

State-to-state transition probabilities for time-dependent Hamiltonians using complex absorbing potentials

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Abstract. Earlier work has derived a new expression for the time-independent scattering probability for time-dependent Hamiltonians for cases where the motion is free at infinitely large times. Here we introduce a new technique which provides an efficient numerical algorithm for the calculation of multiphoton event probabilities based on using complex absorbing potentials along the scattering coordinate. The (t, t') method is used allowing an analytical propagation of the initial state and avoiding long propagation times and accumulation of numerical errors. An iterative technique for the solution of non-Hermitian linear systems is used which allows us to tackle large time-dependent systems, both in internal degrees of freedom and in the number of Fourier components in the time-dependent potential term. A numerical example illustrating the usefulness of the theory is given.

1. Introduction

Numerical solution of the time-dependent Schrödinger equation has become one of the main tools of molecular dynamics simulations. Powerful numerical algorithms have been developed [1–4] allowing one to approach a variety of problems such as reactive scattering calculations [5], molecular surface encounters [6], multiphoton processes [7] and many others. Calculation of state-to-state transition probabilities is the main goal in simulations of these problems. For time-independent Hamiltonians, the solution of the time-dependent Schrödinger equation

$$\hat{H}(q)\Psi(q, t) = i\hbar \frac{\partial \Psi(q, t)}{\partial t} \quad (1)$$

is given by

$$\Psi(q, t) = e^{-i\hat{H}t/\hbar} \Phi_i(q), \quad (2)$$

where Φ_i is the initial state at $t = 0$. Then, the state-to-state transition probability from the Φ_i state to the Φ_f state is obtained by projecting $\Psi(t)$ on the final state:

$$P_{i \rightarrow f} = \left| \lim_{t \rightarrow \infty} \langle \Phi_f | \Psi(t) \rangle \right|^2. \quad (3)$$

For the stationary Hamiltonians, equation (1) can be efficiently solved using Chebyshev expansion techniques [1, 2, 8]. However, in many cases the direct propagation of the initial state is not possible due to limited computational power and accumulation of numerical

errors during the time propagation. To avoid long propagation times in the time-independent Hamiltonian case one can use the simple form of the time evolution operator

$$\hat{U} = e^{-i\hat{H}t/\hbar} \quad (4)$$

in equation (2) to propagate the initial state Φ_i analytically to $t = \infty$ and using time-independent scattering theory [9] to obtain the time-independent expression for the state-to-state transition probability:

$$P_{i \rightarrow f}(E) = \left| \frac{i}{\hbar} \langle \Phi_f | V + VG(E)V | \Phi_i \rangle \right|^2, \quad (5)$$

where $G(E) = (E - \hat{H})^{-1}$ is a Green function and V is the potential of interaction between initial and final states. Dimensionality and singularity of $G(E)$ make the calculation of Green function to be the most difficult problem in that approach. The complex-coordinate scattering theory [10, 11] suggests solutions to these problems reducing the number of Hamiltonian eigenstates needed for the Green function calculation and avoiding singularity problem by rotating the coordinate into the complex plane. Another method based on absorbing boundary conditions (ABC) [12–15] combined with discrete variable representation (DVR) [16, 17] allows one to reduce the dimensionality by restricting the DVR grid to the interaction region and avoids the singularity of the Green function by applying complex absorbing potentials (CAPs) [18–22] near the grid boundaries [23–25]. In [23] it is shown that for reactive collisions equation (5) can be written as

$$P_{i \rightarrow f}(E) = \left| -\frac{i}{\hbar} \langle \Phi_f \epsilon_f G(E) \epsilon_i \Phi_i \rangle \right|^2, \quad (6)$$

where ϵ_i and ϵ_f are the absorbing potentials in the initial (reactant) and final (product) regions of coordinate space and $G(E)$ is the ABC–DVR Green function. Both methods have been successfully applied in different scattering calculations [25–29]. However, many studies of molecular dynamics are not restricted to the time-independent Hamiltonian system, but include interaction of the atomic or molecular system with an external electromagnetic field. For sufficiently high intensity fields this interaction can be described semiclassically as time dependent [30], i.e.

$$\hat{H}(q, t) = \hat{H}(q) + \hat{\mu}(q) f(t), \quad (7)$$

where $\hat{\mu}$ is the dipole moment operator. The main origin of difficulties that arise for time-dependent problems is the fact that equation (2) is not valid when the Hamiltonian is time dependent. In that case, the propagator \hat{U} is much more complicated due to the time ordering problem which is usually solved by dividing the propagation into small intervals for which the time variation of the Hamiltonian is small. That, in turn, results in significant growth of the numerical effort. In addition, beyond the lack of powerful propagators when the Hamiltonian is time dependent, one does not have a time-independent scattering theory in this case. Consequently, a time-independent expression for $P_{i \rightarrow f}(E)$ which avoids the long propagation times is not available.

Let us find an equation which, on one hand, will provide us with the solution of the time-dependent Schrödinger equation with time-dependent Hamiltonian and, on the other hand, will make the use of the advantages of time-independent Hamiltonian case possible.

Consider the following differential equation

$$\hat{H}(q, t') \Psi = i\hbar \frac{\partial \Psi(q, t')}{\partial t}, \quad (8)$$

where $\hat{\mathcal{H}}(q, t')$ is the *time-independent* operator defined as

$$\hat{\mathcal{H}}(q, t') = -i\hbar \frac{\partial}{\partial t'} + \hat{H}(q, t'). \quad (9)$$

$\hat{H}(q, t')$ is the Hamiltonian defined in equation (7), such that time t is replaced by the dynamical variable t' . $\hat{\mathcal{H}}(q, t')$ is called the Floquet Hamiltonian and since $\hat{\mathcal{H}}(q, t')$ is time (t) independent, the solution of equation (8) is given by

$$\Psi(q, t, t') = e^{-i\hat{\mathcal{H}}t/\hbar} \tilde{\Phi}_i(q, t', t=0) = \hat{U}(t \leftarrow 0) \tilde{\Phi}_i(q, t', t=0), \quad (10)$$

i.e. both powerful numerical propagation techniques and analytical propagation can be used to solve equation (8). Moreover, it can be shown [3] that the physical solution $\Psi(q, t)$ is obtained from $\Psi(q, t, t')$ at the cut of $t = t'$ in the generalized space containing an additional t' coordinate:

$$\Psi(q, t) = \Psi(q, t, t')|_{t'=t}. \quad (11)$$

Equation (11) is correct both for time periodic and non-periodic potentials. In the periodic case, e.g. for a system driven by continuous lasers (cw), $0 < t' < T$, where T is the time period. In a general non-periodic case, e.g. in the pulsed laser case, T is taken as any large number for which the pulse dies off, imposing periodic boundary conditions on the Ψ function. If T is large enough it does not effect the accuracy of the physical solution.

Using (t, t') method one can use the close form of the time-independent propagator in equation (10) to propagate analytically the initial state $\tilde{\Phi}_i(q, t', t=0)$ to $t = \infty$. In such a case, similarly to the time-independent Hamiltonian case, one can obtain [31] an expression for the time-independent transition probability

$$P_{i \rightarrow f}^{(n)}(E_f) = \left| \frac{i}{\hbar} \langle\langle \tilde{\Phi}_f | \tilde{V} + \tilde{V} \tilde{G}(E_f) \tilde{V} | \tilde{\Phi}_i \rangle\rangle \right|^2, \quad (12)$$

where $\tilde{V}(q, t') = \hat{H}(q, t') - \hat{H}(q) = \hat{\mu}(q)f(t')$ and \tilde{G} is defined as

$$\tilde{G}(E) = (E - \hat{\mathcal{H}}(q, t'))^{-1}. \quad (13)$$

$P_{i \rightarrow f}^{(n)}(E_f)$ is the transition probability from the initial state (i, E_i) to the final state (f, E_f) as a result of the overall exchange of $n\hbar\omega$ amount of energy between the system and field with frequency ω . The main difference from the stationary scattering theory is the change of the definition of the inner product, such that the time regarded as a dynamical variable. ' $\langle\langle \dots \rangle\rangle$ ' in equation (12) stands for double integration along q and t' coordinates. $\tilde{\Phi}_f$ is a final state, which is an eigenstate of a *field-free* Hamiltonian with kinetic energy E_f . In order to define E_f , both time-dependent and time-independent parts of the interaction term should vanish asymptotically. Only in this case can the kinetic energy of the scattered particle be measured, although the laser is still 'on'. The asymptotic behaviour of the time-dependent Hamiltonian is gauge dependent. For example, in the length gauge, the Hamiltonian of a cw field interacting with one-dimensional particle reads:

$$\left[\frac{\hat{p}_x^2}{2m} + V(x) + \epsilon_0 x \cos(\omega t) \right] \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}, \quad (14)$$

and the time-dependent potential term $\hat{\mu}(q)f(t) = \epsilon_0 x \cos(\omega t)$ diverges as $x \rightarrow \pm\infty$. This problem can be solved using the accelerating frame representation of the time-dependent Hamiltonian. Applying translational operator ($\exp[\frac{i}{\hbar}\alpha\hat{p}]$) on the TDSE in equation (14) one obtains a different equation of the form [32, 33]

$$\left[\frac{\hat{p}_x^2}{2m} + V(x + \alpha_0 \cos(\omega t)) \right] \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}, \quad (15)$$

which has the same solution as equation (14) ($\alpha_0 = \epsilon_0/m\omega^2$). In equation (15), however, the time-dependent potential term $V(x + \alpha_0 \cos(\omega t))$ vanishes as $x \rightarrow \pm\infty$ if $V(x) \rightarrow 0$ as $x \rightarrow \pm\infty$. Therefore, at infinitely large times, after the particle leaves the interaction region, it will become an eigenstate of the field-free Hamiltonian ($\hat{H} = \frac{\hat{p}^2}{2m}$) with well-defined asymptotic kinetic energy (E_f in equation (12)). Since the Hamiltonian is time dependent, there is no energy conservation limitation during the process. Therefore the initial energy of the particle (which is also well defined since $V(x + \alpha_0 \cos(\omega t))|_{t=0} \rightarrow 0$ as $x \rightarrow -\infty$) does not have to be equal to the final energy. Rather, they are related by a net number of absorbed or emitted photons, namely

$$E_f = E_i + \hbar\omega n; \quad n = 0, \pm 1, \pm 2, \pm 3 \dots \quad (16)$$

The initial state $\tilde{\Phi}_i(x, t')$ in equation (12) is both a x - and t' -dependent function describing the asymptotic motion of a particle along x coordinate and the ‘motion’ of photons along the t' coordinate. Therefore,

$$\tilde{\Phi}_i(x, t') = v_i^{-1/2} \exp(ik_i x) \exp(in\omega t'). \quad (17)$$

Similarly, $\tilde{\Phi}_f$ is given by

$$\tilde{\Phi}_f(x, t') = v_f^{-1/2} \exp(ik_f x), \quad (18)$$

which is both a x - and t' -independent function describing the free motion of the scattered particle after it is absorbed or emitted n photons. The $v_{i,f}^{-1/2} = \sqrt{\frac{m}{\hbar k_{i,f}}}$ normalization factor comes from the flux normalization as in standard time-independent scattering theory.

As in standard time-independent scattering theory, the main difficulty in calculating state-to-state scattering probabilities using equation (12) is a calculation of a generalized Green function $\tilde{G}(E) = (E_f - \hat{\mathcal{H}})^{-1}$. The problem now is even more complicated than in the stationary case, since $\tilde{G}(E)$ contains an additional coordinate (t'), and the spectrum of the t' -dependent part of the generalized Hamiltonian $\hat{\mathcal{H}}(q, t')$ may have a very wide range and the spectral representation of $\tilde{G}(E)$ becomes numerically impossible.

We suggest here a new computational technique for the calculation of time-independent scattering probabilities for time-dependent Hamiltonians provided that the asymptotic motion of the scattered particles is free.

2. State-to-state transition probabilities for time-dependent Hamiltonians using complex absorbing potentials

The key point of the suggested approach is that by introducing a new dynamical variable t' the time-dependent problem has been transformed to a time-independent one with one degree of freedom more. That allows one to use various techniques developed in stationary scattering theory. In particular, we refer here to the DVR–ABC Green function method developed by Miller and coworkers [23, 24]. In addition, the time-independent expression for state-to-state transition probabilities combined with powerful iterative methods for the solution of the inhomogeneous equation allows one to tackle very large time-dependent problems without a need to deal with huge time-dependent Hamiltonian matrices.

The first step of the approach is based on using absorbing boundary operators to impose the scattering boundary conditions. ABC are widely used by those carrying out time-dependent wavepacket calculations [12, 13] on a coordinate grid and it prevents the wavepacket from unphysical reflection from the edge of the grid back to interaction region. ABC were also applied in reactive scattering calculations [14, 15, 24], in which a coordinate-dependent optical potential which is essentially zero in the physically relevant region of

space, and rises at the edge of the coordinate grid in order to absorb flux that reaches this region in space is added to the Hamiltonian. Consequently, the physical solution is distorted (damped) near the edge of the grid, however, for a proper absorbing potential it approaches the exact solution far from the boundaries and in the interaction region. The conditions on the absorbing potential are that it should be turned on rapidly enough to absorb the flux over as short distance as possible, but not too rapidly, so as to cause reflection back to the physically relevant region. For the price of distortion of the solution near the grid boundaries one avoids the singularity in the Green function, which now has the form

$$\tilde{G}(E) = (E_f - \hat{\mathcal{H}} + i\epsilon)^{-1}, \tag{19}$$

where $\epsilon = \epsilon(q)$ is an optical potential added to the generalized Hamiltonian $\hat{\mathcal{H}}(q, t')$. Coordinate-dependent complex absorbing potential imposes absorbing boundary conditions on the physical coordinates, whereas periodic boundary conditions are imposed along the t' coordinate.

Using the new definition of the Green function in equation (19) one obtains from equation (12) for the one-dimensional case (generalization to higher dimensions is straight forward),

$$P_{i \rightarrow f}^{(n)}(E_f) = \left| \frac{i}{\hbar} \left\langle \left\langle \tilde{\Phi}_f(x) | \tilde{V}(x, t') + \tilde{V}(x, t') \frac{1}{E_f - \hat{\mathcal{H}}(x, t') + i\epsilon(x)} \tilde{V}(x, t') | \tilde{\Phi}_i(x, t') \right\rangle \right\rangle \right|^2, \tag{20}$$

where

$$\hat{\mathcal{H}}(x, t') = -i\hbar \frac{\partial}{\partial t'} + \hat{H}(x, t'). \tag{21}$$

As we saw in equation (15), in the accelerating frame representation

$$\hat{H}(x, t') = \frac{\hat{p}_x^2}{2m} + \tilde{V}(x, t'), \tag{22}$$

and, therefore,

$$\begin{aligned} \tilde{V}(x, t') &= \hat{\mathcal{H}}(x, t') - \left(-i\hbar \frac{\partial}{\partial t'} + \frac{\hat{p}_x^2}{2m} \right) \\ &= \hat{\mathcal{H}}(x, t') - \hat{\mathcal{H}}_0(x, t'), \end{aligned} \tag{23}$$

where $\hat{\mathcal{H}}_0(x, t')$ describes a free particle and the photons without interaction. Since, $\tilde{\Phi}_i(x, t') = v_i^{-1/2} \exp(ik_i x) \exp(i\omega t')$, it is an eigenfunction of $\hat{\mathcal{H}}_0(x, t')$ with an eigenvalue $E_f = \frac{\hbar^2}{2m} k_i^2 + \hbar\omega = E_i + \hbar\omega$. Therefore, one can rewrite equation (20) as

$$P_{i \rightarrow f}^{(n)}(E_f) = \left| \frac{i}{\hbar} \left\langle \left\langle \tilde{\Phi}_f | \tilde{V} + \tilde{V} \frac{1}{E_f - \hat{\mathcal{H}} + i\epsilon} (\hat{\mathcal{H}} - E_f) | \tilde{\Phi}_i \right\rangle \right\rangle \right|^2. \tag{24}$$

Noting that $\frac{1}{E_f - \hat{\mathcal{H}} + i\epsilon} (\hat{\mathcal{H}} - E_f) = -1 + \frac{1}{E_f - \hat{\mathcal{H}} + i\epsilon} i\epsilon$, one obtains

$$P_{i \rightarrow f}^{(n)}(E_f) = \left| \frac{i}{\hbar} \left\langle \left\langle \tilde{\Phi}_f \tilde{V} \frac{1}{E_f - \hat{\mathcal{H}} + i\epsilon} i\epsilon \tilde{\Phi}_i \right\rangle \right\rangle \right|^2. \tag{25}$$

Here we recall that the DVR [16, 17] is used for both x and t' coordinates. In DVR the local operators (e.g. $\tilde{V}(x, t')$) are diagonal. Therefore one can rewrite equation (25) as

$$\begin{aligned}
 P_{i \rightarrow f}^{(n)}(E_f) &= \left| \frac{i}{\hbar} \left\langle \left\langle \tilde{V} \tilde{\Phi}_f \frac{1}{E_f - \hat{\mathcal{H}} + i\epsilon} i\epsilon \tilde{\Phi}_i \right\rangle \right\rangle \right|^2 \\
 &= \left| \frac{i}{\hbar} \left\langle \left\langle \tilde{\Phi}_f (\hat{\mathcal{H}} - E_f) \frac{1}{E_f - \hat{\mathcal{H}} + i\epsilon} i\epsilon \tilde{\Phi}_i \right\rangle \right\rangle \right|^2 \\
 &= \left| \frac{i}{\hbar} \left\langle \left\langle \tilde{\Phi}_f \left(-1 + i\epsilon \frac{1}{E_f - \hat{\mathcal{H}} + i\epsilon} \right) i\epsilon \tilde{\Phi}_i \right\rangle \right\rangle \right|^2 \\
 &= \left| \frac{1}{\hbar} \langle \langle \tilde{\Phi}_f \epsilon \tilde{\Phi}_i \rangle \rangle - \frac{i}{\hbar} \langle \langle \tilde{\Phi}_f \epsilon \tilde{G}(E_f) \epsilon \tilde{\Phi}_i \rangle \rangle \right|^2. \tag{26}
 \end{aligned}$$

Usually, the initial ($\tilde{\Phi}_i$) and the final ($\tilde{\Phi}_f$) states are located in different regions of the coordinate space. $\tilde{\Phi}_i$ is located in the asymptotic region from which the free particle approaches the interaction region and $\tilde{\Phi}_f$ is located in other asymptotic region in which the scattered particle moves freely. In this case, the first term in equation (26) vanishes and one obtains that the time-independent transition probability in terms of ABC–DVR generalized Green function is given by

$$P_{i \rightarrow f}^{(n)} = \left| -\frac{i}{\hbar} \langle \langle \tilde{\Phi}_f \epsilon \tilde{G} \epsilon \tilde{\Phi}_i \rangle \rangle \right|^2. \tag{27}$$

Since $\tilde{\Phi}_f$ and $\tilde{\Phi}_i$ represent two different asymptotic regions, ϵ can be replaced by two optical potentials ϵ_i and ϵ_f , each localized in the appropriate region of space. In such a way, ϵ_i and ϵ_f themselves distinguish between different asymptotic regions. Namely,

$$P_{i \rightarrow f}^{(n)} = \left| -\frac{i}{\hbar} \langle \langle \tilde{\Phi}_f \epsilon_f \tilde{G} \epsilon_i \tilde{\Phi}_i \rangle \rangle \right|^2. \tag{28}$$

In the case of elastic scattering, i.e. when the incoming particle and the scattered one are located in the same region of space, the first term in equation (26) no longer vanishes, and it was shown (for a time-independent Hamiltonians) [34] that in that case the most accurate way to calculate the elastic probability is

$$P_{i \rightarrow i}^{(n)} = \left| \frac{i}{\hbar} \langle \langle \tilde{\Phi}_i \epsilon_i (\tilde{G} - \tilde{G}_0) \epsilon_i \tilde{\Phi}_i \rangle \rangle \right|^2, \tag{29}$$

where $\tilde{G}_0 = (E_f - \hat{\mathcal{H}}_0 + i\epsilon)^{-1}$ is the free particle and the field Green function.

Equation (28) allows one to calculate the state-to-state transition probability as a result of a particle–light interaction in an efficient way, both reducing the number of grid points needed to be added to the grid and avoiding the singularity of the Green function. A more important advantage of the time-independent approach is that using equation (28) one can calculate the scattering probability for very large time-dependent Hamiltonians. For large atomic or molecular systems interacting with light, both calculation of the propagation operator ($\hat{U}(t \leftarrow 0) = e^{-i\hat{\mathcal{H}}t/\hbar}$, equation (10)) and a direct calculation of the generalized Green function $\tilde{G}(E)$ by inversion is impossible. Moreover, for large systems even the storage of the matrix elements of the Hamiltonian $\hat{\mathcal{H}}(q, t')$ is impossible due to memory limitations. The time-independent approach allows one to overcome this problem using iterative techniques for the solution of inhomogeneous linear systems.

Equation (28) can be rewritten as follows

$$P_{i \rightarrow f}^{(n)} = \left| -\frac{i}{\hbar} \langle \tilde{\Phi}_f | \epsilon_f \chi \rangle \right|^2, \quad (30)$$

where $\chi = \tilde{G}_0 \epsilon_i \tilde{\Phi}_i$. Therefore, χ is a solution of the following inhomogeneous equation

$$(E_f - \hat{\mathcal{H}} + i\epsilon)\chi = \epsilon_i \tilde{\Phi}_i. \quad (31)$$

This equation can be solved iteratively, and, in particular, we refer to the quasiminimal residual (QMR) algorithm developed by Freund and Nachtigal [35, 36] for the numerical solution of non-Hermitian inhomogeneous linear systems. QMR is an iterative method that searches for a converging set of approximate solutions in the span of the Krylov space vectors and combines short recurrences with implicit minimization of the residual vector. The iterative solution avoids the need to store all matrix elements of the Floquet Hamiltonian ($\hat{\mathcal{H}}$) and replaces direct inversion by successive operation of the Hamiltonian matrix on a vector.

The efficiency of the solution of equation (31) can be improved greatly by applying preconditioners. The rate of convergence of the iterative procedure for solution of equation (31) depends on the spectral range of the left-hand side operator ($E_f - \hat{\mathcal{H}} + i\epsilon$). If one could find an operator such that its inverse can be numerically calculated and at the same time it is close to the inverse of ($E_f - \hat{\mathcal{H}} + i\epsilon$), then the spectral range of the left-hand side could be reduced by applying this operator on the inhomogeneous equation and the convergence rate will grow significantly [37]. It has recently been shown that one could find an efficient separable preconditioner, which improves the convergence rate of the iterative procedure and allows us to tackle large multidimensional problems [38]. Following this idea, let us replace equation (31) by

$$\tilde{G}_0(E_f - \hat{\mathcal{H}} + i\epsilon)\chi = \tilde{G}_0 \epsilon_i \tilde{\Phi}_i, \quad (32)$$

where \tilde{G}_0 is an ABC-DVR Green function given by

$$\tilde{G}_0 = (E_f - \hat{A}_0 + i\epsilon)^{-1}, \quad (33)$$

where \hat{A}_0 is any separable operator. The most natural choice for \hat{A}_0 is a free-particle generalized Hamiltonian with complex absorbing potential $\hat{\mathcal{H}}_0 = -i\hbar \frac{\partial}{\partial t'} + \frac{\hat{p}_x^2}{2m} - i\epsilon(x)$. However, \hat{A}_0 may also include additional information from the full Hamiltonian, e.g.

$$\hat{A}_0(x, t') = -i\hbar \frac{\partial}{\partial t'} + \frac{\hat{p}_x^2}{2m} + V_{\text{eff}}(x) - i\epsilon(x), \quad (34)$$

where $V_{\text{eff}}(x) = \frac{1}{T} \int_0^T V(x, t') dt'$ is an one optical cycle average of the particle-field interaction term. For \hat{A}_0 as in equation (34), equation (32) becomes

$$(1 - \tilde{G}_0 V)\chi = \tilde{G}_0 \epsilon_i \tilde{\Phi}_i, \quad (35)$$

where $V = \hat{\mathcal{H}}(x, t') - \hat{A}_0(x, t')$. The iterative solution of equation (35) involves successive operations of \tilde{G}_0 , which are very sparse due to its separability. \tilde{G}_0 matrix is given by three successive operators

$$\tilde{G}_0 = U_R (\lambda^d)^{-1} U_L \quad (36)$$

where λ^d is the diagonal eigenvalue matrix of \hat{A}_0

$$A_0 U_R = U_R \lambda^d \quad (37)$$

and $U_L = U_R^{-1}$. Because \hat{A}_0 is separable, for the one-dimensional case, for example, $U_R = U_R(x)U_R(t')$, where $U_R(x)$ and $U_R(t')$ are the eigenvector matrices of each degree of freedom separately, i.e.

$$\left[\frac{\hat{p}_x^2}{2m} + V_{\text{eff}}(x) - i\epsilon(x) \right] U_R(x) = U_R(x)\lambda_x^d \quad (38)$$

and

$$\left[-i\hbar \frac{\partial}{\partial t'} \right] U_R(t') = U_R(t')\lambda_{t'}^d. \quad (39)$$

$U_L(x) = U_R^{-1}(x)$, $U_L(t') = U_R^{-1}(t')$ and $\lambda_x^d + \lambda_{t'}^d = \lambda^d$.

Although \tilde{G}_0 itself is not separable and may include many degrees of freedom, its application can be carried out separately in successive steps for different degrees of freedom. In addition, potential term V in equation (35) that couples different degrees of freedom is diagonal because of the DVR for the coordinates and, therefore, retains the sparseness of the algorithm. The spectral range of the left-hand side operator in equation (35) is much smaller than that in equation (31), and they have the same solution. Once equation (35) is solved, the solution $\chi(x, t')$ is substituted into equation (30) which provides all state-specific transition probabilities.

Note, that equation (28) (or equation (30)) only includes the information about the initial and final energy. That means that the state-to-state transition probability only depends on the *overall* amount of absorbed or emitted photons. The overall transition probability to a final state with given kinetic energy is then a sum over all probabilities of absorption and emission of quanta of photon energy from different initial states plus the probability of the case in which zero photons were absorbed/emitted and the initial and final energies are the same.

In section 3, a numerical illustration of the usefulness of the suggested algorithm is given.

3. Illustrative numerical example

As an example we chose a system of an electron and a potential barrier interaction under an external electromagnetic field influence. The interest in this physical system was motivated by a recent study of the Ramsauer–Townsend effect in driven systems [39].

The time-dependent Hamiltonian in this case is given by

$$\hat{H}(x, t) = \frac{\hat{p}_x^2}{2m} + V(x) + \epsilon_0 x \cos(\omega t), \quad (40)$$

where $V(x)$ is a barrier potential, e.g. of the following form:

$$V(x) = \begin{cases} V_0 & \text{if } |x| < a \\ 0 & \text{elsewhere.} \end{cases} \quad (41)$$

In the Kramers–Hannerberger oscillating frame representation, equation (40) becomes

$$\hat{H}(x, t) = \frac{\hat{p}_x^2}{2m} + V(x + \alpha_0 \cos(\omega t)), \quad (42)$$

where $\alpha_0 = \epsilon_0/m\omega^2$. α_0 is a maximal amplitude and $T = 2\pi/\omega$ is period of the potential barrier oscillations along the x -coordinate.

The Floquet operator (equation (9)) is given by

$$\hat{H}(q, t') = -i\hbar \frac{\partial}{\partial t'} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \tilde{V}(x, t'). \quad (43)$$

We have shown [39] that the Fourier components of $\tilde{V}(x, t')$,

$$\mathcal{V}_n(x) = \frac{1}{T} \int_0^T \exp(in\omega t') \tilde{V}(x, t') dt', \quad (44)$$

can be obtained analytically and are given by

$$\mathcal{V}_n(x) = \frac{V_0}{\pi n} [\sin(\omega n t_2(x)) - \sin(\omega n t_1(x))], \quad (45)$$

where

$$t_1(x) = \begin{cases} \frac{1}{\omega} \arccos\left(\frac{x + a/2}{\alpha_0}\right), & \text{if } -\alpha_0 \pm a/2 \leq x \leq \alpha_0 - a/2 \\ 0, & \text{if } \alpha_0 - a/2 \leq x \leq \alpha_0 + a/2. \end{cases} \quad (46)$$

and

$$t_2(x) = \begin{cases} \frac{1}{\omega} \arccos\left(\frac{x - a/2}{\alpha_0}\right), & \text{if } \mp\alpha_0 \pm a/2 \leq x \leq \alpha_0 \mp a/2 \\ T/2, & \text{if } -\alpha_0 - a/2 \leq x \leq \alpha_0 + a/2. \end{cases} \quad (47)$$

The $n = 0$ Fourier component is given by

$$\mathcal{V}_0(x) = \frac{V_0}{\pi} \begin{cases} \arccos\left(\frac{x - a/2}{\alpha_0}\right) - \arccos\left(\frac{x + a/2}{\alpha_0}\right), & \text{if } -\alpha_0 + a/2 \leq x \leq \alpha_0 - a/2 \\ \arccos\left(\frac{\pm x - a/2}{\alpha_0}\right), & \text{if } \pm\alpha_0 - a/2 \leq x \leq \pm\alpha_0 + a/2. \end{cases} \quad (48)$$

Figure 1 shows the average value of the x -dependent Fourier components as a function of n . As one can see, in the studied case the Fourier components decay very slowly (as $1/n$, equation (45)) and, therefore, a large number of Floquet channels should be used to obtain converged results. If one uses at least 100 grid points or basis function for the x -coordinate, then, for example 100 Floquet channels taken would result in a Floquet Hamiltonian matrix of $10\,000 \times 10\,000$, for which both straightforward diagonalization of series expansion methods are not applicable due to the computational power and memory limitations. However, if one wishes to calculate the probability of an incoming particle to be transmitted through the barrier with given final energy, the method presented here can deal with even larger dimensions very efficiently.

We solved equation (35), with $V_{\text{eff}}(x) = \mathcal{V}_0(x)$ (see equations (33) and (34)), namely, the preconditioner included an effective potential obtained by one optical cycle averaging of the time-dependent potential. The absorbing potential is given by

$$\epsilon(x) = \begin{cases} A \left(\frac{|x| - x_{\text{abs}}}{x_{\text{max}} - x_{\text{abs}}} \right)^4 & \text{if } |x| > x_{\text{abs}} \\ 0 & \text{elsewhere} \end{cases} \quad (49)$$

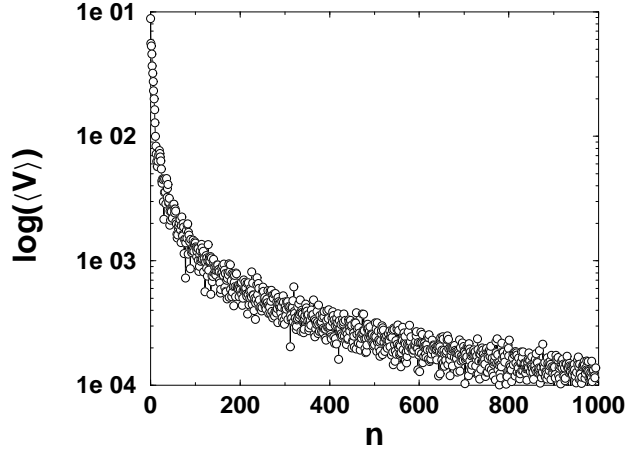


Figure 1. A logarithm of the averaged Fourier components of the time-dependent potential as function of the component number. $\langle V \rangle = \int_{-\infty}^{\infty} |\mathcal{V}_n(x)| dx$. $\mathcal{V}_n(x)$ are given by equation (44). $\omega = 0.03$ au and $\epsilon_0 = 0.018$ au, which corresponds to $\alpha_0 = 200$ au (equation (42)).

and

$$\epsilon_i(x) = \begin{cases} \epsilon(x) & \text{if } x < 0 \\ 0 & \text{elsewhere} \end{cases} \quad (50)$$

$$\epsilon_f(x) = \begin{cases} \epsilon(x) & \text{if } x > 0 \\ 0 & \text{elsewhere.} \end{cases} \quad (51)$$

The static potential barrier parameters were (equation (41)) $V_0 = 0.0147$ au, $a = 80$ au, $m = 0.1$ au, which are similar to those met in the processes of tunnelling in semiconductors [40] (m is an effective electron mass). The number of DVR grid points for x and t' coordinates respectively are $N_x = 301$, $N_{t'} = 101$. $x_{\min} = -2000$ au, $x_{\max} = 2000$ au, $x_{\text{abs}} = 1000$ au, $A = 10$. The results has been checked not to be dependent on the parameters of the complex absorbing potential and of the DVR grid. The field frequency was $\omega = 0.03$ au throughout the calculation.

In figure 2 we show the transmission probability through the ‘oscillating’ potential barrier as a function of energy for different field intensities. As one can see, as the field intensity grows the transmission probability grows. Moreover, for the highest intensity an interesting structure in the probability spectrum is obtained. At certain energies, well below the barrier height, the probability function has peaks of almost 100% transmission. We have shown [39] that this structure is associated with resonances obtained in the effective potential

$$V_{\text{eff}}(x) = \mathcal{V}_0(x) = \frac{1}{T} \int_0^T V(x, t') dt'. \quad (52)$$

The effective potential, $V_{\text{eff}}(x)$, governs the dynamics, because the field frequency is much larger than the semiclassical frequency of the particle which is temporarily trapped in the interaction region [39]. Therefore, as in some other cases [41, 42], the one optical cycle averaged potential can give a good insight into the properties of time-dependent systems driven by high-intensity fields. In our studied case, for high field intensity, the effective potential supports a number of resonance states, which are responsible for the structure in the

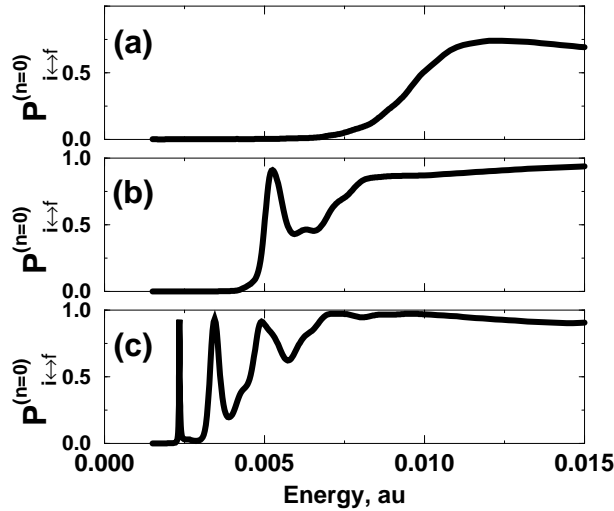


Figure 2. The state-to-state transition probability (equation (28)) through the driven barrier for the case in which the final and initial energies are the same (the overall number of emitted or absorbed photons is zero ($n = 0$)) as a function of the energy of the incoming particle. (a) $\epsilon_0 = 0.0045$ au, $\alpha_0 = 50$ au; (b) $\epsilon_0 = 0.0090$ au, $\alpha_0 = 100$ au; (c) $\epsilon_0 = 0.018$ au, $\alpha_0 = 200$ au. $\omega = 0.03$. Initial and final states are as in equations (17) and (18). For each field intensity the probability of the process in which the initial energy of the electron is conserved dominated over the processes in which the number of absorbed photons was different from the number of emitted ones ($\sum_{n=-\infty}^{\infty} P^{(n)} = P_{\text{tot}} \simeq P^{(0)}$).

probability spectrum. The presence of the resonances makes the suggested technique even more favourable because long-lived resonance states make the propagation techniques much more difficult. We show that using the scattering theory for time-dependent Hamiltonians we can calculate the probability structure very efficiently in this case. Moreover, in the low-frequency case, in which the propagation times are very long and many Floquet states are strongly coupled, the suggested technique was also shown to be very efficient [39].

4. Conclusions

A new method for calculating the scattering probability in a system driven by time-dependent electromagnetic field was introduced. The suggested approach allows us to calculate multiphoton event probabilities for very large systems, both time periodic and general time dependent, provided that the asymptotic motion is free. The usefulness of the technique has been illustrated on a particularly difficult example of a driven rectangular barrier potential. The method was shown to deal efficiently with dynamical problem which includes long-lived resonances, therefore avoiding very long propagation times. The use of the complex absorbing potentials leads to an elegant expression for the state-to-state scattering probability, which can be used in the cases, where other analytical continuation techniques are difficult to implement.

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