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WATERWAVES: wave particles dynamics on a complex triatomic potential ☆

Simone Taioli, Jonathan Tennyson *

Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

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Abstract

The WATERWAVES program suite performs complex scattering calculations by propagating a wave packet in a complex, full-dimensional potential for non-rotating ($J = 0$) but vibrating triatomic molecules. Potential energy and decay probability surfaces must be provided. Expectation values of geometric quantities can be calculated, which are useful for following the wave packet motion. The programs use a local complex potential approximation (LCP) for the Hamiltonian and Jacobi coordinates. The bottleneck of the calculation is the application of each term of the Hamiltonian to the wave packet. To solve this problem the programs use a different representation for each term: normalized associated Legendre polynomials $P_j^K(x)$ as a functional basis for the angular kinetic term and an evenly spaced grid for the radial kinetic term yielding a fully point-wise representation of the wave functions. The potential term is treated using an efficient Discrete Variable Representation (DVR) being diagonal in the coordinate representation. The radial kinetic term uses a fast Fourier transform (FFT) to obtain an operator which is diagonal in the momentum space. To avoid artificial reflection at the boundaries of the grid a complex absorbing potential is included for calculating continuum quantities. Asymptotic analysis is performed to obtain scattering observables such as cross sections and other dynamical properties.

Program summary

Program title: WATERWAVES
Catalogue identifier: ADXT_v1_0
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/ADXT_v1_0
Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland
Licensing provisions: Freely available from CPC
Programming language: Fortran 77
Computer(s) for which the program has been designed: PC
Operating system(s) for which the program has been designed: Linux
RAM required to execute with typical data: case dependent: test run requires 976 024 kB
No. of bytes in distributed program, including test data, etc.: 11 262 681
No. of lines in distributed program, including test data, etc.: 2 510 113
Distribution format: tar.gz
Number of processors used: 1
External routines/libraries used: None
CPC Program Library subprograms used: None
Nature of problem: The WATERWAVES program suite performs complex scattering calculations for calculating the nuclear dynamics subsequent to excitation by, for example, electron or photon impact and leading to dissociative attachment or vibrational excitation. This program treats in a fully multidimensional way the nuclear motion based on the use of complex potential surfaces of three-atom systems. Complex potential energy surfaces have to be provided from fixed-nuclei calculations.

Solution method: By propagating a wave packet in a complex, full-dimensional potential for non-rotating ($J = 0$) but vibrating triatomic molecules, expectation values of geometric quantities can be calculated, which are useful for following the wave packet motion. The programs use a local complex potential approximation (LCP) for the Hamiltonian and Jacobi coordinates. Potential energy and decay probability surfaces must be provided. To solve this problem the programs use a different representation for each term. To avoid artificial reflection at the boundaries of the grid a complex absorbing potential is included for calculating continuum quantities. Asymptotic analysis is performed to obtain scattering observables such as cross sections and other dynamical properties.

Additional comments: Program asymptot.f for analysing results, test data and shell scripts to make a movie of the results.

Running time: Case dependent: test run requires about 200 minutes on a 3.00 GHz Intel Pentium 4 machine provided with 2 060 044 kB of memory.

1. Introduction and outline of the problem

Increasing computer power and the development of new numerical methods [1,2] makes it possible to perform time-dependent (TD) treatment for studying many phenomena including photodissociation processes [3], reactive collisions [4], Bose–Einstein condensation (BEC) [5] and femtoseconds laser pulse [6]. Such methods can be used to chart the path of atoms bonded in a molecule and to compute dissociative attachment cross section of triatomics on desktop computers.

Evolution in time is the natural frame for dynamics and the energy and time domain are linked by a simple Fourier transform. Resonant electron–molecule collisions such as dissociative attachment (DA) and vibrational excitation (VE) have been traditionally performed in the framework of energy domain quantum mechanics and for molecules with just one degree of freedom [7,8]. Gertitschke and Domcke [2] showed one could solve such problems for diatomic molecules within a time-dependent picture and that the Local Complex Potential (LCP) approximation fails in some circumstances This has led to increasing activity both experimental [9] and theoretical [10] looking at the dynamics of DA with a number of several different methods based on the Feshbach projection approach [11], R-matrix [12] and "boomerang model" [10].

Here we present a new theoretical time-dependent program for calculating the nuclear dynamics subsequent to excitation by, for example, electron or photon impact. This program treats in a fully multidimensional way the nuclear motion based on the use of complex potential surfaces of three-atom systems. Complex potential energy surfaces have to be provided from fixed-nuclei calculations such as R-matrix [13] or complex Kohn variational method [14]. A similar approach has been used in reactive scattering by Gray and Balint-Kurti for the propagation of real wave packets on real potential surfaces [15], for which WATERWAVES also works. They were able to predict the evolution of an initial complex wave packet on a real surface just propagating the real part.

An alternative procedure, based on multiconfigurational representations of the nuclear wave functions (MCTDH), has been developed by Meyer and co-workers [16] and has been successfully applied to the case of water [10]. This study generalises the method used by Gray and Balint-Kurti to consider the dynamics of a wave packet on any complex potential surface, which means that the decay to a state different from that of the evolution is treated. The calculation of impact dissociation or dissociative attachment splits naturally into two parts, the first comprising electron dynamics and the second nuclear motion dynamics. WATERWAVES assumes that the electronic problem has been solved and requires surfaces for characterizing both the position (V) and width (Γ) of resonance features as input files for the program. Following Feshbach [11], after projecting the full time-dependent Schrödinger equation onto discrete metastable state ϕ_d we obtain the equation of motion of the nuclear wave packet. Using a local complex potential (LCP) approximation, which defines a Markovian approximation of the Hamiltonian, the equation of motion is [2]:

$$i\frac{\partial|\Psi_d(R,r,\gamma,t)\rangle}{\partial t} = \left[T_N(r,R,\gamma) + V_d(r,R,\gamma) - \frac{i}{2}\Gamma_L(r,R,\gamma)\right]\Psi_d(R,r,\gamma,t), \qquad (1)$$

where T_N is the nuclear kinetic energy operator, V_d the potential energy of the discrete electronic state and $\Gamma_L(r,R,\gamma) = \Gamma(r,R,\gamma,E_{\text{res}}) = 2\pi \int d\Omega_k |V_{dk_f}(r,R,\gamma)|^2$, the decay probability, which contains the discrete-continuum coupling via the "exit amplitude" V_{dk_f} within a local approximation.

WATERWAVES treats the dissociation dynamics using a time-dependent approach which involves three main steps. First it represents the initial wave packet $\Psi_d(r,R,\gamma;t_0)$ and the Hamiltonian on a finite grid. In the second step the wave packet is then propagated until the end of the dynamical event. Finally in program ASYMPTOT asymptotic wave packet is used to calculate the observables. In the following we present the theory necessary to understand WATERWAVES; a fuller derivation of the novel aspects of this theory will be reported elsewhere.

2. Wave packet dynamics: WATERWAVES

2.1. The coordinate system

WATERWAVES uses a multidimensional discrete variable representation (DVR) in scattering (Jacobi) coordinates.
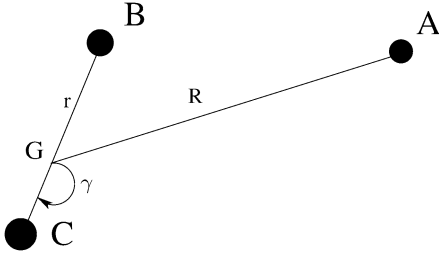
Fig. 1. Body-fixed Jacobi coordinate system: A, B, C represent atoms. The coordinates are given by $r = B - C$, $R = G - A$ and the angle $\gamma = A\hat{G}C$. G is the centre of mass BC.

A sketch of this coordinate system is presented in Fig. 1. In scattering coordinates r represents the diatom distance between atom B and atom C, and R the separation of the atom A from the diatom centre of mass. The angle between $\underline{r}$ and $\underline{R}$ is γ.

A formal definition of the rotational–vibrational wave packet in Jacobi coordinates is:

$$\Psi^{JM}(R, r, \gamma, \alpha, \beta, \zeta) = \sum_{K=-J}^{J} \tilde{D}_{MK}^{J}(\alpha, \beta, \zeta) \frac{\Xi_{K}^{JM}(R, r, \gamma)}{Rr},$$
(2)

where $\tilde{D}_{MK}^{J}(\alpha, \beta, \zeta)$ is the set of normalized Wigner rotation matrices [17], J is the total angular momentum, M is the z component of the total angular momentum in the laboratory frame. The left-hand side of Eq. (2) is written in the laboratory frame, the right-hand side is defined in the body frame where K is the z component of the total angular momentum and (α, β, ζ) are the three Euler angles which orient the body frame to the laboratory frame. WATERWAVES works in the body frame system axes.

2.2. The 3D Hamiltonian matrix and its solution

The zero angular momentum ($J = 0$) Hamiltonian can be written [18] in Bohr

$$H_{J=0} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2}$$
$$- \left[\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2} \right] \hat{j}^2 + V(R, r, \gamma),$$
(3)

where

$$\hat{j}^2 = \frac{1}{\sin\gamma} \frac{\partial}{\partial\gamma} \sin\gamma \frac{\partial}{\partial\gamma}$$
(4)

and the appropriate reduced masses are:

$$\mu_R = \frac{m_{A_1}(m_{A_2} + m_{A_3})}{m_{A_1} + m_{A_2} + m_{A_3}}, \qquad \mu_r = \frac{m_{A_2} m_{A_3}}{m_{A_2} + m_{A_3}}.$$
(5)

In order to minimize the computational time and effort we need an efficient scheme exploiting different representations for describing the action of each term of H on the wave packet. The choice of these different bases takes into account that the bottleneck of the calculation is the product between the representation of H itself and the wave packet. The principle followed in WATERWAVES is to minimize the computational time by

stopping the run when a value of the norm beyond an established threshold is reached.

In what follows we choose three different propagation schemes: Fast Fourier Transform (FFT), Discrete Variable Representation (DVR) and finite basis representation (FBR). A discrete representation on a finite Hilbert space in both DVR and FBR is employed. In FFT methods the grid is evenly spaced in the momentum space and the quadrature scheme is comparable in accuracy to the DVR quadrature. The FFT scales as $N \log N$, while a DVR scheme as N^2, where N is the number of points in the grid.

In Eq. (3) the kinetic operator is written in a coordinate space and can be represented into a grid of evenly spaced points $R_i = i\delta R$, $r_j = j\delta r$, the radial distances along the coordinates δR and δr are uniform. The grid and the values of the wave packet at different times have to be stored in three-dimensional arrays running over $|R_i\rangle$, $|r_j\rangle$, $|\gamma_k\rangle$. In such a way the computational effort increases with the increasing dimension of the grid ($\propto N^2$). As will be clear from the following, our propagation is done in "mathematical" time, u, which is linked through a linear relation to the physical time [19] and which will be defined explicitly below.

The basis set previously cited should satisfy the following requirements ($z = r, R$):

$$\delta z \langle z_i | z_i' \rangle = \delta_{i,i'},$$
(6)

$$\delta z \sum_i \langle z_i | z_i \rangle = 1,$$
(7)

$$\delta z \langle z_i | f(z_i) | z_i' \rangle = \delta_{i,i'} f(z_i)$$
(8)

for any continuous function $f(z)$. Finite Basis Representation (FBR) functions do not satisfy the third condition because in general the second derivatives make the representation tridiagonal rather than diagonal. It is standard procedure to make a linear transformation changing the vectorial space in which the kinetic operator acts: this is done by applying a Fourier transform to the coordinate space and obtaining a reciprocal grid in the momentum space. This is usually centered around the $k = 0$ point and is evenly spaced $\delta k = \frac{2\pi}{L} = \frac{2\pi}{N\delta z}$ where N is the number of grid points in the representation space. The Fourier algorithm is an efficient technique which transforms a periodic sequence from the physical to spectral space defined as follows:

$$\psi(k_j) = \sqrt{\frac{L}{N}} \left[\sqrt{\frac{2}{N}} \sum_i \psi(x_i) \sin\frac{ij\pi}{N} \right] = FFT[\psi(x)].$$
(9)

This forward-FFT brings the diagonal kinetic matrix to diagonal form

$$\langle k | -\frac{1}{2\mu} \frac{\partial^2}{\partial x^2} | k' \rangle = \frac{k^2\pi^2}{2\mu L^2} \delta_{kk'}.$$
(10)

The backward-FFT from the spectral to physical space is given by:

$$\psi(z_j) = \frac{k^2\pi^2}{2\mu N\delta z} \sqrt{\frac{\delta z}{N}} \left[\sqrt{\frac{2}{N}} \sum_i \psi(k_i) \sin\frac{ij\pi}{N} \right]$$
$$= FFT^{-1} \left[\frac{k^2\pi^2}{2\mu N\delta z} \psi(k) \right].$$
(11)

In applying this technique one pays the computational price that all values of the wave packet on the grid are needed at each stage. Finally we obtain for the radial kinetic term:

$$
\left\{ -\frac{1}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r}\frac{\partial^2}{\partial r^2} \right\}\psi(R,r,\gamma,u)
$$
$$
= FFT^{-1}\left[\frac{k_R^2\pi^2}{2\mu_R N_R \Delta R}FFT\psi(R,r,\gamma,u) \right]
$$
$$
+ FFT^{-1}\left[\frac{k_r^2\pi^2}{2\mu_r N_r \Delta r}FFT\psi(R,r,\gamma,u) \right]. \tag{12}
$$

As far as the angular part of the kinetic energy concerns the angular basis functions $|j\rangle$, when $J = 0$, are Legendre polynomials $P_j(x)$ $(x = \cos\gamma)$ [20] which satisfy the simple relation:

$$
\{\hat{j}^2\}P_j(\cos\gamma) = j(j+1)P_j(\cos\gamma), \tag{13}
$$

where j the rotational state of the final diatom. In our experience a reasonable maximum for j is in the range 30 to 40 to satisfy a compromise between efficiency and accuracy.

The treatment of the potential term in Eq. (3) is completely different [15]. There is no problem retaining the diagonal radial matrix previously defined, but the angular matrix in an FBR is not diagonal or sparse. Therefore we choose a more efficient DVR method to solve the angular problem.

A DVR is a unitary transformation of an FBR defined for some quadrature scheme associated with the FBR polynomials [21]. It is defined in terms of points, η, and weights, w_η, of the N-point Gaussian quadrature associated with the orthogonal polynomials used for the FBR in that coordinate [22]:

$$
T(\eta_i, j) = (w_{\eta_i})^{1/2}P_j(\cos(\eta_i)), \tag{14}
$$

where η_i is a discrete angular basis. In such a basis we obtain:

$$
\langle j|V(R,r,\gamma)|j'\rangle_\gamma = \sum_{i=1} P_j(\cos(\gamma_i))w_i^{1/2}V(R,r,\gamma_i)
$$
$$
\times P_{j'}(\cos(\gamma_i))w_i^{1/2}. \tag{15}
$$

The angular part of the potential energy operator is so treated without integration changing the Legendre polynomials basis set (see Eq. (14)) to the chosen angular grid and then changing back through a further similarity transformation.

The 3D Hamiltonian (Eq. (3)) is solved by successive time iteration [19]; the time evolution of the wave packet is governed by Eq. (1) for a given potential. This is first-order differential equation in time: by dividing in two the time coordinate one can split the problem into forward and backward propagation. The wave packet at time $t + \tau$ is related to that at time t and $t - \tau$ as follows:

$$
\Psi(t+\tau) = -\Psi(t-\tau) + 2\left[\cos\left(\frac{H_R\tau}{\hbar}\right)\cosh\left(\frac{\Gamma\tau}{2\hbar}\right) \right.
$$
$$
\left. + i\sin\left(\frac{H_R\tau}{\hbar}\right)\sinh\left(\frac{\Gamma\tau}{2\hbar}\right) \right]\Psi(t), \tag{16}
$$

$$
\Psi(t+\tau) = +\Psi(t-\tau) - 2\left[\cos\left(\frac{H_R\tau}{\hbar}\right)\sinh\left(\frac{\Gamma\tau}{2\hbar}\right) \right.
$$
$$
\left. + i\sin\left(\frac{H_R\tau}{\hbar}\right)\cos\left(\frac{\Gamma\tau}{2\hbar}\right) \right]\Psi(t). \tag{17}
$$

Although the iterations start from a real initial wave packet, the imaginary part in the above equations implies that the wave packet can become complex during the propagation. That means we cannot follow the approach proposed by Gray and Balint-Kurti [23,24] for reactive scattering, where the computer time and the computer memory is halved by just propagating the real part of the wave packet; due to the decay our equations are coupled. The presence of an electromagnetic field or consideration of spin would have the same effect on the equations. To obtain an efficient computational method we merged the benefits of a simple Chebyschev recursion relation [25], which is easy to implement but gives "time-step" dependent results and is useful just for short-time propagators, with our "complex wave packet propagation". To do this we introduce the two real functions:

$$
Q(x,t) = \text{Re}[\Psi], \qquad P(x,t) = \text{Im}[\Psi] \tag{18}
$$

for the real and imaginary part of the wave packet. Starting from the idea that the time coordinate does not to enter in any of the observables, we solve a mapped Schrödinger equation [24], applying a transformation from real time to mathematical time. The modified equation is:

$$
i\frac{\partial|\Psi(u)\rangle}{\partial u} = \left[f(H) + ig(\Gamma) \right]|\Psi(u)\rangle. \tag{19}
$$

The relation between the two representation is linear if we truncate the Taylor expansion of the mapping at first order [19]. The particular functions chosen are the ones which simplify the iterative form:

$$
f(H_R) = -\frac{\hbar}{\tau}\cos^{-1}(H_s), \qquad g(\Gamma) = -\frac{2\hbar}{\tau}\sinh^{-1}\left(\frac{\Gamma}{2}\right), \tag{20}
$$

where we introduce a normalized Hamiltonian H_s, whose eigenvalues are within the interval $[-1, 1]$, which is the domain of arccos; being a probability Γ is already normalized. In the range of complex energies of interest we can consider the mapping to be monotonic and therefore invertible. This is simple to see in the case of bound states but can be usually extended to scattering ones.

Thus the recursion relations implemented in WATERWAVES for the real and imaginary part of the wave packet become:

$$
Q(u+\delta) = -Q(u-\delta) + 2\sqrt{1-\Gamma^2}H_s Q(u)
$$
$$
- 2\left(\frac{\Gamma}{2}\right)\sqrt{1-H_s^2}P(u), \tag{21}
$$

$$
P(u+\delta) = P(u-\delta) + 2\left(\frac{\Gamma}{2}\right)H_s P(u)
$$
$$
+ 2\sqrt{1-\left(\frac{\Gamma}{2}\right)^2}\sqrt{1-H_s^2}Q(u), \tag{22}
$$

where $u = k\delta$ is mathematical time, with δ the time step and k the number of iterations requested in the propagating process of the wave packet. Because the initial wave packet is real the first iteration is different from subsequent iterations. It is:

$$
Q(\delta) = \exp\left(-\frac{\Gamma\delta}{2\hbar}\right)H_s Q(0), \tag{23}
$$

$$P(\delta) = \exp\left(-\frac{\Gamma\delta}{2\hbar}\right)\sqrt{1 - H_s{}^2}\, Q(0). \qquad (24)$$

The solution of the complete system as it is written in Eqs. (21), (22) is computationally slow (it scales as N^3) and the complete Hamiltonian, which has to be read "on the fly", can usually be stored in the memory. Mandelshtam and Taylor proposed [26,27] a new computational approach based on the iterative solution of simultaneous linear equations through a modified Chebyschev polynomial expansion of the root operator acting on the wave packet. They introduced a scaled Hamiltonian

$$H_s = \frac{\hat{H} - \hat{I}(\frac{\Delta E}{2} + V_{\min})}{\Delta E}, \qquad (25)$$

where $\hat{I}$ is the identity operator and $\Delta E = E_{\max} - E_{\min}$. $E_{\max}$ and $E_{\min}$ are the maximum and minimum eigenvalues of the Hamiltonian on the grid, respectively. A rough estimate of such eigenvalues (one can always think that the spectral range is finite due to some L^2 basis) can be obtained from:

$$E_{\max} = \hbar^2\pi^2/2m(\Delta x)^2 + V_{\min}, \qquad (26)$$

$$E_{\min} = V_{\min}, \qquad (27)$$

where $V_{\min}$ is the minimum value of the potential. To evaluate the effect of the square root of the Hamiltonian on the wave packet WATERWAVES uses a Chebyschev series:

$$\sqrt{1 - x^2} = \frac{2}{\pi}\left[1 - 2\sum_{k=1}^{N}\frac{T_{2k}}{4k^2 + 1}\right], \qquad (28)$$

where $T_{2k}(x)$ are the N Chebyschev polynomials of $2k$-order [20], and to calculate such a series it uses the recursion formula

$$T_{k+1}(z) = 2zT_k(z) - T_{k-1}(z), \qquad (29)$$

$$T_0(z) = 1, \qquad (30)$$

$$T_1(z) = z. \qquad (31)$$

One obtains a good evaluation using

$$N = \frac{\Delta E\delta}{2\hbar} \qquad (32)$$

terms (usually 30 terms).

2.3. The initial condition

To start the propagation of the wave packet, it is necessary to introduce initial conditions to define total energy, momentum and what kind of excitation one is dealing with. The initial wave function $\Psi_d(r, R, \gamma; t_0)$ is descretised on a finite grid, the size of which should be large enough to contain all asymptotic channels and to avoid reflections on the boundary of the grid. The angular basis functions can be normalized associated Legendre defined as above for the Hamiltonian, the radial basis functions can be either Morse oscillator-like function or spherical oscillator [28]. The best choice of the initial condition for DA calculation is [29]:

$$\left|\Psi_d(0)\right\rangle = V_{d\mathbf{k_i}}|v\rangle, \qquad (33)$$

where $\mathbf{k_i}$ denotes the momentum of the incoming particle, $|v\rangle$ the initial vibrational state of the molecule and $V_{d\mathbf{k_i}} = \langle k_i(t)|V|\psi_d\rangle = \sqrt{\Gamma/(2\pi)}$ is the "entry amplitude". The calculation of $|v\rangle$ can be carried out using the DVR3D program [30], which calculates ground and excited vibrational states of a triatomic molecule. This initial wave packet sets the clock at $t = 0$ for the dynamical evolution of the system.

2.4. Wavefunctions

The propagated wave packets of the 3D Hamiltonian (Eq. (3)) are obtained as coefficients of the basis. Thus the cost of processing and storing these wave functions depends on the number of points on which one has to calculate the wave packets and this depends from the size of the grid. Furthermore one has to retain in dynamic memory all arrays needed for the propagation at two different times, Eqs. (21), (22), as the wave packet at time $t + \tau$ depends on the values of the wave packets at time $t - \tau$ and t. WATERWAVES optimises its computational effort by writing out and flushing the coefficients in several files at user chosen iteration. For asymptotic analysis purposes WATERWAVES also stores the wave functions at some fixed R coordinate point projected on the vibrational final state of the diatom between the classical turning points. The same is done for the average geometric quantities. During the computation there are several calls to files where the wave packets are stored. If one has to stop the calculation it is in principle possible to restart from these files.

2.5. Absorbing potential

WATERWAVES makes a finite grid representation of a wave packet which is physically unbound and calculates continuum quantities through a discrete approximation. Doing a brute force calculation would cause the wave packet to be reflected back after reaching the boundary of the numerical grid causing interference which destroys the real dynamics [31].

This problem is solved by either using a very large numerical grid or employing a complex absorbing potential. To minimize the computational effort WATERWAVES uses a complex absorbing potential for the two radial coordinates [32,33]. The complex potential is easy to implement and requires only a little extra computational effort. The main drawback in using a complex absorbing potentials is that the Hamiltonian operator becomes non-Hermitian and some parts of the wave packet are effectively lost: this means the norm is not conserved. Instead of suddenly removing the wave packet at one point before the physical barrier we preferred, for reasons of numerical stability [25,34], associated with the Chebyschev propagation scheme, to implement a shaped complex potential useful also for large time steps. At each time step WATERWAVES multiplies the wave packet by a Gaussian functional form [23]:

$$A(x) = \begin{cases} 1, & z \leqslant z_{\text{abs}}, \\ \exp[-A_{\text{abs}}(z - z_{\text{abs}})^2], & z > z_{\text{abs}}, \end{cases} \qquad (34)$$

where z_{abs} is the value of the radial coordinate where the wave packet begins to be absorbed and A_{abs} is an empirical coefficient which gives the strength of the absorption. This procedure

switches on adiabatically the absorbing potential, which does not alter greatly the wave packet shape in one single time step and gives stability to the numerical procedure.

2.6. Potential and centrifugal cut-off

Our experience shows that it is worthwhile to superimpose a cut-off on the values the potential and the centrifugal force can take. This limits the range of the eigenvalues of the Hamiltonian. WATERWAVES requires input values for the cut-off and puts $V = V_{\max}$ if $V > V_{\max}$ and $Cent = Cent_{\max}$ if $Cent > Cent_{\max}$. The same cut-off technique is used in evaluating the vibrational wave functions of the final diatom for calculating the cross section.

2.7. Expectation values

Expectation values of geometrically defined operators can be computed in a straightforward manner simply by summing the square of the wave function and the operator over all grid points. Calculating averaged coordinates or squared averaged coordinates allows one to follow the norms of the evolving wave packet. Furthermore WATERWAVES is able to evaluate both the energy and the norm at a given time iteration. To decide when to stop the calculation it is necessary to calculate what proportion of the norm wave packet is left after the absorption and for the asymptotic analysis it is important to calculate the total amount of wave packet up to the absorbing edges. WATERWAVES does the evaluation of such a norm beyond and behind the starting point of the absorbing potential.

3. Physical observables: ASYMPTOT

After propagating the wave packet one has to extract the observables of interest. In order to obtain the cross section (DA, VE, ...), working in a time-dependent picture, two approaches can be used: asymptotic analysis and flux analysis. Both methods have as a starting point the wave packet at a typical value of the Jacobi coordinate ($R = R_\infty$) where it is certain that dissociation has occurred. In a typical triatomic calculation this means that the final diatom–atom products are formed. The first approach is mainly based on the calculation of the scattering matrix, the later one relies on a T-matrix formalism.

We adopt the asymptotic analysis which requires less computational effort and gives results comparable to those of the flux analysis. Indeed, using a body-frame Jacobi coordinate system, ASYMPTOT obtains the scattering states at a given value of $R = R_\infty$ directly without any need for transformation because the point for analysis is chosen along a line in the direction of the scattering products. A projection onto the final diatomic states is needed to get wave packet coefficients as a function of time. Energy-resolved observables can be obtained through a Fourier transform from the time to the energy domain.

The starting point of our analysis is thus the asymptotic wave packet $\Psi(R_\infty, r, \gamma, u)$. Projection of such a wave packet

onto the final states of the diatom $\phi_{jv}(r)$ gives a set of time-dependent coefficients $A_{jv}(u)$ [35]

$$A_{jv}(u) = \int_0^\infty dr\, \phi_{jv}(r) \int d\gamma\, P_j^0(\gamma) \psi(R_\infty, r, \gamma, u), \qquad (35)$$

where j and v are the quantum numbers of the final rovibrational state of the diatom. To find an analytic expression for the cross section we need to return to the time-independent formal theory of scattering where the dissociative wave packet has an asymptotic behaviour analogous to an outgoing wave in the laboratory frame:

$$\Psi^{JM}(R, r, \gamma, \alpha, \beta, \zeta) = \sum_{K=-J}^{J} \tilde{D}_{MK}^J(\alpha, \beta, \zeta) \frac{\Xi_K^{JM}(R, r, \gamma)}{Rr},$$

$$\widetilde{R \to \infty} \sum_{jv} C_{jv}(E) \tilde{D}_{MK}^J(\alpha, \beta, \zeta) \frac{e^{ikR - ij\pi/2}}{Rr} \phi_v, \qquad (36)$$

where ϕ_v are the vibrational wave functions of the diatom product, $E = E_m + E_{\rm kin}$ is the total energy written as a sum of the initial state energy of the triatomic molecule and the energy of the exciting process. $C_{jv}(E)$ are the partial wave amplitudes for the dissociative process. After projecting the asymptotic wave function onto ϕ_v the coefficients $C_{jv}(E)$ and $F_{jv}(E)$ are the real and imaginary part of the Fourier transform coefficients from u of the $A_{jv}(u)$ previously defined in Eq. (35). Mathematically:

$$C_{jv}\big(f(E)\big) = \frac{1}{2\pi} \int_0^\infty du \exp\big(if(E)/\hbar\big) \,{\rm Re}\big[A_{jv}(u)\big], \qquad (37)$$

$$F_{jv}\big(g(E)\big) = \frac{1}{2\pi} \int_0^\infty du \exp\big(ig(E)/\hbar\big) \,{\rm Im}\big[A_{jv}(u)\big]. \qquad (38)$$

There are two different ways of representing the cross section: one can obtain it from the outgoing projected flux or derive it from the asymptotic form of the solution of the time-dependent Schrödinger equation. Following this last path one obtains the dissociative cross section resolved by quantum number of the final fragments [2] as:

$$\begin{aligned}
\sigma^{jv}(E) &= \left(\left|\frac{df(E)}{dE}\right|^2\right)\sigma^{jv}\big(f(E)\big) + \left(\left|\frac{dg(E)}{dE}\right|^2\right)\sigma^{jv}\big(g(E)\big) \\
&= \frac{\hbar^4 a_s^2}{\delta(1 - E_s^2)} \frac{k}{\mu_R}\big(\big|C_{jv}(E_{v_i} + k^2/2)\big|^2 \\
&\quad + \big|F_{jv}(E_{v_i} + k^2/2)\big|^2\big),
\end{aligned} \qquad (39)$$

where k is the relative nuclear momentum of the fragments, g is a statistical ratio, μ_R the reduced mass of the fragments.

4. Programs structure

User input is needed for both the modules. The modules follow the convention that names beginning with letters A–H and O–Y are for 8-byte real variables, I–N are for integers.
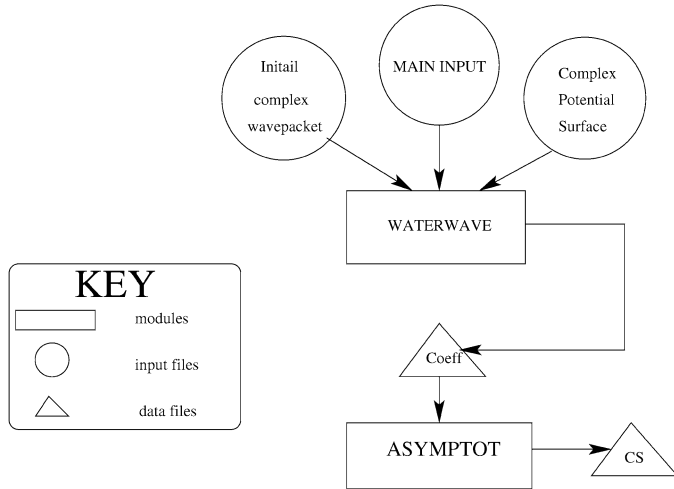
Fig. 2. Structure and data flow for the WATERWAVES and ASYMPTOT program suite.

The data flow through the modules is given in Fig. 2. The role of the individual subroutines is described in comments included in the source programs and briefly summarized below. All modules, except the interpolation routines, are written in FORTRAN 77 (a preliminary version in C++ also exists for getting optimal efficiency in the dynamical storage). In addition calls to calculate FFT (VRFFTF) [36] and Gauss–Legendre quadrature (GAULEG) [37] have been implemented. The local implementation of these routines should be used where possible otherwise FORTRAN sources can be downloaded from the web.

Internally WATERWAVES works and passes data entirely in atomic units. Atomic mass units, used for input, are converted using $1u = 1822.8883 m_e$. A factor of 1.7475329251 is used to change the units from degrees to radiants for the calculation of geometric quantities. To return to physical time after propagation the transformation factor used is

$$t = \frac{\hbar a_s}{\sqrt{1.0 - E_s^2}} u = \frac{1.0545887 * 10^{-34} * a_s}{\sqrt{1.0 - E_s^2}} u, \tag{40}$$

where $E_s = a_s * E + b_s$ is the energy scaled by the factor a_s [19] and assumed to be in Hartree.

4.1. The main program: WATERWAVES.F

The main driving module, named WATERWAVES.F, calls the various subroutines needed for the time propagation of the wave packet, carries out the first and main iterations. The main program includes tools for calculating of the norm of the complex wave packet, the density, the energy and many expectation values of geometric quantities. WATERWAVES includes the commons given in the file COMMONS.DAT (masses of the atoms, Hamiltonian terms, etc.) used both in the propagation and absorption of the wave packet and in the asymptotic analysis. For large runs, the CPU time requirement of WATERWAVES.F is usually dominated by the propagation of the wave packet on the complex potential, implemented as explained in Section 2.2: significant computational time depending on the

size of the grid used to approximate the wave packet and on the numbers of polynomials used in Eq. (28) can result.

4.2. Setting parameters: SETPARAM.F

This module sets all the parameters needed in the calculation. After reading from the standard input, it calculates the reduced masses, the numerical size of the problem and the parameters for scaling the Hamiltonian. It also fixes the evenly spaced radial grid calling the function GRIDR.F, and the weights and Gauss–Legendre quadrature points calling ANGDEV.F [37]. Furthermore it reads the input files of the complex triatomic potential surface (real and imaginary part separately) as specified in Section 5.1.

4.3. The initial condition: INICON.F

Since we have to solve a first order differential equation in time we need an initial condition for the wave packet. IN-ICON.F fixes this initial condition which has to be provided for both the real and imaginary part of the complex wave packet in Jacobi coordinate system as specified below in Section 5.1. This condition is used to start the propagation in the first time iteration which is different from the main ones.

4.4. The action of the Hamiltonian on the wave packet: subroutine HPW.F

An essential part, which is widely used in the code, is the HPW.F module. This function is devoted to the application of each term of the Hamiltonian to the wave packet; that means the routine needs to know the Hamiltonian tensor and the wave packet both written in a suitable basis to calculate the product of these two quantities. Along with GRIDR.F, which calculates just the kinetic part, HPW.F utilises the subroutine FFT.F [36] for computing the Fourier coefficients of a number of real periodic sequences. The routine applies the radial r and R kinetic terms to the wave packet through a FFT algorithm as explained in Section 2.2, the centrifugal part, the potential by transforming backward to a DVR basis and forward to the FBR basis and afterwards adds the different contributions.

4.5. Energy values: subroutine GETENERGY

The calculation of the expectation value of the Hamiltonian is performed in the subroutine GETENERGY.

4.6. Expectation values: subroutine GETNORM

The calculation of the expectation values of some geometric quantities, such as the average and squared average position of the centre of mass of the wave packet, is performed in the subroutine GETNORM of the main code. The values of the norm up to the edges of the absorption, the total amount of wave packet in the region where the asymptotic analysis is conducted, the total amount of the wave packet for a given $r = \bar{r}$, and the total norm are also calculated and stored in RNORMABS, RNORMBR, RNORMSR, RNORM, respectively.

4.7. Absorption: subroutine ABSORB

The absorption of the wave packet at the boundaries is performed by calling ABSORB. ABSORB uses a Gaussian type absorbing function and allows the user to choose also the time iteration after which wave packet absorption starts.

5. Programs use

5.1. Potential, decay and property subroutines

WATERWAVES requires the user to provide the appropriate potential energy surface in Hartree as a one column file using the format $V(R_i, r_j, \gamma_k)$ where r runs NV steps from SRMIN to SRMAX, R runs NR steps from RMIN to RMAX, γ runs NJ steps from -1 to 1, where the sequence runs over i fastest, k slowest. The subroutine GETPOT calculates also the minimum and maximum values of the potential energy and whenever $V >$ VCUT sets $V =$ VCUT. WATERWAVES also requires the user to provide the appropriate decay probability surface in Hartree as a one column file using the format $\Gamma(R_i, r_j, \gamma_k)$ where coordinates run in the same order as above.

Finally the user must provide a one column file with the appropriate vibrational wave functions $\phi_v(r)$ of the final diatom, where r runs in NV steps from SRMIN to SRMAX and the sequence is from $v = 0$ to NVAB.

5.2. Data input for WATERWAVES

WATERWAVES requires two different user defined input files. All input is free format. The first file is a 2 lines file needed to fix the maximum size of the array used in the wave packet propagation and is a standard FORTRAN parameter file linked by the compiler.

Line 1: COORDINATE PARAMETERS

NRMAX	= the max number of points requested in the R-grid.
NVMAX	= the max number of points requested in the r-grid.
NJMAX	= the max number of points requested in the γ-grid.
NCOSMAX	= the max number of Legendre polynomials for the diatomic rotational basis.

Line 2: VIBRATIONAL PARAMETER

NVABMAX	= the max number of vibrational states of the final diatom.

The second input file is a more complex one and requires 29 lines of user input for all runs.

Line 1: NCHEB

NCHEB	= number of terms used in Chebyschev expansion.

Line 2: IWRITE, ICOOUT

IWRITE	= write to the standard output significant data every IWRITE iterations.

ICOOUT	= write to file the coefficients every ICOOUT iterations.

Line 3: IABST

IABST	= the number of time steps after which absorbing starts.

Line 4: PROCODAT

PROCODAT	= string with the name of the projected coefficients output file.

Line 5: CODAT

CODAT	= string with the name of the coefficients output file.

Line 6: DENS, NORMFL

DENS	= string with the name of the density output file.
NORMFL	= string with the name of the norm output file.

Line 7: RAVDAT

RAVDAT	= geometric averages output file.

Line 8: WFNR, WFNI

WFNR	= string with the file name where the real part of the initial wave packet is stored as defined above.
POT	= string with the file name where the real part of the potential is stored as defined above.
GAM	= string with the file name where the imaginary part of the potential is stored as defined above.

Line 10: JBIG

JBIG	= total angular momentum (only $J = 0$ implemented).

Line 11: RMA, RMB, RMC

RMA	= mass of the atom A in a.m.u.
RMB	= mass of the atom B in a.m.u.
RMC	= mass of the atom C in a.m.u.

Line 12: BRDAG

BRDAG	= R coordinate point for the asymptotic analysis in a_0.

Line 13: RDAGGER, BROUT

RDAGGER	= starting r point for the flux analysis in a_0.
BROUT	= R coordinate point for the flux analysis in a_0.

Line 14: NJ

NJ	= number of points requested in the γ-grid.

Line 15: RMIN, RMAX, NR

RMIN	= minimum value of R in a_0.
RMAX	= maximum value of R in a_0.
NR	= number of points requested in the R-grid.

Line 16: SRMIN, SRMAX, NV

SRMIN	= minimum value of r in a.u.
SRMAX	= maximum value of r in a.u.

NV   = number of points requested in the *r*-grid.

Line 18: VCUT

VCUT   = cut-off of the potential in E_h.

Line 19: CENCUT

CENCUT   = cut-off of the centrifugal energy in E_h.

Line 20: RAB, CRAB

RAB   = value of the *R*-coordinate where the wave packet begins to be absorbed in a_0.

CRAB   = pure value of the coefficient in the Gaussian-like absorbing potential in E_h.

Line 21: SRAB, CSRAB

SRAB   = value of the *r*-coordinate in a_0 where the wave packet begins to be absorbed.

CSRAB   = pure value of the coefficient in the Gaussian-like absorbing potential.

Line 22: NSTEP

NSTEP   = number of time steps used in the propagation.

Line 23: EKIN

EKIN   = kinetic energy of the impinging particle in eV.

Line 24: EGRN

EGRN   = ground state energy of the triatomic molecule in E_h.

Line 24: ERESON

ERESON   = resonant state energy of the triatomic anion in E_h.

Line 24: EVIB

EVIB   = zero vibrational state energy of the triatomic molecule in eV.

Line 25: WIDTH

WIDTH   = finite spread of the initial wave packet.

Line 26: NVAB, NJAB

NVAB   = number of vibrational states included in the final diatomic state.

NJAB   = number of rotational states included in the final diatomic state.

Line 27: TMPFILCA

TMPFILCA   = string with the name of temporary file for data storage.

Line 28: TMPFILCB

TMPFILCB   = string with the name of temporary file for data storage.

Line 29: TMPFILCC

TMPFILCC   = string with the name of temporary file for data storage.

6. ASYMPTOT

ASYMPTOT requires the unformatted output of WATER-WAVES containing the coefficients of the wavepacket at differ-ent times. The routines ASYMPTOTIC.F and PROJECTION.F carry out the asymptotic analysis and extract the necessary in-formation from the evolved wave packet at a value of *R* large enough to be sure that the fragments are far from each other.

6.1. Input for ASYMPTOT

Most of the data for ASYMPTOT, which must be pro-vided by WATERWAVES, are taken from unformatted files which contain the coefficients of the asymptotic wave packet (the evolved wave packet at some $R = R_\infty$). ASYMPTOT re-quires the same parameters file previously provided for WA-TERWAVES and 6 lines of data are read from the input stan-dard.

Line 1: TSTART

TSTART   = starting time *t* requested for the analysis in fs.

Line 2: FLUX.DAT

FLUX1.DAT   = string with the name of the coeffi-cients data of the wave packets as given by WATERWAVES.

Line 3: PFLUX

PFLUX   = string with the name of the output file of the total cross section.

Line 4: PFLUXVIB

PFLUXVIB   = output file of the cross section as a function of the vibrational state of the final diatom.

Line 5: EMIN, EMAX, NE

EMIN   = min kinetic energy of the impinging particle in eV.

EMAX   = max kinetic energy of the impinging particle in eV.

NE   = number of points in the energy grid.
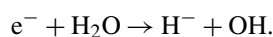
Line 6: NTIME, DELTAT

NTIME   = number of time point used in the propaga-tion of the wavepacket.

DELTAT   = time interval used in the propagation of the wavepacket in fs.

7. Test run

Short scripts, input data and associated output files have been included with the program.

The test case which ensures that there is a test run for each module, is based on a calculation for dissociative attachment (DA) of water:

$$e^- + H_2O \rightarrow H^- + OH.$$

The tests use the complex potential energy surfaces of Haxton et al. [10] provided as explained in Section 5.1. The calcula-tions use Jacobi products coordinates (OH + H) and run both the modules WATERWAVES and ASYMPTOT.

Table 1
Parameter file for WATERWAVES: test case

parameter(nrmx = 200, nvmx = 110, njmx = 40, ncosmx = 40, nkmx = 1)
parameter(nvabmx = 45)

Table 2
Input file for WATERWAVES: test case

10	! no. Cheb. polys for $t = 1$
4 4	! iwrite, icoout
0	! iabst
'scr/projcoeff.dat'	! Projected coeff file
'scr/coeff.dat'	! Coeff output file
'scr/density.dat' 'scr/normwp.dat'	! density and norm output files
'scr/rav.dat'	! averages output file
'scr/wfnewr.dat'	! initial wfn input file
'scr/pot.dat'	! potential input file
'scr/gamma.dat'	! gamma input file
0	! J
15.994915 1.0079 1.0079	! O + H2 masses/amu
10.00	! Rdag for ASYMPTOT
5.00 10.0	! rdag, Rout for flux
39	! nj
0.1 11.98 199	! Rmin, Rmax, nr
0.6 6.9 106	! rmin, rmax, nv
1	! rkin choice
2.5	! vcut/a.u.
0.7	! cencut/a.u.
9.0 0.015	! R abs and coeff
5.5 0.015	! r abs and coeff
852	! nstep
6.4	! etran/eV
76.1	! eh20 a.u.
75.8	! eh20—a.u.
0.7	! eh20 zero energy a.u.
0.10	! width
11 39	! nvab, njab
'scr/catmp.dat'	! ca temporary file
'scr/cbtmp.dat'	! cb temporary file
'scr/cctmp.dat'	! cc temporary file

An example of user provided parameter file and input for the test case of WATERWAVES is given in Tables 1 and 2, respectively.

The grid chosen is a compromise between accuracy and computational effort and it is evenly spaced in both radial Jacobi coordinates: r runs over 106 points in the range 0.6 to 6.9, while R runs over 198 points in the interval 0.1 to 11.98. The angular grid is made of 39 Gauss–Legendre quadrature points. The total size of the test grid is 822666. In the case of water we choose the initial condition, Eq. (33) [29], where $|v\rangle$ is the $(0, 0, 0)$ vibrational state of water in its X^1A_1 ground state and $V_{d\mathbf{k_i}}$ is the value of the square root of Γ, the probability, at the equilibrium distance, of excitation into the resonance state X^2B_1 at about 6.5 eV.

The DVR3D program [30] was used to calculate the initial state. This gives the values on a DVR grid. WATERWAVES requires values of the wave function on a DVR grid which means the amplitudes of the wave packet at different points from these of the Gaussian quadrature scheme. Routine INTERP.F makes the 3D B-spline interpolation based on carefully tested versions of BSPLINE LIBRARY VERSION 2.2 by Schadow [38].

Table 3
Input file for ASYMPTOT: test case

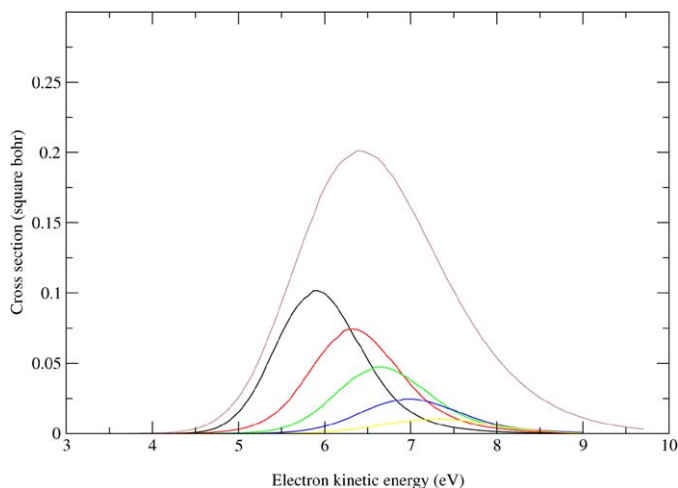| 0	! tstart
'scr/coeff.dat'	! probability output file
'scr/probab.dat'	! probability output file
'scr/probabvib.dat'	! probability output file
3 8 200	! emin, emax, ne
852 2.458232345287928E–002	! ntime, dt

Fig. 3. Cross section for H_2O with increasing vibrational quantum number from left to right.

The routine uses as input the old grid and values provided by DVR3D and the new grid on which one transforms the wave packet. This routine which requires a FORTRAN 90 compiler, is supplied with test run data. An input file for the test run is provided containing the initial condition The initial capture of the electron into the resonant state marks time $t = 0$. The total energy is the sum of:

$$E = E_{\text{trans}} + \epsilon_v = \frac{k^2}{2} + \epsilon_v,$$

where E_{trans} is the collision energy of the impinging electron and ϵ_v the initial vibrational energy of water, where the zero point energy is supposed to be taken. The test calculation is for $J = 0$ and the absorption of the wave packet starts at $z_{\text{abs}} = 9.0a_0$ a.u. with a strength of $A_{\text{abs}} = 0.015$.

After the calculation the file "coeff.dat" contains the values of the wave packet snapshots at different times (750 in this case) in unformatted form besides other files (density.dat, normwp.dat, rav.dat) with information on the propagation of the wave packet. To extract the dissociative attachment cross section one has to run ASYMPTOT. An example of input for ASYMPTOT is given in Table 3.

ASYMPTOT reads coeff.dat and after the run produces two different files, probab.dat and probabvib.dat, in which the total probability and the probability as a function of the final diatom vibrational state increasing from left to right are given. The time grid consists of 850 points separated uniformly in time by 0.02458232; intervals, the energy domain is divided in 800 intervals between 0.5 to 15 eV.

The test runs requires the creation of a directory called "scr" and use the Intel Fortran compiler which we found significantly better than others we tested for use under Linux. All the results in the test run are fully converged. For both the programs a makefile is provided. Sample results are given in Fig. 3. These have been compared with those given by Haxton et al. [10] and are nearly indistinguishable.

To plot the snapshots at different times two shell scripts are provided for producing mpeg movies.

Acknowledgement

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