - 1) \Delta t' \) and \( X = (N_x - 1) \Delta x \). The DVR for the transition probability amplitude is then given by [see Eq. (27)]

\[
S_{f,i} = S^0_{f,i} + 2 \pi i \varphi^\dagger_f [i \hat{e} + \hat{e}\hat{G}(E)\hat{e}] \cdot \varphi_i
\]

where the initial and final distorted waves are represented by the vectors

\[
[\varphi_i, \dot{\varphi}_i]_{i_x, i_t} = \varphi_{i_x, i_t}(x_{i_x}, t'_i),
\]

and the coordinate-dependent optical potential is represented by a diagonal matrix

\[
[\epsilon],_{i_x, j_x, i_t, j_t} = \epsilon(t'_i, x_{i_x}) \delta_{i_x, j_x} \delta_{i_t, j_t}.
\]

\( \mathbf{H} \) is the DVR of the extended Hamiltonian, \( \hat{\mathcal{H}} \)

\[
\mathbf{H} = \mathbf{V} + \mathbf{H}_M + \mathbf{W}.
\]

The time-dependent interaction operator is a local function of both \( x \) and \( t' \) and therefore its matrix representation is also diagonal:

\[
[\mathbf{V}],_{i_x, j_x, i_t, j_t} = \mathbf{V}(x_{i_x}, t'_i) \delta_{i_x, j_x} \delta_{i_t, j_t}.
\]

The molecular Hamiltonian is composed of the molecular potential term, \( \mathbf{V}_M \), whose DVR is diagonal, and a kinetic energy operator \([-\hbar^2/(2\mu)](\partial^2/\partial x^2)\)]. For the kinetic energy we use the infinite order finite difference approximation for the second derivative\(^ {19}\) such that

\[
[\mathbf{H}_M],_{i_x, j_x, i_t, j_t} = \begin{cases} 
\delta_{i_x, j_x} \left( \frac{V_M(x_{i_x}) + \hbar^2}{2\mu \Delta x^2} \right), & i_x = j_x \\
\frac{\hbar^2}{2\mu \Delta x^2} \frac{2}{(i_x - j_x)^2} & i_x \neq j_x.
\end{cases}
\]

The last term in Eq. (32) refers to the energy operator along the time coordinate, \(-i\hbar(\partial / \partial t')\). Its DVR within the infinite order finite difference approximation for the first derivative is\(^ {19}\)

\[
[\mathbf{W}],_{i_x, j_x, i_t, j_t} = \begin{cases} 
0, & i_x = j_x \\
\delta_{i_x, j_x} (-i\hbar) \left( -1 \right)^{i_x - j_x} (i_x, j_x) \frac{1}{\Delta t'} & i_x \neq j_x.
\end{cases}
\]

The computational task in the application of Eq. (29) is the calculation of the vector \( \Psi = \hat{G}(E)\epsilon \cdot \varphi_i \) which implies solving the coupled linear equations

\[
[E + \epsilon - \mathbf{H}] \Psi = \epsilon \cdot \varphi_i.
\]

For this matter different numerical algorithms are available. In the present work the generalized minimal residual method\(^ {20}\) (GMRES) has been used. The method is based on minimizing the error in \( \Psi \) iteratively. It avoids the need to store the entire DVR Hamiltonian matrix in the computer core memory, requiring only the operation of the Hamiltonian onto a vector in each iteration, and it makes full advantage of the sparse DVR of the Hamiltonian. For each initial state, the transition probabilities for all possible final states are obtained via Eq. (29) with practically no additional computational effort.

\[\text{IV. BOUND-TO-BOUND TRANSITIONS (PHOTOEXCITATION)}\]

Let us consider first a simple system in which both the initial state, \( \varphi_i(x) \), and the final state, \( \varphi_f(x) \), are bound states of a Hamiltonian with a discrete spectrum. In the extended Hilbert space these functions are multiplied by functions of \( t' \) with the asymptotic behavior of free “time waves.” A convenient choice for the distorted asymptotic states is

\[
\varphi_f(x, t') = \varphi_f(x)f(t' - t_e) (e^{i(E - E_i)t'/\hbar}) e^{i\hbar/(2\pi \hbar)},
\]

\( \varphi_i(x, t') = \varphi_i(x)[1 - f(t' - t_e)] (e^{i(E - E_i)t'/\hbar}) e^{i\hbar/(2\pi \hbar)}. \)

Formally, the total energy in the extended space (i.e., \( E \)) is arbitrary. It is advised, however, that \( E \) be chosen such that the oscillations of the asymptotic time waves are minimized. Throughout the present work \( E \) was chosen as the initial bound state energy, \( E = E_i \). \( f(\tau) \) in Eq. (37) is a switching function

\[
f(\tau) = e^{\tau/(1 + e^{\tau})}
\]

with a positive switching parameter, \( t_e \). Since for this choice the initial state is different from zero only for asymptotic negative times, and similarly for the final state for positive times, \( \varphi_f \cdot e \cdot \varphi \), and \( S_{f,i} \) vanish, so that Eq. (29) becomes
First order time-dependent perturbation theory

\[ S_{f,i} = 2\pi i \varphi_f \cdot e^{-i\mathcal{H}(E)T} \cdot e^{i\mathcal{H}(E)T} \cdot \varphi_i. \]  

(39)

When bound-to-bound transitions are considered, the only coordinate which is associated with a continuous spectrum is \( t' \), i.e., the “reaction coordinate” in the extended Hilbert space. Therefore the absorbing boundary conditions are imposed only for that coordinate. A useful choice\(^\text{14}\) of the optical potentials is the power law switching functions,

\[ e_f(t') = \begin{cases} 
  e_0 \left( \frac{t' - t_0}{T/2 - t_0} \right)^2, & t' > t_0 \\
  0, & t' < t_0
\end{cases} \]  

(40a)

and

\[ e_i(t') = \begin{cases} 
  e_0 \left( \frac{-t' - t_0}{T/2 - t_0} \right)^2, & t' < -t_0 \\
  0, & t' > -t_0
\end{cases} \]  

(40b)

where \( t_0 \) is positive and localized in the asymptotic region such that

\[ t_0 > t_c. \]  

(41)

A. The pulsed driven harmonic oscillator

As a representative test case of bound-to-bound transitions we consider the pulsed driven harmonic oscillator that was studied in Refs. 9 and 21. The Hamiltonian in the extended Hilbert space is given by (with \( \hbar = m = 1 \))

\[ \hat{\mathcal{H}}(x,t') = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{x^2}{2} + \lambda x e^{-t'^2/2\sigma^2} - i \frac{\partial}{\partial t'} \]  

(42)

with the pulse width parameter \( \sigma = 2 \). The undisturbed system is represented by the harmonic oscillator and the initial state is taken as its ground \( (n=0) \) state. In Fig. 1 excitation probabilities for the \( n=1 \) level of the oscillator are plotted as a function of the the field intensity parameter \( \lambda \). The results of the present calculation as obtained according to Eq. (39) are compared to results of a time-dependent \((t,t')\) calculation using the Newton–Chebychev propagator, as introduced in Ref. 9. The time-dependent calculation was performed such that the error in the averaged oscillator position with respect to the analytical (classical) result did not exceed \( 10^{-4} \). The state-to-state probabilities were obtained by projecting the propagated wave packet onto the first excited state of the oscillator at sufficiently long times, such that the result is invariant. The agreement between the time-dependent calculation and the present ABC-DVR results is complete, and both methods are shown to provide the same probabilities well beyond the perturbative regime.

The DVR parameters in the present calculation are \( T=32 \) and \( N_x=60 \) for the time coordinate \( t' \), and \( X=12 \) and \( N_x=30 \) for the spatial coordinate. These values were found to be sufficient for the convergence of the calculated probabilities as the density of points and the “box” sizes \((X,T)\) were increased. The asymptotic scattering states as defined in Eqs. (37) and (38) were switched on at \( t_c = 5 \). For illustrative purposes, the time-dependent interaction potential (for \( \lambda x = 2 \)) is plotted in Fig. 2 along with the asymptotic distorted time waves and the optical potentials. The stability of the calculated probabilities with respect to the absorbing potential parameters is demonstrated in Fig. 3 for the field intensity \( \lambda = 2 \). It is seen that the accuracy of the calculated probability increases rapidly as \( e_0 \) increases. We relate this behavior to the fact that there are no reflections along the time axis. In the conventional case of coordinate-scattering such reflection, which are typical of the wave (second order) equation, must be avoided by chosing the optical potential to rise “slowly.” However, as illustrated in Fig. 3, in a given DVR (i.e., \( N_x \) and \( T \)), the stability of the results depends on the switching point of the imaginary potential, \( t_0 \). The latter must not be taken too large, in order to sample the optical potential with a sufficient number of grid points. The values \( t_0 = 11.5 \) and \( e_0 = 9.0 \) were used for the calculations presented in Fig. 1.

V. BOUND TO CONTINUUM TRANSITIONS (PHOTOCHEMISTRY)

In reality, any molecular system may dissociate due to its interaction with an external field. The initial state, \( \phi_0(x) \), in
the physical (coordinate) Hilbert space is usually a bound state of the molecular Hamiltonian, but the final states, \( \{ \phi_f(x) \} \), may be either bound states of the molecular Hamiltonian (photoexcitation) or continuum states which are associated with bond breaking (photodissociation). In the extended Hilbert space the initial bound system is associated with a distorted wave in time as defined in Eq. (37a). The continuum final states are associated with a free asymptotic motion along the spatial reaction coordinate as well as along \( t' \). Here the final continuum states are represented by an energy normalized distorted incoming plane wave along \( x \), and free undistorted time waves along \( t' \). For dissociation to “the right hand side” of coordinate space, one has

\[
\Psi_f(x,t') = f(x-x_c) \left( \frac{\mu}{2 \pi \hbar^2 k_f} \right)^{1/2} e^{-ik_f(x-x_c)} e^{i (E_f-E) t'/2 \hbar} \sqrt{2 \pi \hbar},
\]

where \( k_f \) is the final wave vector characterizing the asymptotic free motion,

\[
\frac{k_f^2 \hbar^2}{2 \mu} = E_f,
\]

and \( f \) is the switching function defined in Eq. (38) with the switching parameter \( x_c \). As before, this choice of the asymptotic states assures that \( \Psi_f^I \) and \( \varphi^I_2 \cdot \epsilon \cdot \varphi \) vanish, such that the transition probability is given by Eq. (39). To absorb outgoing flux along the spatial coordinate, \( x \) dependent optical potentials are added to the final optical potential such that

\[
\epsilon_f(x,t') = \epsilon_f(t') + \epsilon_f^R(x) + \epsilon_f^L(x),
\]

where

\[
\epsilon_f^R(x) = \begin{cases} \epsilon_0 \frac{(x-x_0)^2}{X/2-x_0}, & x > x_0 \\ 0, & x < x_0 \end{cases}
\]

and

\[
\epsilon_f^L(x) = \begin{cases} \epsilon_0 \frac{(x-x_0)^2}{X/2-x_0}, & x < x_0 \\ 0, & x > x_0 \end{cases}
\]

A. Above threshold ionization with a finite pulse

As a typical example for a dissociative system we refer to a generalized version of the Rosen–Morse model.\(^{22}\) The Rosen–Morse model serves as a bench mark for the study of the above threshold ionization (ATI) of rare gas atoms in time-periodic fields.\(^{3,12,23}\) In order to account for fields which are localized in time (i.e., a laser pulse), the time-periodic field, characterized by a carrier frequency \( \omega \), is multiplied by a Gaussian envelope. The Hamiltonian in the extended Hilbert space is given by (in a.u.)

\[
\hat{H}(x,t') = -i \frac{\partial}{\partial t'} - \frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{V_0}{\cosh^2(\alpha x)} \left[ 1 + \lambda \cos(\omega t') e^{-t'/2\sigma^2} \right]
\]

with the parameters \( V_0 = 2.0 \) and \( \alpha = 1/\sqrt{3} \) characterizing the field-free Hamiltonian.

In Fig. 4 a contour map of the potential is plotted in the two-dimensional \((x,t')\) extended coordinate space for the field parameters \( \lambda = 1, \omega = 4/3, \) and \( \sigma = 3.\) For asymptotic negative and positive times the potential surface is time independent, and the field-free interaction is represented by a potential well. The initial state is chosen as the first excited bound state in the well, associated with the (analytic) eigenvalue \( E_i = -2/3 \). This function is the only odd bound function in the well, and since the full Hamiltonian is symmetric with respect to \( x \), this bound state is coupled to the continuum but not to other bound states. The symmetry property also implies that the dissociation probabilities to either side of the potential well (right or left) are the same.

FIG. 3. The excitation probability (0 to 1) for the pulsed driven harmonic oscillator with \( \lambda = 2 \), as obtained for increasingly larger optical potentials (i.e., increasing \( \omega \)). The circles, squares, diamonds, and triangles, correspond to the different switching points \( t_0 = 9.5, 10.5, 11.5, 12.5 \) a.u. The probability as obtained from a time-dependent \((t,t')\) calculation is \( P = 0.3666 \).

FIG. 4. Contour plot of the two-dimensional potential in the extended Hilbert space, for the Hamiltonian in Eq. (47). The arrows illustrate the possible routes of the process: As \( t' \) increases, the initially bound molecular system may dissociate to the right \((R)\), to the left \((L)\), or it may stay bounded \((F)\), for forward scattering.
when the pulse duration and the bound-to-bound transition probabilities should sum to one. The numerical finding is in agreement with the observation of Bental et al.\textsuperscript{15} for harmonic generation spectra, and suggests that the Floquet theory description of the process (i.e., regarding the field as time periodic) is quite accurate even for pulses which are not much broader than a few optical cycles.

VI. INCLUSIVE (PARTIAL STATE-RESOLVED) PHOTOREACTION PROBABILITIES

In many practical applications information about state-to-state reaction probabilities may not be of interest. Therefore, one is interested in obtaining directly the photoreaction probability for a specific product rearrangement (i.e., chemical species) regardless of the final internal quantum states. The ABC-DVR is a convenient framework for that purpose. In the case of field-free reactive scattering, cumulative reaction probabilities\textsuperscript{13} and partial state-resolved (inclusive)\textsuperscript{14} probabilities have been calculated directly from the ABC-DVR Green’s operator. Applying the derivation of Thompson and Miller\textsuperscript{14} for the “reactive” scattering matrix in the extended Hilbert space, one can show that the inclusive reaction probability for a specific final rearrangement \( \gamma \) is given by

\[
P_\gamma = \sum_{f, \gamma} |S_{f, \gamma}|^2 = 4 \pi \varphi_i^\dag \mathbf{e}_\gamma (E) \mathbf{e}_\gamma (E) \mathbf{e}_\gamma \mathbf{e}_\gamma \mathbf{e}_\gamma \mathbf{v}.
\]

For the one-dimensional case studied in Sec. V, the arrangement index \( \gamma \) corresponds to the right- or left-hand sides of the potential well (dissociation), or to the well itself (no dissociation). For the right-hand side one has

\[
\mathbf{e}_\gamma (x, t') = \begin{cases} \mathbf{e}_f (x) + \mathbf{e}_f (t'), & x > x_c, \\ \mathbf{e}_f (x), & x < x_c. \end{cases}
\]

where \( x = x_c \) is chosen as the “dividing surface” between the interaction and the asymptotic regions. Similarly,

\[
\mathbf{e}_{\gamma L} (x, t') = \begin{cases} \mathbf{e}_f (x) + \mathbf{e}_f (t'), & x < -x_c, \\ \mathbf{e}_f (x), & -x_c < x < x_c. \end{cases}
\]

The probability for no-dissociation (the “forward” scattering) is associated with

\[
\mathbf{e}_{\gamma F} (x, t') = \begin{cases} 0, & x > x_c, x < x_c, \\ \mathbf{e}_f (t'), & -x_c < x < x_c. \end{cases}
\]

In Fig. 7 dissociation probabilities are plotted as a function of the field intensity parameter \( \lambda \) along with the complimentary (no-dissociation) probabilities. The probability of dissociation to the right-hand side is multiplied by a factor of 2 to account for the total dissociation out of the symmetric well. Probability conservation in the physical space implies that

\[
P_\gamma + P_{\gamma L} + P_{\gamma F} = 1,
\]

which holds for the numerical results in Fig. 7. The direct calculations are shown to be equivalent to state-to-state calculations according to Eq. (39), where the no-dissociation probability is obtained from the bound-to-bound \( S \)-matrix element as discussed in Sec. IV, and the total dissociation probability is obtained by numerically integrating \( |S_{f, \gamma}|^2 \) over
the final kinetic energies (i.e., integrating the spectra in Fig. 5). We note that for the one-dimensional case the computational effort associated with the state-to-state calculation is actually comparable to the effort in a direct calculation. However, for multidimensional systems the direct calculation should be much more efficient since the number of final specific states will be much larger.

VII. CONCLUDING REMARKS

Transitions in a molecular system (bound-to-bound or bound-to-continuum) which are induced by external time-dependent fields can be rigorously formulated as a time-independent scattering problem in an extended Hilbert space with an additional time coordinate. Regarding the time-coordinate, \( t' \), in this space as the scattering coordinate, transition probability amplitudes are expressed in terms of standard reactive scattering matrix elements. This enables one to use any computational method that was originally developed for the study of time-independent reactive scattering also for the study of field-induced processes, avoiding the traditional “time ordering” problem. In the present work we introduced a new computational method, in which absorbing boundary conditions are imposed on the time coordinate in terms of \( t' \)-dependent optical potentials, with a DVR for \( t' \). We point out, however, that other variational methods in which outgoing wave boundary conditions are applied (such as the method of Siegert waves\(^{26} \) or the complex coordinate method\(^{27} \)) could be applied for \( t' \) as well. The ABC-DVR enables one to calculate detailed state-to-state transition probabilities as well as partial state-resolved probabilities (inclusive reaction probabilities), and thus avoiding the need to sum (or integrate) over all the final open channels in a photochemical process.

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APPENDIX: AN ALTERNATIVE DERIVATION OF THE TRANSITION AMPLITUDES

Here we follow the derivation of Ref. 12 for a “full collision” process in the presence of a time-periodic field and generalize it to any scattering process (bound-to-bound, bound-to-continuum, or continuum-to-continuum process) with an external time-dependent field. This derivation is based on associating the initial and final states with the exact asymptotic evolution of specific solutions of the time-dependent Schrödinger equation. When the interaction of the time-dependent field with the bound region of the molecular system does not vanish in time (e.g., a time-periodic interaction), eigenstates of the molecular Hamiltonian cannot be obtained asymptotically. However, free motion can be obtained at infinite times due to the local nature of the interaction in coordinate space (such as in the Kramers–Henneberger representation\(^{18,28} \)), and this was the basis for the scattering theory for time-periodic Hamiltonians in Ref. 12. In the present work we explicitly assume that the interaction with the external time-dependent field vanishes for asymptotic times, such that the asymptotic states in the “usual” Hilbert space \( |\phi_{i,j}\rangle \) can be any eigenstates of the time-independent molecular Hamiltonian (bound or continuum states), according to Eq. (5). Each state is associated with the asymptotic time evolution of an exact solution \( |\Psi_{i,j}\rangle \) of the time-dependent Schrödinger equation at time \( t=0 \). This asymptotic condition reads as\(^{15} \)

\[
\lim_{t \to -\infty} U(t,0)|\Psi_i\rangle = \lim_{t \to -\infty} e^{-iE_i t/h} |\phi_i\rangle, \quad (A1a)
\]

\[
\lim_{t \to -\infty} U(t,0)|\Psi_f\rangle = \lim_{t \to -\infty} e^{-iE_f t/h} |\phi_f\rangle, \quad (A1b)
\]

where \( U(t,t_0) \) is the exact time evolution operator. The probability amplitude for the transition is given by the overlap of \( |\Psi_i\rangle \) and \( |\Psi_f\rangle \) at \( t=0 \), i.e.,

\[
S_{i,f} = \langle \Psi_f | \Psi_i \rangle = \lim_{t \to -\infty} \langle \phi_f | e^{iE_f t/h} U(t,-t) e^{-iE_i t/h} |\phi_i\rangle. \quad (A2)
\]

According to the \( (t,t') \) representation of the Schrödinger equation, the time evolution operator can be written as\(^{29} \)

\[
U(t,t_0) = \int_{-\infty}^{\infty} dt' \, \delta(t' - t) e^{-i[E(t'-t_0)/h]} \hat{\mathcal{H}}(t'), \quad (A3)
\]

where

\[
\hat{\mathcal{H}}(t') = \mathcal{H}(t') - i\hbar \frac{\partial}{\partial t'}, \quad (A4)
\]
and it is understood that the delta-integral follows the exponential operation, maintaining the conventional order of writing. By using the following representation for the $\delta$ function in Eq. (A.3),

$$\delta(t' - t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dE' e^{-iE'(t' - t)/\hbar},$$  \hspace{1cm} (A5)$$
one obtains from Eq. (A2)

$$S_{f,i} = \lim_{t \to \infty} \frac{1}{2\pi i} \int_{-\infty}^{\infty} dE' \int_{-\infty}^{\infty} dt' e^{-iE't'/\hbar} \times \left( \phi_f \left| e^{i(E_f + E') t/\hbar} e^{-2i\hat{H}(t')/\hbar} e^{iE't'/\hbar} \phi_i \right| \right)$$

$$= \lim_{t \to \infty} \int_{-\infty}^{\infty} dE' \left( \langle \phi_f, E' \rangle e^{i(E_f + E') t/\hbar} \times e^{-2i\hat{H}(t')/\hbar} e^{iE't'/\hbar} \left| \phi_i, 0 \right\rangle \right).$$  \hspace{1cm} (A6)$$

$\langle \cdots \cdots \rangle$ stands for the inner product in the extended Hilbert space with $t'$ regarded as an additional coordinate and with the asymptotic states as defined in Eq. (15) in the text. The limit $t \to \infty$ can be replaced by an integral. Following the standard procedure, \cite{12,13} this finally gives

$$S_{f,i} = \langle \phi_f | \phi_i \rangle - \int_{-\infty}^{\infty} dE' (2\pi i) \delta(E_i - (E_f + E'))$$

$$\times \left( \langle \phi_f, E' \rangle \left| \hat{T} \left( \frac{E_i + E_f + E'}{2} \right) | \phi_i, 0 \right\rangle \right),$$  \hspace{1cm} (A7)$$

where the $T$ matrix in the extended Hilbert space is given by

$$\hat{T}(z) = (\hat{H} - \hat{H}_0) + (\hat{H} - \hat{H}_0) \left[ z + i e^{-\hat{H}} \right]^{-1} (\hat{H} - \hat{H}_0).$$  \hspace{1cm} (A8)$$

Carrying out the integral over $E'$ in Eq. (A7), one obtains the "on shell" scattering matrix in the extended Hilbert space,

$$S_{f,i} = \delta_{f,i} - 2\pi i \langle \phi_f, E_i - E_f \rangle \hat{T}(E_i) | \phi_i, 0 \rangle),$$  \hspace{1cm} (A9)$$

precisely the result of Eq. (23) for $E = E_i$. Note that according to the definition of the extended inner product, $S_{f,i}$ in Eqs. (23) and (24) depends explicitly only on the difference between the total energy in the extended space, $E$, and the molecular energies, $E_{i,f}$. Therefore, any choice of $E$ is correct. (For computational purposes, however, it is advised that $E$ should be chosen such that the oscillations of the asymptotic time-waves are minimized.) Equation (A9) is very similar to Eq. (3.44) in Ref. 12 for the continuum-to-continuum scattering matrix. Regarding the field frequency in the latter as a continuous variable (i.e., assuming an infinite time period), these two equations are identical. However, in Ref. 12 the derivation applies only to continuum-to-continuum transitions (or bound-to-continuum transitions with an instantaneous switching of the field).