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A wave packet method for treating nuclear dynamics on complex potentials

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Abstract

A general time-dependent description of the dissociative attachment of a triatomic molecule is presented. The approach presented works within the Feshbach projection operator formalism and gives an algorithm for solving the nuclear motion problem which reduces the computational effort required. The method uses a complex potential energy surface to characterize the formation and decay of resonances as modified by the coupling to the nuclear motion which are treated using multidimensional complex wave packets. A basis-independent wave packet method is developed and used to treat the propagation of a wave packet on a complex three-dimensional potential appropriate for resonance states of the water anion. A complete derivation of the system of linear equations used in the time iteration is presented. The method can be applied to resonant vibrational excitation, for which the electron impact vibrational excitation of water is considered.

1. Introduction

Calculations on scattering processes have been traditionally performed in the framework of energy domain quantum mechanics and for molecules with just one degree of freedom (Bardsley 1966, Morgan *et al* 1990). In the last few years advances in computer memory and development in computation techniques have made it possible to numerically solve the time-dependent Schrödinger equation (Balakrishnan *et al* 1997, Gertitschke and Domcke 1993, Schneider *et al* 2006) for a variety of processes including photodissociation (Kulander *et al* 1990), atom–molecule reactive collisions (Zhang and Zhang 1994), Bose–Einstein condensation (BEC) (Inguscio *et al* 1999), resonant dissociative collisions (dissociative recombination (Orel and Kulander 1993) and electron attachment (Haxton *et al* 2004b)) and vibrational excitation via resonance (Schulz 1973). The evolution in time is the most intuitive and appealing frame for dynamics for at least two different reasons. First, the use of the laws of quantum mechanics in time-dependent approach is analogous to the classical mechanics description. It gives an intuitive insight into the dynamics, often hidden in time-independent calculations, because one can view snapshots of the wave packets by simply plotting probability densities at various stages of the time evolution and hence obtain a feel for the dynamics. Indeed, by studying wave packets one touches the border between classical and quantum behaviour as it is well known that a wave packet must be associated with a bunch of deterministic classical trajectories. Second, the Schrödinger equation is first order in time and thus the scattering problem can be solved for a variety of energies with just one wave packet run by performing a simple Fourier transform. These results can then be directly compared to the experiment, where time resolution of the interacting systems can be difficult to achieve.

Time-dependent methods can be used to compute both the dynamics of atoms bound in a molecule and the dynamics of dissociation following an excitation by an impinging particle. Whereas our understanding of non-dissociative collisions has advanced greatly recently, largely due to the development of theories capable of treating correctly the strong forward peak of most such cross sections, less is known about collisions which dissociate the molecule. Impact dissociation is important for astrophysics, radiation damage of living tissue and in the ionosphere. Dissociative electron–molecule collisions such as dissociative electron attachment (DEA), which competes with vibrational excitation (VE), cause strand breaks in DNA and, as a result of fragmentation or recombination of the molecules, produce chemically reactive radicals (Boudaiffa *et al* 2000, Pimblott and LaVerne 2002). It is now widely accepted that such collisions often proceed via a resonant state in which the impinging particle loses its kinetic energy for a period of time of the same order as the vibrational motion and can decay by a variety of different paths.

While the dynamics of resonant collisions in the simple case of a one-dimensional potential, such as electron collision with diatomic molecules (Morgan 1986, Hazi *et al* 1981, Robicheaux 1991, Brems *et al* 2002) seems to be well established, the best general method for treating fully multidimensional nuclear motion is still the subject of discussion. In general multidimensional problems have different reaction paths which yield different products, each with different probability amplitudes. This means that quantal effects due to sharing energy between electronic and nuclear motion have to be treated in all the nuclear degrees of freedom to correctly model the vibrations and dissociation of the molecule. Alternative computational procedures are represented by the path-integral approach of Feynman (1981) and Feynman and Hibbs (1965), the multiconfigurational time-dependent Hartree representation of the wavefunctions (MCTDH), developed by Beck *et al* (2000), and the spectral method due to Feit and Fleck (1982).

All have been used to develop approximation methods for treating both local and non-local dynamics (Winterstetter and Domcke 1993). The path-integral approach, which is motivated by the linear scaling with the number of degrees of freedom if one uses the harmonic oscillator approximation for the vibrational modes, suffers problems with choosing suitable weights for the electronic paths and from the need to introduce a discrete basis at every intermediate time. The MCTDH approach makes use of the time-dependent representation of the nuclear wave packet as a linear combination of single-particle functions: the greater the number of terms, the more precise is the calculation. It has been used to treat the dissociative attachment of water in all three vibrational degrees of freedom using a method tailored *ad hoc* to this system (Haxton *et al* 2004b). The spectral method has been used (Kazansky and Sergeeva 1994, Kazansky 1995) for calculating both inelastic and DEA cross sections of slow electrons with carbon dioxide. In such a case the solution of the time-dependent Schrödinger equation was obtained using the split time propagation method where the propagation of the wave packet is split into a free-particle propagation over a half-time, a whole time propagation for the potential part and a third free particle action step to end the propagation. This method, as the authors acknowledge, relies on the existence of the fast Fourier transform algorithm (FFT) and on the explicit independence of the kinetic energy from the spatial coordinates. Furthermore this method appears unsuitable for joining with a Chebyshev propagation scheme. Our method has a different prospective: it actively uses Chebyshev propagation and can be used with or without an FFT algorithm.

The purpose of this paper is to present a new method, both theoretical and computational, for calculating the dynamics subsequent to excitation of a polyatomic molecule. This method still retains the time-dependent view but, in contrast to standard methods for solving the Schrödinger equation which are basis dependent, uses a grid Hamiltonian. The method uses a complex potential to represent the resonance state, can take into account all nuclear degrees of freedom and can treat both DEA and resonant VE. The algorithm we present transforms the decaying partial differential equation to a set of coupled linear equations for the real and imaginary parts of the wave packet. It gives a rigorous treatment of the non-separability in time between the real and imaginary parts due to the decay.

This distinguishes the method and the computation procedures from some employed previously (Kulander *et al* 1990). The coupled linear equations, as explained below, are solved iteratively, using large time steps due to an efficient Chebyshev expansion scheme. This enables us to handle the exponential growth in the computational effort with the number of degrees of freedom by a combination of minor improvements in the theory and major changes to the computational procedure. In particular we choose different suitable coordinate systems, and consequently grids, as well as representations of the Hamiltonian operator.

We limit ourselves to the discussion of nuclear excitation and dissociation processes in a sample triatomic molecule, water. However we believe that the methods we present are sufficiently general to be applied to the analysis and interpretation of different physical problems, such as resonances in tetratomic molecules or processes involving the interaction between matter and light.

2. Method

The calculation of electron–molecule impacts resulting in dissociative electron attachment (DEA) or resonant vibrational excitation (VE) splits naturally into two parts: the first comprising electron dynamics and the second nuclear motion dynamics. Our goal is to combine accurate first principles electronic motion calculations with a wave packet treatment of the nuclear dynamics with multiple nuclear degrees of freedom. The computation of the complex potential surfaces of the combined electron–molecule complex is not the subject of this paper: the electronic motion can be studied using standard methods such as *ab initio* complex Kohn variational calculations (McCurdy and Rescigno 1989) or the molecular *R*-matrix method (Burke and Berrington 1993). Fixed-nuclei calculations are used to obtain complex potential energy surfaces. As result of the collision the molecule can be excited to one or more short-lived resonant states embedded in the continuum which decay with time. Excitation of such quasi-bound resonances results mainly in two different physical processes: vibrational excitation and dissociative attachment. In the former the molecule is left in its electronic ground state but vibrationally excited; in the latter there must be sufficient energy for a bond to be broken and the molecule follows a dissociative path. For the following general analysis it is not necessary to specify if we are dealing with a shape or a Feshbach resonance: we just assume a single complex electronic state which is discrete, as opposed to the continuum of states with which it interacts. Generalization to more than one distinct discrete state is straightforward.

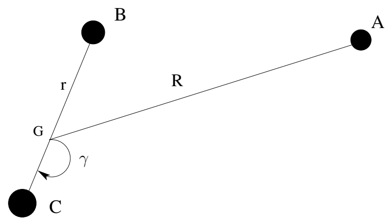

Figure 1. Body-fixed Jacobi coordinate system: A, B, C represent atoms. The coordinates are given by $r = \mathrm{B} - \mathrm{C}$, $R = \mathrm{G} - \mathrm{A}$ and the angle $\gamma = \mathrm{A}\hat{\mathrm{G}}\mathrm{C}$. G is the centre of mass of BC.

2.1. The nuclear motion: the model Hamiltonian

The time-dependent projection operator formulation has been described in detail elsewhere (Gertitschke and Domcke 1993), so here we just give a brief outline. For an isolated resonance we assume that the Hilbert space of the electronic configurations is spanned by a simple L^2 function $|\phi_d\rangle$. This assumption is clearly based on the Born–Oppenheimer approximation. Partitioning the total wavefunction into resonant and non-resonant components defines two projectors (Feshbach 1962)

$$Q = |\phi_d\rangle\langle\phi_d|, \qquad P = 1 - Q. \tag{1}$$

One can reduce the treatment of nuclear dynamics in a complex energy-dependent and non-local potential to a local complex potential, which is known as the Markov approximation for the decay dynamics (Cederbaum and Domcke 1981). Projecting out the electronic motion, we are left with the equation of motion of the nuclei

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

where T_N is the nuclear kinetic energy operator, V_d is the potential energy of the discrete electronic state and

$$\Gamma_L(r, R, \gamma, E_{\mathrm{res}}) = \Gamma_L(r, R, \gamma) = 2\pi \int \mathrm{d}\Omega_k |V_{dk_f}(r, R, \gamma)|^2 \tag{3}$$

in which $\Gamma_L(r, R, \gamma)$ is the width taken at the resonance energy and the discrete–continuum coupling enters via the 'exit amplitude' V_{dk_f}.

2.2. Jacobi coordinate system

To treat the dissociative and vibrational problem, we use Jacobi coordinates. A sketch of this coordinate system is presented in figure 1. In scattering coordinates r represents the diatom distance between atom B and atom C, and R the separation of 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 body-fixed Jacobi coordinates is

$$\Psi^{JM}(R, r, \gamma, \alpha, \beta, \zeta) = \sum_{K=-J}^{J} \tilde{D}^J_{MK}(\alpha, \beta, \zeta)\frac{\Xi^{JM}_K(R, r, \gamma)}{Rr} \tag{4}$$

where $\tilde{D}^J_{MK}(\alpha, \beta, \zeta)$ is the set of normalized Wigner rotation matrices (Wigner 1939), J is the total angular momentum, and M is the z component of the total angular momentum in the laboratory frame. In equation (4), K is the projection of the total angular momentum on the body-fixed z axis which we take as $R \equiv z$, and (α, β, ζ) are the three Euler angles which orient the body frame to the laboratory frame. The left-hand side of equation (4) is thus in the laboratory frame and the right-hand side is in the body frame.

3. Solution of the equation of motion

A single nuclear dynamics problem, defined by equation (2), is considered for DEA and VE. It is solved in three different steps: wave packet creation, wave packet evolution and extraction of the observables of interest.

3.1. The initial condition

To begin the propagation of the wave packet, we need to introduce an initial condition that sets the total energy as a sum of the collision energy of the impinging particle E_{trans} and the initial vibrational energy of the triatomic molecule ϵ_ν:

$$E = E_{\text{trans}} + \epsilon_\nu = \frac{k^2}{2} + \epsilon_\nu. \tag{5}$$

The best choice for the initial condition for DEA and VE calculations is (Domcke 1991)

$$|\Psi_d(0)\rangle = V_{d\mathbf{k_i}}|\upsilon\rangle \tag{6}$$

where $\mathbf{k_i}$ denotes the momentum of the incoming particle, $|\upsilon\rangle$ the initial vibrational state of the molecule and

$$V_{d\mathbf{k_i}} = \langle k_i(t)|V|\psi_d\rangle = \sqrt{\Gamma/(2\pi)} \tag{7}$$

is the 'entry amplitude'. This is known as 'vertical transition' approximation and defines the initial wave packet which sets the clock at $t = 0$ for the dynamical evolution of the system.

3.2. Evolution in time

Equation (2) can be formally solved by introducing the operator

$$\hat{U} = \exp\left(-\frac{\mathrm{i}}{\hbar}\int H(\hat{t})\,\mathrm{d}t\right), \tag{8}$$

which gives the state of a system at a later time. In our case the total Hamiltonian, equation (2), is not Hermitian because the wave packet can bifurcate and decay to the ground state:

$$H_T = H_R + \mathrm{i}H_c = T_N + V_d - \mathrm{i}\frac{\Gamma}{2}. \tag{9}$$

The real part of the body frame Hamiltonian in Jacobi coordinates is written (Tennyson and Sutcliffe 1982), in atomic units:

$$\begin{aligned} H_R = &-\frac{1}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r}\frac{\partial^2}{\partial r^2} - \left[\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2}\right]\hat{j}^2 \\ &- \frac{1}{2\mu_R R^2}\left[J(J+1) - 2K^2 + C^J_{K,K-1}\left(-\frac{\partial}{\partial\gamma} + K\cot(\gamma)\right)\right. \\ &\left. + C^J_{K,K+1}\left(\frac{\partial}{\partial\gamma} + K\cot(\gamma)\right)\right] + V_d(R, r, \gamma) \end{aligned} \tag{10}$$

where K is the projection of the total angular momentum on the R axis and

$$\hat{j}^2 = \frac{1}{\sin\gamma}\frac{\partial}{\partial\gamma}\sin\gamma\frac{\partial}{\partial\gamma} - K^2\operatorname{cosec}^2\gamma \tag{11}$$

$$C^J_{K,K\pm1} = [J(J+1) - K(K\pm1)]^{1/2} \tag{12}$$

and the appropriate reduced masses are

$$\mu_R = \frac{m_A(m_B+m_C)}{m_A+m_B+m_C}, \qquad \mu_r = \frac{m_B m_C}{m_B+m_C} \tag{13}$$

and the atoms are defined by figure 1. Putting $J = 0$ means K is a good quantum number and the wave packets are not coupled by the Coriolis terms. Previous calculations (Schulz 1973, Haxton *et al* 2004b) suggest that the rotational state of the triatomic has negligible effect on the cross section for DEA and VE. The same is not true for different initial vibrational modes of the target.

The 3D Hamiltonian (equation (10)) is solved by successive time iteration (Balint-Kurti *et al* 1998); the time evolution of the wave packet is governed by equation (2) for a given potential. A similar approach has been used in reactive scattering by Gray (1992) and Gray and Balint-Kurti (1998) for the propagation of real wave packets on real potential surfaces. These workers were able to predict the evolution of an initial complex wave packet on a real surface by only propagating the real part. We cannot follow this approach, which halves the computer time and the memory, due to the complex potential. The presence of an electromagnetic field or consideration of spin would have the same effect on the Hamiltonian.

By dividing the time coordinate into two, one can split the problem into forward

$$\begin{aligned}\Psi(\vec{R}, t+\tau) &= U(t+\tau, t)\Psi(\vec{R}, t) = \exp\frac{-\mathrm{i}H_T\tau}{\hbar}\Psi(\vec{R}, t)\\ &= +\exp\frac{-\Gamma\tau}{2\hbar}\left[\cos\left(\frac{H_R\tau}{\hbar}\right) - \mathrm{i}\sin\left(\frac{H_R\tau}{\hbar}\right)\right]\Psi(\vec{R}, t)\end{aligned} \tag{14}$$

and backward propagation

$$\begin{aligned}\Psi(\vec{R}, t-\tau) &= U(t-\tau, t)\Psi(\vec{R}, t) = \exp\frac{+\mathrm{i}H_T\tau}{\hbar}\Psi(\vec{R}, t)\\ &= +\exp\frac{+\Gamma\tau}{2\hbar}\left[\cos\left(\frac{H_R\tau}{\hbar}\right) + \mathrm{i}\sin\left(\frac{H_R\tau}{\hbar}\right)\right]\Psi(\vec{R}, t).\end{aligned} \tag{15}$$

Adding the right-hand side of the two previous equations one obtains

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

$$\begin{aligned}\Psi(\vec{R}, t+\tau) = +\Psi(\vec{R}, t-\tau) - 2\left[\cos\left(\frac{H_R\tau}{\hbar}\right)\sinh\left(\frac{\Gamma\tau}{2\hbar}\right)\right.\\ \left. + \mathrm{i}\sin\left(\frac{H_R\tau}{\hbar}\right)\cosh\left(\frac{\Gamma\tau}{2\hbar}\right)\right]\Psi(\vec{R}, t)\end{aligned} \tag{17}$$

where the $\vec{R}$ represents (R, r, γ). This enables us to relate the wave packet at time $t+\tau$ to that at time t and $t-\tau$. Even if the iteration starts from a real initial wave packet, the imaginary part in the above equations implies that the wave packet can become complex during the propagation and our equations are coupled. To obtain an efficient computational method we merged the benefits of a simple Chebyshev recursion relation (Tal-Ezer and Kosloff 1984), which is easy to implement but gives 'time-step' dependent results and is useful only for short-time propagators, with our 'complex wave packet propagation'. for the real and imaginary part of the wave packet. Starting from the idea that the time coordinate does not enter in any of the observables, we solve a mapped Schrödinger equation. To do this, we apply a transformation from real time to 'mathematical time', u and from the physical decay to the 'mapped decay', Γ_s. The modified equation is

$$\mathrm{i}\frac{\partial|\Psi(u)\rangle}{\partial u} = [f(H) + \mathrm{i}g(\Gamma)]|\Psi(u)\rangle. \tag{18}$$

The particular functions chosen for the transformation are those which simplify the iterative form,

$$f(H) = -\frac{\hbar}{\delta}\cos^{-1}(H_s) \qquad g(\Gamma) = -\frac{2\hbar}{\delta}\sinh^{-1}\left(\frac{\Gamma_s}{2}\right) \tag{19}$$

where δ is the time step in mathematical time and we have introduced the normalized Hamiltonian H_s and width Γ_s. The former is defined below as that whose eigenvalues are within the interval $[-1, 1]$, which is the domain of arccos; the latter is taken to be in the domain of the $\sinh^{-1}$

$$\Gamma_s = \frac{\Gamma - \Gamma_{\mathrm{av}}}{\Delta\Gamma/2} = c_s\Gamma + d_s \tag{20}$$

where $\Delta\Gamma = \Gamma_{\mathrm{max}} - \Gamma_{\mathrm{min}}$, Γ_{max} and Γ_{min} are the maximum and minimum values of the width on the grid, respectively. Γ_{av} is the average value of Γ and the scaling quantities c_s and d_s are defined by the equation.

In the range of complex energies of interest the mapping is monotonic and therefore invertible. This is simple to see in the case of bound states but can usually be extended to continuum problems.

Taking the real part of equation (16) and the imaginary part of equation (17), we introduce the two real functions:

$$Q(\vec{R}, t) = \mathcal{RE}[\Psi], \qquad P(\vec{R}, t) = \mathcal{IM}[\Psi]. \tag{21}$$

In terms of these the recursion relations the wave packet become

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

$$P(u+\delta) = P(u-\delta) + 2\left(\frac{\Gamma_s}{2}\right)H_s P(u) + 2\sqrt{1 + \left(\frac{\Gamma_s}{2}\right)^2}\sqrt{1 - H_s{}^2}Q(u) \tag{23}$$

where $u = k\delta$ is the mathematical time and k is the number of iterations requested for propagating the wave packet.

As the initial wave packet is real for DEA and VE calculations, the first iteration is different from subsequent iterations and the initial conditions are given by

$$Q(\delta) = \exp\left(-\frac{\Gamma\delta}{2\hbar}\right)H_s Q(0) \tag{24}$$

$$P(\delta) = \exp\left(-\frac{\Gamma\delta}{2\hbar}\right)\sqrt{1 - H_s{}^2}Q(0). \tag{25}$$

The solution of the complete system as it is written in equations (22) and (23) is computationally slow (it scales as N^3) but the complete Hamiltonian, which has to be read 'on the fly', can usually be stored in the memory. (Mandelshtam and Taylor 1995a, 1995b) proposed a new computational approach based on the iterative solution of simultaneous linear equations through a modified Chebyshev polynomial expansion of the root operator acting on the wave packet. They introduced a scaled Hamiltonian

$$\hat{H}_s = \frac{\hat{H} - \hat{I}\left(\frac{\Delta E}{2} + V_{\mathrm{min}}\right)}{\Delta E/2} = a_s\hat{H} + b_s \tag{26}$$

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

$$E_{\mathrm{max}} = \hbar^2\pi^2/2m(\Delta x)^2 + V_{\mathrm{min}} \tag{27}$$

$$E_{\mathrm{min}} = V_{\mathrm{min}} \tag{28}$$

where V_{min} is the minimum value of the potential; this gives for the scaled eigenvalues

$$E_s = a_s E + b_s. \tag{29}$$

For dealing with a mapped decay, a transformation between the physical and mathematical time is necessary

$$t = \frac{\hbar a_s}{\sqrt{1.0 - E_s^2}}u. \tag{30}$$

This equation is obtained by linearizing and truncating the Taylor expansion of the first equation of the mapping system, equation (19), at first order (Balint-Kurti *et al* 1998).

To evaluate the effect of the square root of the Hamiltonian on the wave packet we use a Chebyshev series:

$$\sqrt{1 - x^2} = \frac{2}{\pi}\left[1 - 2\sum_{k=1}^{N}\frac{T_{2k}}{4k^2 - 1}\right] \tag{31}$$

where $T_{2k}(x)$ are the N Chebyshev polynomials of $2k$-order (Abramowitz and Stegun 1972), calculated by the recursion formula

$$T_{k+1}(z) = 2zT_k(z) - T_{k-1}(z) \tag{32}$$

$$T_0(z) = 1 \tag{33}$$

$$T_1(z) = z. \tag{34}$$

3.3. Computational procedures

To minimize the computational time we need an efficient scheme of propagation which exploits the optimal 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. We chose three different propagation schemes: fast Fourier transform (FFT) to treat the kinetic term, discrete variable representation (DVR) for the angular part and finite basis representation (FBR) for the radial part of the potential. 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 scales as N^2, where N is the number of points in the grid. The Fourier algorithm is an efficient technique which transforms a periodic sequence from the physical to spectral space defined as follows:

$$\psi(k_j) = \sqrt{\frac{L}{N}} \left[\sqrt{\frac{2}{N}} \sum_i \psi(x_i) \sin \frac{ij\pi}{N} \right] = FFT[\psi(x)]. \tag{35}$$

When applying this technique one pays the computational cost of dealing with non-local operators, but it is possible to employ a less dense grid for a given accuracy. The angular part of the kinetic energy is treated using Legendre polynomials $P_j^K(x)$ ($x = \cos\gamma$) (Abramowitz and Stegun 1972). In treating the potential term we retain the radial FBR basis set, but for the angular part we use a DVR method.

It should be clear that, in the case of DEA, we are trying to represent the wave packet which is physically unbound on a finite grid and to calculate continuum quantities through a discrete approximation. This could result in reflection of the wave packet back at the boundary of the numerical grid, causing interference which destroys the real dynamics (Manolopoulos 2002). Instead of enlarging the grid we solved the problem by employing a complex absorbing potential (Migdley and Wang 2000, Muga *et al* 2004). As a consequence of using a formalism that is easy to implement we pay the price of having a non-Hermitian Hamiltonian operator and of losing some parts of the wave packet.

The complex absorbing potential causes the wave packet to be shaped by a Gaussian function (Gray 1992):

$$A(x) = \begin{cases} 1 & z \leqslant z_{\mathrm{abs}} \\ \exp[-A_{\mathrm{abs}}(z - z_{\mathrm{abs}})^2] & z > z_{\mathrm{abs}} \end{cases} \tag{36}$$

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 the absorbing potential adiabatically, which does not greatly alter the wave packet shape in one single time step and gives stability to the numerical procedure. To estimate vibrational excitation we avoided the absorption in order to retain the entire wavefunction after reaching the boundaries. We therefore perform an additional calculation which propagates using $\Gamma = 0$ which means the wave packet lives indefinitely on the resonance surface. The difference between the two calculated amplitudes is the total amount of wave packet which decays by autoionization of the resonance into the ground electronic state. As an example we consider below the case of water excited to its stretching and bending vibrational fundamental states after an electron collision.

3.4. Observables

After propagating the wave packet one can extract the physical observables, such as the cross sections for DEA, VE, etc, using two approaches: asymptotic analysis and flux analysis. The starting point of the analysis in both methods is the value of the wave packet at a grid point ($R = R_\infty$) where dissociation has occurred. In a typical triatomic calculation, this means that the final diatom–atom products are formed. Results are comparable for each method; differences are simply due to the final quantities one wants to achieve: the scattering matrix in the first case, the T-matrix in the second one. We have chosen asymptotic analysis which gives the scattering states directly without any need for transformation as the point where the analysis is conducted is chosen to lie 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 analysis thus starts from the asymptotic value $\Psi(R_\infty, r, \gamma, u)$. Projection of such a wave packet onto the final states of the diatom $\phi_{j\nu}(r)$ gives a set of time-dependent coefficients $A_{j\nu}(u)$

$$A_{j\nu}(u) = \int_0^\infty \mathrm{d}r\, \phi_{j\nu}(r) \int \mathrm{d}\gamma\, P_j^0(\gamma)\psi(R_\infty, r, \gamma, u) \tag{37}$$

where j and ν are the quantum numbers of the final rovibrational state of the diatom. Returning 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, we find

$$\begin{aligned}\Psi^{JM}(R, r, \gamma, \alpha, \beta, \zeta) &= \sum_{K=-J}^{J} \tilde{D}^J_{MK}(\alpha, \beta, \zeta) \frac{\Xi^{JM}_K(R, r, \gamma)}{Rr} \\ &\widetilde{R \to \infty} \sum_{j\nu} C_{j\nu}(E) \tilde{D}^J_{MK}(\alpha, \beta, \zeta) \frac{\mathrm{e}^{\mathrm{i}kR - ij\pi/2}}{Rr} \phi_\nu\end{aligned} \tag{38}$$

where ϕ_ν are the vibrational wavefunctions of the diatom product, E is the total energy. $C_{j\nu}(E)$ are the partial wave amplitudes for the dissociative process. After projecting the asymptotic wavefunction onto ϕ_ν the coefficients $C_{j\nu}(E)$, $F_{j\nu}(E)$ are the Fourier transform coefficients from u of the real and imaginary parts of the $A_{j\nu}(u)$ previously defined in equation (37). Mathematically:

$$C_{j\nu}(f(E)) = \frac{1}{2\pi} \int_0^\infty \mathrm{d}u\, \exp(\mathrm{i}f(E)/\hbar)\, \mathrm{Re}[A_{j\nu}(u)] \tag{39}$$

$$F_{j\nu}(g(E)) = \frac{1}{2\pi} \int_0^\infty \mathrm{d}u\, \exp(\mathrm{i}g(E)/\hbar)\, \mathrm{Im}[A_{j\nu}(u)]. \tag{40}$$

The dissociative cross section resolved by quantum numbers of the final fragments can now be obtained from the asymptotic form of the solution of the time-dependent Schrödinger equation (Gertitschke and Domcke 1993) as

$$\begin{aligned}\sigma^{j\nu}(E) &= \left(\left|\frac{\mathrm{d}f(E)}{\mathrm{d}E}\right|^2\right)\sigma^{j\nu}(f(E)) + \left(\left|\frac{\mathrm{d}g(E)}{\mathrm{d}E}\right|^2\right)\sigma^{j\nu}(g(E)) \\ &= \frac{2\pi^2}{E}\frac{\kappa}{\mu_R}\left(\frac{\hbar^2 a_s^2}{\delta\left(1 - E_s^2\right)}\left|C_{j\nu}\left(f\left(E_{\nu_i} + k^2/2\right)\right)\right|^2 + \frac{\hbar^2 c_s^2}{\delta\left(1 - \Gamma_s^2\right)}\left|F_{j\nu}\left(g\left(E_{\nu_i} + k^2/2\right)\right)\right|^2\right)\end{aligned} \tag{41}$$

where κ is the relative nuclear momentum of the fragments and μ_R the reduced mass of the fragments.

That part of the vibrationally inelastic excitation which proceeds via the resonant process differs from the treatment of DEA only in the way the cross sections are obtained. The asymptotic states of water in the adiabatic approximation are in this case the electronic ground state and the vibrationally excited states; it is onto these states we have to consider the projection of the evolved wave packet. In a similar fashion to equations (37) and (39), we define the quantities:

$$A_\nu(u) = \int_0^\infty \mathrm{d}R\, \mathrm{d}r \int_{-1}^{1} \mathrm{d}\gamma\, \phi_\nu(R, r, \gamma) P_j^0(\gamma)\psi(R, r, \gamma, u) \tag{42}$$

where, this time, $\phi_\nu(R, r, \gamma)$ are the final vibrationally excited states of water, and

$$C_\nu(f(E)) = \frac{1}{2\pi}\int_0^\infty \mathrm{d}u \exp(\mathrm{i}f(E)/\hbar)\,\mathrm{Re}[A_\nu(u)] \tag{43}$$

$$F_\nu(g(E)) = \frac{1}{2\pi}\int_0^\infty \mathrm{d}u \exp(\mathrm{i}g(E)/\hbar)\,\mathrm{Im}[A_\nu(u)]. \tag{44}$$

Following Domcke and Cederbaum (1977) and Narevicius and Moiseyev (1998), one can obtain for the cross section the expression:

$$\sigma^\nu(E) \propto \frac{|E - E_\nu|^{1/2}}{|E|}(|C_\nu(f(E_\nu + k^2/2))|^2 + |F_\nu(g(E_\nu + k^2/2))|^2). \tag{45}$$

We derive an expression for the normalized cross section within the framework of the local complex potential approximation which describes an impinging electron with energy $E = E_{\mathrm{trans}}$ which leaves the molecule in the vibrationally excited state ν and departs with energy $E_{\mathrm{trans}} - E_\nu$:

$$\begin{aligned}\sigma^\nu(E) &= \left(\left|\frac{\mathrm{d}f(E)}{\mathrm{d}E}\right|^2\right)\sigma^\nu(f(E)) + \left(\left|\frac{\mathrm{d}g(E)}{\mathrm{d}E}\right|^2\right)\sigma^\nu(g(E))\\ &= \frac{2\pi^3}{E}\left(\frac{\hbar^2 a_s^2}{\delta\big(1-E_s^2\big)}|C_\nu(f(E_\nu + k^2/2))|^2 + \frac{\hbar^2 c_s^2}{\delta\big(1-\Gamma_s^2\big)}|F_\nu(g(E_\nu + k^2/2))|^2\right)\end{aligned} \tag{46}$$

which gives the resonant contribution to the absolute vibrational excitation cross section.

4. Test calculations

To demonstrate our method we applied the theory to the study of both electron dissociative attachment (DEA) and vibrational excitation (VE) of water. The $\mathrm{X}\,^2\mathrm{B}_1$ resonance state of the water anion is known to be dissociative (Haxton *et al* 2004a) for a kinetic energy of the impinging electron equal to 6.4 eV. There are two higher resonances at 8.4 eV and 11.2 eV which are also believed to be important for the dissociative electron attachment of water. The processes under consideration are then

$$\mathrm{e}^- + \mathrm{H_2O}(v_i) \longrightarrow \mathrm{H_2O}^{*-} \longrightarrow \mathrm{HO}(v, j) + \mathrm{H}^- \tag{47}$$

$$\mathrm{e}^- + \mathrm{H_2O}(v_i) \longrightarrow \mathrm{H_2O}^{*-} \longrightarrow \mathrm{H_2O}(v_f) + \mathrm{e}'^- \tag{48}$$

for the DEA and VE, respectively. In both cases we take the initial vibrational state, v_i, to be the vibrational ground state. In the case of DEA $\mathrm{HO} + \mathrm{H}^-$ are thought to be the most likely direct products although energetically less favourable (Melton 1972).

Both calculations used the centrifugal sudden approximation, which means putting $J = 0$ in the Hamiltonian. The total size of the grid chosen is $(106 \times 198 \times 39)$ in r, R, γ, respectively, running in the range 0.6 to 6.9 for r and in the interval 0.1 to 11.98 for R; the angular grid is made of 39 Gauss–Legendre quadrature points. Initial excitation $V_{d\mathbf{k_i}}$ was taken as the square root of Γ, the probability of excitation into the $\mathrm{X}\,^2\mathrm{B}_1$ resonance state, at the equilibrium geometry of water. The resonance width value we used is 0.004 eV. The DVR3D program (Tennyson *et al* 2004) was used to calculate wavefunctions for initial, v_i, and final, v_f, states of water involved in the analysis. A separate program was written for projecting onto the different vibrational states of OH.

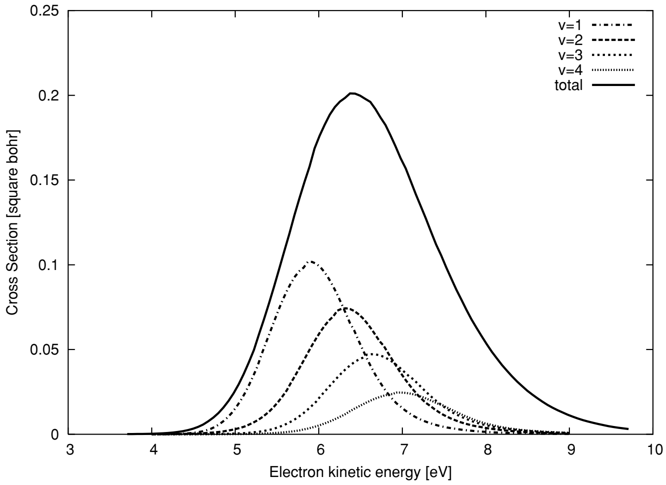

Figure 2. DEA cross section for H_2O with increasing OH vibrational quantum number v, from left to right. The top curve is the total cross section calculated as the sum of the underlying vibrational spectra.

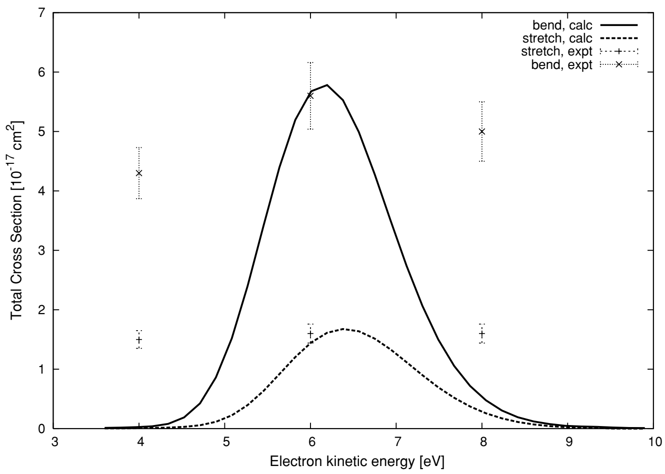

Figure 3. Resonant vibrational excitation cross sections for electron collisions with H_2O in its (0, 0, 0) vibrational ground state. Experimental points (cross and square) by Shyn *et al* (1988).

Our test calculations use the complex potential energy surfaces of Haxton *et al* (2004b) in Jacobi products coordinates ($OH + H^-$). In the DEA process the time grid used consists of 852 points separated uniformly in time by 0.024 582 32 fs; at the end we obtain a dissociation time of about 21 fs. To obtain the VE cross section we used a grid of 736 time steps separated by the same evenly spaced amount without any absorption. We performed calculations using two different values of Γ, one with the actual Γ as for the DEA calculation, and the other with $\Gamma = 0$. We consider the case of water excited to its stretching, (0, 0, 1) and (1, 0, 0), and bending, (0, 1, 0), excited vibrational states since these are the cases for which experimental data are available.

Sample results for the DEA and VE cross sections are given in figures 2 and 3, respectively. They were obtained using about 136 min of CPU time on a Intel Pentium M processor 1.5 GHz with 1 GB of available memory. The DEA results given in figure 2 can be compared directly with those given by Haxton *et al* (2004b) from which they are nearly indistinguishable. These results are in agreement with the experimental results for the total cross section obtained by Melton (1972), Compton and Christophorou (1967) and Trajmar and Hall (1974) which peak at about 7×10^{-18} cm^2, and show similar behaviour for the partial cross sections for excitation of the increasing vibrational states of OH (Belic *et al* 1981). See Haxton *et al* (2004b) for a thorough analysis of this process.

Our method of studying VE is only appropriate at energies where VE is predominantly via a resonance. There is a broad resonance contribution to the VE cross section around 6 eV (Jain and Thompson 1983, Seng and Linder 1976). Experiments by Shyn *et al* (1988) and Seng and Linder (1976) have studied excitation of the bending and the two stretching fundamental vibrations of water. The two stretching states are not resolved at the energy resolution of the experiment. Figure 3 presents our results for these excitations in the 6 eV region. Our calculations give a ratio of about 3.5 at 6 eV for the two VE processes considered, in good agreement with the measurements of Shyn *et al* (1988). The other energies considered by Shyn *et al* (1988) lie outside the main resonance region.

5. Conclusions

We present a general method and its implementation for calculating the nuclear motion wavefunctions on a complex potential energy surface. This method is particularly appropriate for the calculation of dissociative electron attachment and resonant electron impact vibrational excitation cross sections. It allows, within the Born–Oppenheimer approximation, a full dimensional treatment of vibrational and dissociative problems. The dynamics of the collision are studied by using the evolution of wave packets in the time domain. A sample application of the method to dissociative electron attachment and vibrational excitation of water is presented. The code used in this work has been made generally available (Taioli and Tennyson 2006).

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