Time-dependent and time-independent wavepacket approaches to reactive scattering and photodissociation dynamics

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Time-dependent and time-independent wavepacket approaches to reactive scattering and photodissociation dynamics

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Quantum mechanical wavepacket treatments of reactive scattering and photo-dissociation dynamics are reviewed and discussed. Initially these treatments arose within a time-dependent framework, but as the cross sections of interest depend on energy rather than on time, it was realised that by Fourier transforming the basic equations over time an equivalent time-independent wavepacket methodology could be formulated. Other methods, namely the real wavepacket method and the polynomial propagation method were also developed. The review discusses all these methods and their relationship to each other. In the case of photodissociation, the real wavepacket method is clearly formulated for the first time.

Keywords: quantum dynamics; molecular reactive scattering; photodissociation; wavepackets

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1. Introduction

The first time-dependent wavepacket treatment of reactive scattering was published by Mazur and Rubin [1] in 1959 and was followed by several further investigations [2–9]. An important breakthrough in this approach to the calculation of reactive scattering probabilities and cross-sections came in 1982 with the work of Feit and coworkers [10,11] and of Kosloff and Kosloff [12] who introduced the Fourier transform method for evaluating the action of the time evolution operator on the wavepacket. Another crucial development followed in 1984 with the introduction by Kosloff *et al.* [13–15] of a very stable and numerically accurate Chebyshev polynomial expansion technique for evaluating the action of the time evolution operator on a wavepacket and the subsequent application of these methods to the reactive scattering problem by Neuhauser, Baer and co-workers [16–18]. This approach subsequently led to a huge advance in both time-dependent [19–50] and time-independent [51–57] theoretical molecular dynamics. In this review I will concentrate exclusively on the Chebyshev polynomial expansion approach to the evaluation of the time evolution operator and on its relationship to time-independent wavepacket methods. The split-operator method of Feit and Fleck [10,11] also continues to be widely used in time-dependent wavepacket calculations, but will not be further discussed.

The wavepacket approach to photodissociation and to Raman spectra was introduced in a series of ground breaking papers by Heller [58–61]. While some exact, two mathematical dimensional calculations were carried out in these early works [62], including the evaluation of product quantum state distributions, the main emphasis was on semi-classical methods of solving photodissociation dynamics. The use of the Chebyshev expansion of the time evolution operator [12–15] again had a great impact on the field

of photodissociation theory and has resulted in many time-dependent [63–77] and time-independent applications [78].

This review will outline the application of Chebyshev expansion methodology to quantum wavepacket dynamics both in the time-dependent and time-independent domains. The main applications we will have in mind are those of reactive scattering theory and the theory of photodissociation processes, though there are also many valuable applications to the calculation of bound states. [54,79–81].

In the case of both reactive scattering and of photodissociation the quantities of interest, such as the reactive cross-section or the absorption cross-section, are functions of the energy, and not of time. Time is therefore seen to play an ancillary role. The initial quantities calculated are functions of time, but these functions are not of interest in their own right. Their Fourier transforms over time yield the cross-sections, which are functions of energy and are the principal quantities of interest. This realization leads to two important conclusions: (1) It is clearly possible to perform the Fourier transform of the relevant expressions, i.e. the expansion of the time evolution operator, before operating on the wavepacket and thus obtain time-independent expressions for the cross-sections directly [82–85]. (2) As time is just an ancillary variable, which is eventually integrated away when the Fourier transform is performed, it should be possible to substitute a different variable, e.g. the recursion number in the Chebyshev recursion formula, for time [86,87]. It turns out that both these approaches lead to essentially the same results. It has also subsequently been shown that the same equations arise from a cosine mapping of the Hamiltonian operator [86] coupled with a three term recursion relationship permitting the forward evolution of the wavepacket one time step at a time [25]. This approach provided the insights which have led to the formulation of the real wavepacket approach [53,86], that permits the calculation of all cross-sections of interest from the propagation and analysis of only the real part of the wavepacket.

The computationally intensive part of a quantum dynamical wavepacket calculation is always the repeated action of the Hamiltonian on the wavepacket. The details of this aspect of the computation is not covered in this review. The reader is rather referred to other reviews by the present author [88–90].

2. The time-dependent Schrödinger equation and its solution

2.1. *The Schrödinger equation and its iterative equation equivalent*

The time-dependent Schrödinger equation is:

$$i\hbar \frac{\partial \Phi(t)}{\partial t} = \hat{\mathbf{H}} \Phi(t). \tag{1}$$

If the Hamiltonian, $\hat{\mathbf{H}}$, does not depend on time, this equation has the analytic solution:

$$\Phi(t) = \exp\left[\frac{-i\hat{\mathbf{H}}t}{\hbar}\right] \Phi(t = 0) = \hat{\mathbf{U}}(0, t)\Phi(t = 0). \tag{2}$$

The operator $\hat{U}(0, \tau) = \exp[(-i\hat{H}\tau/\hbar)]$ is the time evolution operator and propagates the wavepacket forward in time from $t = 0$ to $t = \tau$. Expanding the propagator in terms of cosines and sines, we may write:

$$\Phi(t + \tau) = \exp\left[\frac{-i\hat{H}\tau}{\hbar}\right]\Phi(t)$$

$$= \cos\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t) - i\sin\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t). \tag{3}$$

The corresponding expression for the backward propagation, from t to $t - \tau$ is:

$$\Phi(t - \tau) = \cos\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t) + i\sin\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t). \tag{4}$$

By adding Equations (3) and (4) we obtain [25]:

$$\Phi(t + \tau) = 2\cos\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t) - \Phi(t - \tau). \tag{5}$$

This equation is exact and constitutes an iterative equation equivalent to the time-dependent Schrödinger equation [25,91,92]. The iterative process itself does not involve the imaginary number i and therefore, if $\Phi(t)$ and $\Phi(t - \tau)$ were the real parts of the wavepacket then $\Phi(t + \tau)$ would also be real and would be the real part of the exact wavepacket at time $(t + \tau)$. Thus the real part of a complex wavepacket can be propagated forward in time without reference to the imaginary part. This is the basis of the real wavepacket method.

2.2. The Chebyshev expansion of the time evolution operator

Kosloff [12–15] introduced a very stable 'Chebyshev' series expansion of the exponential time evolution operator, Equation (2). The series has the form (see Appendix A for a detailed derivation):

$$\exp\left(\frac{-i\hat{H}t}{\hbar}\right) = \exp\left(\frac{-i((\Delta E/2) + V_{\min})t}{\hbar}\right)\sum_{n=0}^{N}(2 - \delta_{no})J_n\left(\frac{\Delta E\,t}{2\hbar}\right)Q_n(-i\hat{H}_s). \tag{6}$$

Q_n are Chebyshev polynomials of complex argument. They obey the recursion formula:

$$Q_{n+1} = -2i\hat{H}_s Q_n + Q_{n-1} \tag{7}$$

where $\hat{H}_s$ is a 'normalized' Hamiltonian. It is normalized in such a way as to limit its 'spectrum' to lie between -1 and $+1$. The spectrum of the Hamiltonian is the range of possible eigenvalues it can have. This normalization is performed by finding the range of

the Hamiltonian operator:

$$\Delta E = E_{\max} - E_{\min} \tag{8}$$

and subsequently defining the scaled and shifted Hamiltonian $\hat{\mathbf{H}}_s$ in the manner:

$$\hat{\mathbf{H}}_s = \frac{\hat{\mathbf{H}} - \hat{\mathbf{I}}((\Delta E/2) + V_{\min})}{(\Delta E/2)} \tag{9}$$

where we have replaced $E_{\min}$ by $V_{\min}$. As $V_{\min} \leq E_{\min}$ this is always permissible and just leads to a slight overestimate of the range of the Hamiltonian operator.

The first few Chebyshev polynomials are;

$$Q_0(-ix) = 1; \quad Q_1(-ix) = -ix; \quad Q_2(-ix) = -2x^2 + 1. \tag{10}$$

The J_n (in Equation (6)) are Bessel functions. These play a very important role in the convergence of the expansion. For n values greater than the argument, $(\Delta E t/2\hbar)$, these Bessel functions decrease exponentially in value. We can therefore predict that the number of terms needed in the expansion is approximately:

$$N \approx \frac{\Delta E t}{2\hbar}. \tag{11}$$

This is in fact an important conclusion. The number of terms required to expand the time evolution operator is proportional to the range of the Hamiltonian operator. Or equivalently this is the number of operations of the Hamiltonian operator which must be performed in order to propagate the wavepacket forward by t.

We can now define the wavefunction iterates Φ_n as:

$$\Phi_n = Q_n(-i\hat{\mathbf{H}}_s)\Phi(t=0). \tag{12}$$

Successive iterates are now generated using the recursion relationship:

$$\Phi_{n+1} = -2i\hat{\mathbf{H}}_s\Phi_n + \Phi_{n-1}. \tag{13}$$

The wavepacket at time t is then given by:

$$\Phi(t) = \exp\left(\frac{-i((\Delta E/2) + V_{\min})t}{\hbar}\right) \sum_{n=0}^{N} (2 - \delta_{no}) J_n\left(\frac{\Delta E t}{2\hbar}\right) Q_n(-i\hat{\mathbf{H}}_s)\Phi(t=0)$$

$$= \exp\left(\frac{-i((\Delta E/2) + V_{\min})t}{\hbar}\right) \sum_{n=0}^{N} (2 - \delta_{no}) J_n\left(\frac{\Delta E t}{2\hbar}\right) \Phi_n. \tag{14}$$

Clearly the summation in Equation (14) must be taken to sufficiently large values of n to ensure convergence.

Note that the form of the three term recursion formulae in Equations (5) and (13) are almost identical in form. This is an important factor in the relationship between the time-dependent Chebyshev expansion method, the time-independent wavepacket approach and the real wavepacket approach.

3. Reactive scattering

3.1. Time-dependent treatment

Only a brief summary is given here of the steps needed to calculate the reactive scattering cross-sections. The reader is referred to [47,89] for a more detailed discussion. In the treatments discussed in this review different Jacobi coordinates will be used for reactant and product arrangements. Considering a reaction of the type $A + BC \rightarrow AB + C$, reactant coordinates will be denoted by R for the scattering coordinate and by $\mathbf{r}$ for the other coordinates (i.e. for the vibrational and angular Jacobi coordinates). The analogous coordinates in the product arrangement channel will be denoted by R' and $\mathbf{r}'$.

The initial wavepacket is defined to be of the form:

$$\Phi_K^J(R, \mathbf{r}, t = 0) = \exp[-ikR]f(R)\phi_{i,K}(\mathbf{r}) = g(R)\phi_{i,K}(\mathbf{r}) \tag{15}$$

where the exponential $\exp[-ikR]$ provides some inward momentum directing the wavepacket towards the reaction region; $f(R)$ is either a Gaussian [29] or a sinc type function [93]; $\phi_{i,K}(\mathbf{r})$ is the vibrational-rotational eigenfunction of the initial molecular fragment; K is the quantum number for the body-fixed z-component of the rotational angular momentum and $g(R)$ is defined as $\exp[-ikR]f(R)$.

In order to determine the reactive cross-sections the amplitude of the initial wavepacket with a specified initial translational momentum must be known. This is obtained from the Fourier transform of the initial wavepacket:

$$g(-k) = \frac{1}{2\pi} \int_0^\infty e^{ikR} g(R)\mathrm{d}R. \tag{16}$$

An analysis line is drawn corresponding to a fixed value of the product Jacobi scattering coordinate $R' = R'_\infty$ across the exit channel in the the asymptotic region of the potential energy surface [29,94]. A cut is now taken through the wavepacket, $\Phi_K^J(R', \mathbf{r}', t)$, along the analysis line and this cut through the wavepacket is projected onto the product vibrational-rotational eigenfunctions, $\chi_{v'j'K'}(\mathbf{r}')$. This yields a time-dependent coefficient, $C_{v'j'}^{JK'}(t)$:

$$C_{v'j'}^{JK'}(t) = \langle \chi_{v'j'K'}(\mathbf{r}')|\Phi_K^{JK'}(R' = R'_\infty, \mathbf{r}', t)\rangle. \tag{17}$$

The angular brackets indicate integration over the product internal coordinates $\mathbf{r}'$ and the superscripts K' indicate the component of total angular momentum about the body-fixed z-axis which is taken to be the product scattering coordinate. The angular momentum aspects of the calculation are not discussed in the present review. The reader can find a discussion of these aspects in [47,89].

A half-Fourier transform of this time-dependent coefficient is then taken to yield an energy dependent quantity, $A_{v'j'}^{JK'}(E)$:

$$A_{v'j'}^{JK'}(E) = \frac{1}{2\pi} \int_0^\infty \exp(iEt/\hbar) C_{v'j'}^{JK'}(t)\mathrm{d}t. \tag{18}$$

The analysis of [94] (see also [86,89]) enables us to relate this to the reactive $\mathbf{S}$ matrix elements through the expression:

$$S_{j'K', jK}^J(E) = -\left(\frac{\hbar^2 k_j k_{j'}'}{\mu\mu'}\right)^{(1/2)} \exp(-ik_{j'}'R'_\infty) \frac{A_{v'j'}^{JK'}(E)}{g(-k_j)}. \tag{19}$$

For non-zero total angular momentum some phase corrections are required to the above expression for the body-fixed **S** matrix elements. These arise from the fact that the analysis line cannot, in general, be located at a sufficiently large R' value for the centrifugal repulsion to be zero at the analysis line. They are discussed in detail in [47]. The **S** matrix elements calculated in this way then yield the desired cross-sections through the use of standard formulae [47].

Once we have computed the **S** matrix elements we may calculate all the cross-sections and reaction probabilities from them [47,89,90,95].

3.2. *Time-independent wavepacket treatment*

The time-independent wavepacket treatment of reactive scattering was first introduced by Kouri [82–84,96–100] and very soon afterwards placed on a sounder footing through the work of Mandelshtam and Taylor [51,85].

Let us start the derivation of these equations by substituting Equation (18) into (19):

$$S_{j'K',jK}^{J}(E) = -\left(\frac{\hbar^2 k_j k_{j'}'}{\mu\mu'}\right)^{1/2} \exp(-ik_{j'}'R_\infty')\frac{1}{2\pi}\int_0^\infty \exp(iEt/\hbar)C_{v'j'}^{JK'}(t)\mathrm{d}t\frac{1}{g(-k_j)}. \quad (20)$$

Now using Equation (17) to substitute for $C_{v'j'}^{JK'}(t)$ we obtain:

$$S_{j'K',jK}^{J}(E)$$

$$= -\left(\frac{\hbar^2 k_j k_{j'}'}{\mu\mu'}\right)^{1/2}\frac{1}{2\pi\, g(-k_j)}\exp(-ik_{j'}'R_\infty')\int_0^\infty \exp(iEt/\hbar)\langle\chi_{v'j'K'}(\mathbf{r}')|\Phi_K^{JK'}(R'=R_\infty',\mathbf{r}',t)\rangle\mathrm{d}t$$

$$= -\left(\frac{\hbar^2 k_j k_{j'}'}{\mu\mu'}\right)^{1/2}\frac{1}{2\pi\, g(-k_j)}\exp(-ik_{j'}'R_\infty')$$

$$\times \int_0^\infty \mathrm{d}t\, \exp(iEt/\hbar)\int_0^\infty \mathrm{d}R'\,\delta(R'-R_\infty')\,\langle\chi_{v'j'K'}(\mathbf{r}')|\Phi_K^{JK'}(R',\mathbf{r}',t)\rangle. \quad (21)$$

We can now substitute for the time-dependent wavepacket using the Chebyshev expansion (see Equation (14)).

$$S_{j'K',jK}^{J}(E)$$

$$= -\left(\frac{\hbar^2 k_j k_{j'}'}{\mu\mu'}\right)^{1/2}\frac{1}{2\pi\, g(-k_j)}\exp(-ik_{j'}'R_\infty')\int_0^\infty \mathrm{d}t\,\exp(iEt/\hbar)\int_0^\infty \mathrm{d}R'\delta(R'-R_\infty')$$

$$\times \left\langle\chi_{v'j'K'}(\mathbf{r}')\left|\exp\left(\frac{-i((\Delta E/2)+V_{\min})t}{\hbar}\right)\sum_{n=0}^N(2-\delta_{no})J_n\left(\frac{\Delta E\,t}{2\hbar}\right)\Phi_n\right.\right\rangle$$

$$= -\left(\frac{\hbar^2 k_j k_{j'}'}{\mu\mu'}\right)^{1/2}\frac{\exp(-ik_{j'}'R_\infty')}{g(-k_j)}\sum_{n=0}^N(2-\delta_{no})$$

$$\times \left\{\frac{1}{2\pi}\int_0^\infty \mathrm{d}t\,\exp(iEt/\hbar)\exp\left(\frac{-i((\Delta E/2)+V_{\min})t}{\hbar}\right)J_n\left(\frac{\Delta E\,t}{2\hbar}\right)\right\}$$

$$\times \langle\chi_{v'j'K'}(\mathbf{r}')|\Phi_n(R'=R_\infty')\rangle \quad (22)$$

where the nth wavefunction iterate Φ_n is defined as in Equation (12) to be the wavepacket arising from operating on the initial wavepacket with the Chebyshev polynomial of order n:

$$\Phi_n = Q_n(-i\hat{\mathbf{H}}_s)\Phi_K^J(R', \mathbf{r}', t = 0) \tag{23}$$

and the notation $\Phi_n(R' = R'_\infty)$ indicates that a cut is taken through this wavepacket at a fixed value of the product scattering coordinate $R' = R'_\infty$.

The integral in curly brackets in Equation (22) is the half Fourier transform of the Bessel function coefficients in the Chebyshev expansion of the time evolution operator (see Equation (6)). After we have performed this integration, time will no longer appear anywhere in the formulation and the methodology will then have been transformed into one involving time-independent wavepackets. The integral in Equation (22) is cast into a simpler form in Appendix B. Substituting into Equation (22) from Equation (109) of Appendix B we obtain:

$$S_{j'K', jK}^J(E) = -\left(\frac{k_j k_{j'}'}{\mu\mu'}\right)^{1/2} \frac{\exp(-ik_{j'}' R'_\infty)}{g(-k_j)} \frac{\hbar^2}{\pi\Delta E}$$
$$\times \sum_{n=0}^N (2 - \delta_{no}) \frac{\exp[-in\phi]}{\sin\phi} i^n \langle \chi_{v'j'K'}(\mathbf{r}')|\Phi_n(R' = R'_\infty)\rangle \tag{24}$$

where:

$$\alpha = \left(\frac{1}{2}\Delta E + V_{\min}\right), \quad \beta = \left\{\frac{\Delta E}{2}\right\} \tag{25}$$

and

$$\cos\phi = \frac{E - \alpha}{\beta}. \tag{26}$$

If we incorporate an extra 'i' into the definition of the wavepacket iterates, i.e.

$$\eta_n = i^n \Phi_n. \tag{27}$$

We can rewrite the expression for the **S** matrix element as:

$$S_{j'K', jK}^J(E) = -\left(\frac{k_j k_{j'}'}{\mu\mu'}\right)^{1/2} \frac{\exp(-ik_{j'}' R'_\infty)}{g(-k_j)} \frac{\hbar^2}{\pi\Delta E} \sum_{n=0}^N (2 - \delta_{no}) \frac{\exp[-in\phi]}{\sin\phi} \langle \chi_{v'j'K'}(\mathbf{r}')|\eta_n(R' = R'_\infty)\rangle \tag{28}$$

where

$$\begin{aligned}
\eta_0 &= \Phi(t = 0) \\
\eta_1 &= iQ_1(-i\hat{\mathbf{H}}_s)\Phi(t = 0) = \hat{\mathbf{H}}_s\Phi(t = 0) \\
\eta_2 &= 2\hat{\mathbf{H}}_s\eta_1 - \eta_0 \\
\eta_{n+1} &= 2\hat{\mathbf{H}}_s\eta_n - \eta_{n-1}
\end{aligned} \tag{29}$$

and as before the notation $\eta_n(R' - R'_\infty)$ indicates that a cut is taken through the wavepacket iterate η at a fixed value of the product scattering coordinate $R' = R'_\infty$.

Equation (28) provides a time-independent wavepacket method for calculating the all important **S** matrix elements. The squares of these elements then provide us with the integral and differential cross-sections we can compare with experimental measurements. In order to transform the time-dependent method to a time-independent one we have formally performed the Fourier transform of the basic time-dependent expressions for the **S** matrix elements. In this way we have eliminated time from the formalism and have transformed it from a time-dependent to a time-independent method. The expression in Equation (28) is very similar to the one derived in [101,102] directly from the use of time-independent wavepackets. It differs from these by a minus sign and through the presence of a factor of $(1/\mu\mu')^{1/2}$ instead of a factor of $(1/\mu)$, where μ and μ' are the reduced masses associated with the reactant and product scattering coordinates respectively. The minus sign in Equation 28 will only effect elastic cross-sections, where the **S** matrix determines the relative sign of the incoming and outgoing radial waves (see Equation (4.64) of [103], Equation (21) of [104] or [95]).

3.3. *Damped iterations and the time-independent wavepacket method*

In the time-dependent wavepacket approach a negative imaginary potential is normally added to the Hamiltonian to prevent the wavepacket from reaching the edge of the coordinate grid [15,105–116]. The nature of this artificially added potential destroys the Hermitian property of the Hamiltonian operator. This problem has been elegantly analysed by Mandelshtam and Taylor [85] who have shown that instead of a negative imaginary absorbing potential a modified form of the Chebyshev recursion relationship should be used, in the case of the time-independent wavepacket formalism. This modified relationship replaces Equation (29) and is given by:

$$
\begin{aligned}
\eta_0 &= \Phi(t = 0) \\
\eta_1 &= \hat{\mathbf{A}}\hat{\mathbf{H}}_s\Phi(t = 0) \\
\eta_{n+1} &= \hat{\mathbf{A}}\left\{2\hat{\mathbf{H}}_s\eta_n - \hat{\mathbf{A}}\eta_{n-1}\right\}
\end{aligned}
\tag{30}
$$

where $\hat{\mathbf{A}}$ is a damping operator and may have the form $\exp[-V_{abs}(r)]$, such that $V_{abs}(r)$ is non-zero only in an absorbing region close to the edge of the grid and is in general similar in form to the negative imaginary part of the more widely used negative imaginary absorbing potentials [105,106]. A very similar damping procedure was introduced by Gray in relation to the iterative equation approach to wavepacket dynamics [25].

3.4. *The real wavepacket method*

The formulation of the real wavepacket method [86] starts from consideration of Equation (5), the iterative equation equivalent to the time-dependent Schrödinger equation [91,92]. In Appendix A of [86] it was shown that if only the real part of a wavepacket was analysed to obtain time-dependent coefficients such as occur in Equations (17) and (18), then the same formula as before (i.e. Equation (19)) is still valid for the **S** matrix elements, but that it should now be multiplied by 2 to account for the missing imaginary part of the wavepacket.

This is however not the full story. The method which has now become known as the real wavepacket method contains a further aspect which contributes greatly to its efficiency. A major obstacle to to using the iterative procedure of Equation (5) is the fact that it involves the evaluation of the cosine of $\hat{\mathbf{H}}_s$ acting on a wavepacket. This is a difficult operation to perform and would involve computational effort equivalent to that needed in the evaluation of the Chebyshev series of Equation (14). The real wavepacket method overcomes this problem by using a mapping of the Hamiltonian operator.

$$f(\hat{\mathbf{H}}_s) = -\frac{\hbar}{\tau}\cos^{-1}(\hat{\mathbf{H}}_s). \tag{31}$$

The use of this mapping means that we are no longer solving the time-dependent Schrödinger equation, but rather a modified equation of the form:

$$i\hbar\frac{\partial\Phi_f(t)}{\partial t} = f(\hat{\mathbf{H}}_s)\Phi_f(t), \tag{32}$$

where a subscript 'f' has been placed on the wavefunction to emphasize that it is the solution of a mapped equation rather than of the original time-dependent Schrödinger equation. The same arguments which led to the iterative equation equivalent to the time-dependent Schrödinger equation Equation (5), now lead to the simplified form:

$$\Phi_f^R(t+\tau) = 2\hat{\mathbf{H}}_s\Phi_f^R(t) - \Phi_f^R(t-\tau) \tag{33}$$

where the superscript R in $\Phi_f^R(t)$ indicates that only the real part of the wavepacket is used.

Gray [25] has shown that, when an absorbing technique is included in the propagation of the wavepacket to prevent it from reaching the edge of a finite grid, the absorption should be performed in the same way as was later discussed by Mandelstam and Taylor [85] namely:

$$\Phi_f^R(t+\tau) = \hat{\mathbf{A}}\Big\{2\hat{\mathbf{H}}_s\Phi_f^R(t) - \hat{\mathbf{A}}\Phi_f^R(t-\tau)\Big\}. \tag{34}$$

Note that the time-step, τ, has been included in the mapping of the Hamiltonian operator (Equation (31)). In practice all the Fourier transforms over time (see Equation (18)) are performed using a trapezoid rule approach. With this in mind we can now replace the integrations over time by summations over the Chebyshev iteration number. Therefore we replace time using $t = k\tau$, where k is the iteration number and τ is the time-step. The time-dependent coefficients, $C_{\upsilon'j'}^{JK'}(t)$, in Equation (17) are then replaced by the iteration number dependent coefficients $C_{f,k}^{JK'\upsilon'j'}$:

$$C_{f,k}^{JK'\upsilon'j'} = C_{f,\upsilon'j'}^{JK'}(t=k\tau) = \langle\chi_{\upsilon'j'K'}(\mathbf{r})|\Phi_{f,k}^R(R'=R'_\infty,\mathbf{r})\rangle \tag{35}$$

where $\Phi_{f,k}^R$ is the kth iterate of the iteration process in Equation (34) and corresponds to time $t = k\tau$. Equation (34) is then replaced by the recursion relationship:

$$\Phi_{f,k+1}^R = \hat{\mathbf{A}}\Big\{2\hat{\mathbf{H}}_s\Phi_{f,k}^R - \hat{\mathbf{A}}\Phi_{f,k-1}^R\Big\}. \tag{36}$$

The first function used to start the iteration process is given by Equation (15), but note that only the real part of the wavefunction is used in the iteration process (see discussion below).

The equation analogous to Equation (18), giving the discretized Fourier transform of the $C_{f,k}^{JK'v'j'}$ coefficients, is:

$$A^{JK'v'j'}(f) = \frac{\tau}{2\pi} \sum_{k=0}^{N} \left(1 - \frac{\delta_{k,0}}{2}\right) \exp(ifk\tau/\hbar) C_{f,k}^{JK'v'j'}. \tag{37}$$

We now define a new quantity $\tilde{A}^{JK'v'j'}(f)$ such that

$$\tilde{A}^{JK'v'j'}(f) = \frac{A^{JK'v'j'}(f)}{\tau} = \frac{1}{2\pi} \sum_{k=0}^{N} \left(1 - \frac{\delta_{k,0}}{2}\right) \exp(ifk\tau/\hbar) C_{f,k}^{JK'v'j'}$$

$$= \frac{1}{2\pi} \sum_{k=0}^{N} \left(1 - \frac{\delta_{k,0}}{2}\right) \exp(ifk) C_{f,k}^{JK'v'j'}. \tag{38}$$

In the final line of Equation (38) I have set $\tau/\hbar = 1$. This is justified by arguments given in [86] which state that the discrete dynamics of the system cannot depend on any particular chosen value of τ. We may also note that in the mapping equation (Equation (31)) f is proportional to $\hbar/\tau$. The product $f\tau/\hbar$ which occurs in Equation (38) will therefore be independent of the value of τ.

The interpretation of the A coefficients of Equation (18) is discussed in detail in [94]. This analysis involved the use of the identity operator expressed in terms of continuum wavefunctions normalized on the energy scale [117]. As we have now mapped the Hamiltonian (Equation (31)) onto a function of itself, $f(\hat{H}_s)$, the energy is replaced by $f(E_s)$ at every stage of this analysis. Our continuum wavefunctions which appear in the analysis are therefore now normalized on the 'f' scale and the conversion from the 'f' to the 'E' scale is given by the relationship of the Dirac delta functions in the two scales:

$$\delta(E - E') = \frac{df}{dE} \delta(f - f'). \tag{39}$$

But

$$\frac{df}{dE} = \frac{d}{dE}\left[-\frac{\hbar}{\tau}\cos^{-1}(E_s)\right] = \frac{d}{dE_s}\left[-\frac{\hbar}{\tau}\cos^{-1}(E_s)\right]\frac{dE_s}{dE}$$

$$= -\frac{\hbar}{\tau}\frac{d}{dE_s}\left[\cos^{-1}(E_s)\right]\frac{dE_s}{dE} = \frac{\hbar}{\tau}\frac{1}{\sin(\arccos(E_s))}\frac{dE_s}{dE}$$

$$= \frac{\hbar}{\tau}\frac{1}{\sqrt{1-E_s^2}}\frac{dE_s}{dE} = \frac{\hbar}{\tau}\frac{1}{\sqrt{1-E_s^2}}\frac{2}{\Delta E} \tag{40}$$

where I have used Equation (9) to relate E to E_s.

With the above formulae in mind and following the analysis of [94], we obtain an expression for the $\mathbf{S}$ matrix elements in terms of the $\tilde{A}^{JK'v'j'}(f)$ coefficients of Equation (38).

$$S_{j'K',jK}^{J}(E) = -\frac{df}{dE}\left(\frac{\hbar^2 k_j k_{j'}'}{\mu\mu'}\right)^{1/2}\exp(-ik_{j'}'R_\infty')\frac{2\tilde{A}^{JK'v'j'}(f)\tau}{g(-k_j)}$$

$$= -\frac{\hbar}{\tau}\frac{1}{\sqrt{1-E_s^2}}\frac{2}{\Delta E}\left(\frac{\hbar^2 k_j k_{j'}'}{\mu\mu'}\right)^{1/2}\exp(-ik_{j'}'R_\infty')\frac{2\tilde{A}^{JK'v'j'}(f)\tau}{g(-k_j)}$$

$$S_{j'K',jK}^{J}(E) = -\frac{4\hbar^2}{\Delta E\sqrt{1-E_s^2}}\left(\frac{k_j k_{j'}'}{\mu\mu'}\right)^{1/2}\exp(-ik_{j'}'R_\infty')\frac{\tilde{A}^{JK'\upsilon'j'}(f)}{g(-k_j)}. \tag{41}$$

An extra factor of 2 has appeared in the above equation relating the **S** matrix elements with the $\tilde{A}^{JK'\upsilon'j'}(f)$ coefficients. This arises from the analysis of Appendix A of [86] where it was shown that when only the real part of the wavepacket is used the $\tilde{A}^{JK'\upsilon'j'}(f)$ coefficients must be multiplied by this factor.

There is only one additional minor point which needs to be discussed in connection with the real wavepacket method. This is how the iteration process is to be started.

The 0th iterate is taken to be the real part of the initial wavepacket (see Equation (15)).

$$\Phi_{f,k=0}^{R}(R',\mathbf{r}') = \Re\{\Phi_K^J(R',\mathbf{r}',t=0)\}. \tag{42}$$

The solution to the modified Schrödinger equation, Equation (32) is

$$\begin{aligned}\Phi_f(t) &= \exp\left[-if(\hat{\mathbf{H}}_s)\,t/\hbar\right]\Phi_f(t=0)\\ &= \left[\cos\left(f(\hat{\mathbf{H}}_s)\,t/\hbar\right) - i\sin\left(f(\hat{\mathbf{H}}_s)t/\hbar\right)\right]\Phi_f(t=0).\end{aligned} \tag{43}$$

Now using the mapping of Equation (31) we obtain at time $t=\tau$ corresponding to the first iterate:

$$\begin{aligned}\Phi_f(\tau) &= \left[\hat{\mathbf{H}}_s - i\sin\left(-\arccos\left(\hat{\mathbf{H}}_s\right)\right)\right]\Phi_f(t=0)\\ &= \left[\hat{\mathbf{H}}_s + i\sin\left(\arccos\left(\hat{\mathbf{H}}_s\right)\right)\right]\Phi_f(t=0)\\ &= \left[\hat{\mathbf{H}}_s + i\sqrt{1-\hat{\mathbf{H}}_s^2}\right]\Phi_f(t=0).\end{aligned} \tag{44}$$

We require the first iterate, which corresponds to the real part of the wavepacket $\Phi_f(\tau)$.

$$\begin{aligned}\Phi_{f,k=1}^{R}(R',\mathbf{r}') &= \hat{\mathbf{A}}\Re\{\Phi_K^J(R',\mathbf{r}',t=\tau)\}\\ &= \hat{\mathbf{A}}\Re\left\{\left[\hat{\mathbf{H}}_s + i\sqrt{1-\hat{\mathbf{H}}_s^2}\right]\Phi_K^J(R',\mathbf{r}',t=0)\right\}\\ &= \hat{\mathbf{A}}\left\{\hat{\mathbf{H}}_s\Phi_{f,k=0}^{R}(R',\mathbf{r}') - \left[\sqrt{1-\hat{\mathbf{H}}_s^2}\right]\Im\{\Phi_K^J(R',\mathbf{r}',t=0)\}\right\}. \tag{45}\end{aligned}$$

So to obtain the $k=1$ iterate we need to operate on the imaginary part of the initial wavepacket. Subsequent iterates are obtained through the application of the recursion relationship in Equation (36).

The operation of $\sqrt{1-\hat{\mathbf{H}}_s^2}$ on the imaginary part of the initial wavepacket (see Equation (45)) is accomplished using a expansion in terms of Chebyshev polynomials:

$$\sqrt{1-\hat{\mathbf{H}}_s^2} = \frac{2}{\pi}\left[1 - 2\sum_{n=1}^{\infty}\frac{T_{2n}(\hat{\mathbf{H}}_s)}{4n^2-1}\right]. \tag{46}$$

This expansion is derived in Appendix C (see also problem 13.3.27 of [118]).

In the real wavepacket approach to the evaluation of the **S** matrix elements time plays no role. The wavepacket iterates are are evaluated using Equation (34) and then used to calculate the iterate number dependent $C_{f,k}^{JK'v'j'}$ coefficients (Equation (35)). These are then used to compute a discretized Fourier transform (Equation (38)) which yields the **S** matrix elements directly through Equation (41). A similar method, based on a time-independent wavepacket formulation and on the artificial creation of an initially real wavepacket with flux going in both directions (i.e. with both the reactants approaching each other and getting more distant from each other) has been proposed and used by Kroes and Neuhauser [53]. Guo has also proposed and exploited similar techniques, i.e. the polynomial propagation method, both in photodissociation [56,69,70] and in reactive scattering applications [54].

There is clearly a very close relationship between the time-independent prescription for the calculation of the reactive scattering **S** matrix elements (Equation (28) together with Equations (25), (26) and (29)) and the real wavepacket method (Equation (41) together with Equations (35), (36) and (38)). They are indeed absolutely identical. Once the mapping relationship (Equation (31)) and the normalization and scaling procedure of the Hamiltonian or energy (Equation (9)) is taken into account (and noting that we have chosen $\tau/\hbar = 1$) we see that f in Equation (38) is just equal to $-\phi$ in Equation (28). Substitution of Equations (35) and (38) into Equation (41) then yields Equation (28) which was derived from the time-independent wavepacket method.

4. Photodissociation

4.1. *Total photodissociation cross-section – Derivation of time-independent treatment from time-dependent formulation*

The time-dependent expression for the total photodissociation cross-section may be written in the form [89]:

$$\sigma_{\text{tot}}(E) = \frac{2\pi v}{c\epsilon_0 \hbar} \int_0^\infty dt \exp\left[\frac{iEt}{\hbar}\right] \langle \Phi(\mathbf{r}, \mathbf{R}, t=0) | \Phi(\mathbf{r}, \mathbf{R}, t) \rangle \tag{47}$$

where $\Phi(\mathbf{r}, \mathbf{R}, t=0)$ is the 'initial wavepacket' created from the wavefunction of the initial bound vibrational-rotational state of the parent molecule, ψ_i:

$$\left| \Phi(\mathbf{r}, \mathbf{R}, t=0) \right\rangle = \vec{\epsilon} \cdot \vec{\mu} | \psi_i \rangle. \tag{48}$$

The angular momentum aspects of these equations have been discussed elsewhere. [89,119] In the present review I will concentrate on relating this time-dependent treatment to an alternative time-independent approach. As in the case of reactive scattering we will do this by substituting for the time-dependent wavepacket using the Chebyshev expansion of the time evolution operator (Equation (14)) and then performing the Fourier transform over time in Equation (47). Using the Chebyshev expansion of Equation (14) to substitute for

$\Phi(r, \mathbf{R}, t)$ in Equation (47) we obtain:

$$
\begin{aligned}
\sigma_{\text{tot}}(E) = {} & \frac{2\pi\nu}{c\epsilon_0\hbar} \int_0^\infty \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \left\langle \Phi(\mathbf{r}, \mathbf{R}, t=0) \middle| \exp\left(\frac{-i((\Delta E/2)+V_{\min})t}{\hbar}\right) \right. \\
& \times \left. \sum_{n=0}^N (2-\delta_{no}) J_n\left(\frac{\Delta E\,t}{2\hbar}\right) Q_n(-i\hat{H})\Phi(\mathbf{r}, \mathbf{R}, t=0) \right\rangle \\
= {} & \frac{4\pi^2\nu}{c\epsilon_0\hbar} \sum_{n=0}^N (2-\delta_{no}) \left\langle \Phi(\mathbf{r}, \mathbf{R}, t=0) \middle| \left\{ \frac{1}{2\pi} \int_0^\infty \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \right. \right. \\
& \times \left. \left. \exp\left(\frac{-i((\Delta E/2)+V_{\min})t}{\hbar}\right) J_n\left(\frac{\Delta E\,t}{2\hbar}\right) \right\} Q_n(-i\hat{H}) \,\middle|\, \Phi(\mathbf{r}, \mathbf{R}, t=0) \right\rangle. \qquad (49)
\end{aligned}
$$

The integral in curly brackets above is the same as that which occurred in Equation (22) and which is discussed in detail in Appendix B. Using Equation (109) of Appendix B to substitute for the curly bracket in the above equation and following the development used in the discussion of the reactive scattering cross-section above (see Equations (24)–(30)) we obtain:

$$
\sigma_{\text{tot}}(E) = \frac{4\pi\nu}{c\epsilon_0\Delta E} \sum_{n=0}^N (2-\delta_{no}) \frac{1}{\sin\phi} \exp[-in\phi]\zeta_n \qquad (50)
$$

where

$$
\zeta_0 = \langle \Phi(\mathbf{r}, \mathbf{R}, t=0) | \eta_n(\mathbf{r}, \mathbf{R}, t=0) \rangle; \qquad (51)
$$

$$
\begin{aligned}
\eta_0 &= \Phi(\mathbf{r}, \mathbf{R}, t=0) \\
\eta_1 &= \hat{\mathbf{A}}\hat{\mathbf{H}}_s \Phi(\mathbf{r}, \mathbf{R}, t=0) \\
\eta_{n+1} &= \hat{\mathbf{A}}\left\{ 2\hat{\mathbf{H}}_s\eta_n - \hat{\mathbf{A}}\eta_{n-1} \right\},
\end{aligned} \qquad (52)
$$

where $\hat{\mathbf{A}}$ is a damping operator (see discussion beneath Equation (30)) and ϕ is defined in Equations (25) and (26).

4.2. *Partial integral photodissociation cross-section – Derivation of time-independent treatment from time-dependent formulation*

The partial integral photodissociation cross-section measures the probability of producing a particular quantum state of the product fragments. It has been extensively discussed in the literature [89,94]. I will concentrate on the photodissociation of a triatomic molecule to yield a structureless atom and a diatomic having no electronic angular momentum. In Appendix D I relate the expression for the partial differential photodissociation cross-section derived in [89] to an expression for the partial integral photodissociation cross-section.

The initial wavepacket is formed as discussed above (see see Equation (48) and also [89]), the time-dependent procedure then follows closely that used in reactive

scattering (see Section 3.1). A cut is taken through the wavepacket at each time step for a fixed value of the dissociation coordinate, i.e. at $R = R_\infty$, in the asymptotic region of the dissociation channel and the resulting function is projected onto the product fragment eigenfunctions. This yields a time-dependent coefficient, $C_{vj}^{JK}(t)$, for each of the dissociation product quantum states.

$$C_{vj}^{JKp}(t) = \langle \chi_{vjK}(\mathbf{r}) | \Phi^{JKp}(\mathbf{r}, R = R_\infty, t) \rangle \tag{53}$$

where as before $\mathbf{r}$ stands for all the internal coordinates of the fragments. $\Phi^{JKp}(\mathbf{r}, R = R_\infty, t)$ represents the body-fixed component of the wavepacket with total angular momentum quantum number J and body-fixed z-component K (see [119] for a complete discussion). The superscript p denotes the parity of the wavepacket. The half Fourier transform of these coefficients is now computed:

$$A_{vj}^{JKp}(E) = \frac{1}{2\pi} \int_{t=0}^{\infty} \exp(iEt/\hbar) C_{vj}^{JKp}(t) \mathrm{d}t. \tag{54}$$

These equations are identical to those in Section 3.1 above (Equations (17) and (18)), except for the fact that the initial wavepacket from which the time-dependent wavepackets are evolved are different (see Equations (15) and (48)). The partial integral photodissociation cross-section summed over final product m_j states and averaged over the initial M_i states, $\bar{\bar{\sigma}}_{vj}(E)$, is given by (see [89,94] and Equation (134) of Appendix D):

$$\bar{\bar{\sigma}}_{vj}(E) = \frac{2\pi^2 \nu}{3c\epsilon_0} \frac{1}{2J_i + 1} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} \left| T_{vj}^{JKp} \right|^2 \tag{55}$$

where

$$T_{vj}^{JKp} = i(-1)^{K-j} A_{vj}^{JKp}(E) \left(\frac{\pi k_{vj}}{\mu} \right)^{1/2} \sqrt{(1 + \delta_{0,K})} \, e^{-ik_{vj}R_\infty}. \tag{56}$$

Substituting Equation (56) into Equation (55) we obtain:

$$\bar{\bar{\sigma}}_{vj}(E) = \frac{2\pi^3 k_{vj} \nu}{3\mu c \epsilon_0} \frac{1}{2J_i + 1} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} (1 + \delta_{0,K}) \left| A_{vj}^{JKp}(E) \right|^2. \tag{57}$$

Substituting Equations (53) and (54) into Equation (57) now yields:

$$\bar{\bar{\sigma}}_{vj}(E) = \frac{2\pi^3 k_{vj} \nu}{3\mu c \epsilon_0} \frac{1}{2J_i + 1} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} (1 + \delta_{0,K}) \left| \frac{1}{2\pi} \int_{t=0}^{\infty} \exp(iEt/\hbar) \langle \chi_{vjK}(\mathbf{r}) | \Phi^{JKp}(\mathbf{r}, R = R_\infty, t) \rangle \mathrm{d}t \right|^2. \tag{58}$$

The Fourier transform integral over time in Equation (58) is of exactly the same form as that occurring in Equation (21) for the reactive $\mathbf{S}$ matrix elements. This integral is discussed further in Appendix E. Substituting from Equation (141) of Appendix E into Equation (58) we obtain:

$$\bar{\bar{\sigma}}_{vj}(E) = \frac{2\pi k_{vj} \nu}{3\mu c \epsilon_0} \left(\frac{\hbar}{\Delta E \sin\phi} \right)^2 \frac{1}{2J_i + 1}$$
$$\times \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} (1 + \delta_{0,K}) \left| \sum_{n=0}^{N} (2 - \delta_{no}) \exp[-in\phi] \langle \chi_{vjK}(\mathbf{r}) | \eta_n^{JKp}(R = R_\infty) \rangle \right|^2 \tag{59}$$

where (see Equation (30):

$$
\begin{aligned}
\eta_0^{JKp} &= \Phi^{JKp}(\mathbf{r}, R, t = 0) \\
\eta_1^{JKp} &= i\hat{\mathbf{A}}Q_1(-i\hat{\mathbf{H}}_s)\Phi^{JKp}(\mathbf{r}, R, t = 0) = \hat{\mathbf{A}}\hat{\mathbf{H}}_s\Phi^{JKp}(\mathbf{r}, R, t = 0) \\
\eta_2^{JKp} &= \hat{\mathbf{A}}\left\{2\hat{\mathbf{H}}_s\eta_1^{JKp} - \hat{\mathbf{A}}\eta_0^{JKp}\right\} \\
\eta_{n+1}^{JKp} &= \hat{\mathbf{A}}\left\{2\hat{\mathbf{H}}_s\eta_n^{JKp} - \hat{\mathbf{A}}\eta_{n-1}^{JKp}\right\}
\end{aligned}
\tag{60}
$$

and

$$
\cos\phi = \frac{E - \alpha}{\beta}
\tag{61}
$$

where

$$
\alpha = \left(\frac{1}{2}\Delta E + V_{\min}\right), \quad \beta = \left\{\frac{\Delta E}{2}\right\}.
\tag{62}
$$

4.3. *Photodissociation and the real wavepacket method*

4.3.1. *Total integral cross-section*

In analogy with the calculation of the reactive scattering **S** matrix elements, in photodissociation our interest is in various cross-sections. These are dependent on energy and do not directly involve time. We could therefore replace time by another variable, such as the Chebyshev iteration number [69]. In Appendix F I follow the logic of [86] and show that if we use only the real part of the time-dependent wavepacket to evaluate the total integral photodissociation cross-section in Equation (47) we need to multiply the right hand side of the equation by 2. For the case of photodissociation the initial wavepacket (Equation (48)) is real. We will use the same mapping of the Hamiltonian operator as discussed in Section IIID and all the discussion of this section applies also to the present case.

The expression for the total integral photodissociation cross-section (Equation (47)) therefore becomes (see Equation (38) and associated discussion):

$$
\sigma_{\text{tot}}(E) = 2\frac{\mathrm{d}f}{\mathrm{d}E} \times \frac{2\pi\nu}{c\epsilon_0\hbar}\sum_{k=0}^{N}\left(1 - \frac{\delta_{k,0}}{2}\right)\tau\exp(ifk)\left\langle\Phi(\mathbf{r}, \mathbf{R}, t = 0)\middle|\Phi_{f,k}^{R}(\mathbf{r}, \mathbf{R})\right\rangle.
\tag{63}
$$

The superscript 'R' on $\Phi_{f,k}^{R}(\mathbf{r}, \mathbf{R})$ indicates that only the real part of the wavepacket is used. The subscript 'f' indicates that the wavepacket arises from a mapped Schrödinger equation (see Equation (32)) and the subscript 'k' indicates the kth wavepacket iterate (see Equation (36) using real part only). The factor $(\mathrm{d}f/\mathrm{d}E)$ arises from the need to convert the Dirac delta function in the mapped energy $f(E)$ to a Dirac delta function in E in the derivation of the time-dependent expression for the total integral photodissociation cross-section [86,89]. An extra factor 2 has also been inserted as discussed above because of the use of the real part only of the wavepacket.

Using Equation (40) to substitute for (df/dE) we obtain:

$$\sigma_{\text{tot}}(E) = \frac{1}{\Delta E \sqrt{1 - E_s^2}} \frac{8\pi\nu}{c\epsilon_0} \sum_{k=0}^{N} \left(1 - \frac{\delta_{k,0}}{2}\right) \exp(ifk) \langle \Phi(\mathbf{r}, \mathbf{R}, t=0) | \Phi_{f,k}^R(\mathbf{r}, \mathbf{R}) \rangle. \tag{64}$$

The zeroth wavepacket iterate is just the initial wavepacket (see Equation (48)).

$$\Phi_{f,k=0}^R(\mathbf{r}, \mathbf{R}) = \Phi(\mathbf{r}, \mathbf{R}, t=0). \tag{65}$$

As this wavepacket is real, we see from Equation (45) that the first iterate is given by:

$$\Phi_{f,k=1}^R(\mathbf{r}, \mathbf{R}) = \hat{\mathbf{A}}\hat{\mathbf{H}}_s \Phi_{f,k=0}^R(\mathbf{r}, \mathbf{R}). \tag{66}$$

Further iterates are given by the application of the recurrsion relationship of Equation (36).

Equation (64) for the total integral photodissociation cross-section is very similar to the expressions used in the work of Guo *et al.* [56,69,70]. It differs from them in that a complex Fourier transform is used as opposed to a cosine transform. As the cross-section itself should be a real quantity, both formulations should yield the same result.

4.3.2. *Partial integral cross-section*

We start our development of the real wavepacket formulation for the calculation of partial integral photodissociation cross-sections with Equation (58). This equation may be written in the form:

$$\bar{\bar{\sigma}}_{vj}(E) = \frac{2\pi^3 k_{vj}\nu}{3\mu c\epsilon_0} \frac{1}{2J_i + 1} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} (1 + \delta_{0,K}) \left| Z_{vj}^{JKp} \right|^2 \tag{67}$$

where

$$Z_{vj}^{JKp} = \frac{1}{2\pi} \int_{t=0}^{\infty} \exp(iEt/\hbar) \langle \chi_{vjK}(\mathbf{r}) | \Phi^{JKp}(\mathbf{r}, R = R_{\infty}, t) \rangle \mathrm{d}t. \tag{68}$$

The derivation of the formulae for the real wavepacket method now proceeds in an identical manner to the derivation given in Appendix A of [86]. The continuous Fourier transform over time in Equation (68) is replaced by a discrete Fourier transform over iteration number k. An extra facor of 2 is added to account for the use of only the real part of the wavepacket and a factor of (df/dE) is included to transform the Dirac delta function in the mapped variable $f(E)$ to a Dirac delta function in E. With all these changes the expression for the coefficient Z_{vj}^{JKp} in Equation (67) becomes (see also discussion beneath Equation (38) above):

$$Z_{vj}^{JKp} = 2 \frac{df}{dE} \frac{1}{2\pi} \sum_{k=0}^{N} \left(1 - \frac{\delta_{k,0}}{2}\right) \tau \exp(ifk) \langle \chi_{vjK}(\mathbf{r}) | \Phi_{f,k}^{JKpR}(\mathbf{r}, R = R_{\infty}) \rangle \tag{69}$$

where, as before, the superscript 'R' on $\Phi_{f,k}^{JKpR}(\mathbf{r}, R = R_{\infty})$ indicates that only the real part of the wavepacket iterate is used, the subscript 'f' indicates that the Hamiltonian has been mapped according to Equation (31) and the subscript 'k' indicates the kth wavepacket

iterate (see Equations (66) and (36)). Just as in the discussion below Equation (38) we have chosen the time step such that $(\tau/\hbar) = 1$ and f is consequently related to the scaled energy by $f(E_s) = -\cos^{-1}(E_s)$ (see Equation (31)) where:

$$E_s = \frac{E - ((\Delta E/2) + V_{\min})}{(\Delta E/2)}. \tag{70}$$

The zeroth iterate is real and corresponds to:

$$\Phi_{f,k=0}^{JKpR}(\mathbf{r}, R) = \Phi^{JKp}(\mathbf{r}, R, t = 0) \tag{71}$$

with subsequent iterates being generated using Equations (65), (66) and (36).

Using Equation (40) to substitute for $(\mathrm{d}f/\mathrm{d}E)$ in Equation (69) we obtain:

$$Z_{vj}^{JKp} = \frac{1}{\Delta E \sqrt{1 - E_s^2}} \frac{2}{\pi} \frac{\hbar}{} \sum_{k=0}^{N} \left(1 - \frac{\delta_{k,0}}{2}\right) \exp(ifk) \left\langle \chi_{vjK}(\mathbf{r}) \middle| \Phi_{f,k}^{JKpR}(\mathbf{r}, R = R_\infty) \right\rangle. \tag{72}$$

Equations (67) and (72) together with the iterative Equations (71), (66) and (36) constitute the real wavepacket method for the calculation of partial integral photodissociation cross-sections. As with all real wavepacket methods they involve iteration of only the real part of the wavepacket. In the case of photodissociation there is the added benefit that the initial wavepacket is real, with the consequence that the first wavepacket iterate does not involve the imaginary part of the initial wavepacket (compare Equations (45) and (66)). Equation (67), for the partial integral photodissociation cross-section in the real wave wavepacket approach, differs considerably from the expressions developed by Guo *et al.* [56,69] in their Chebyshev polynomial propagation approach. This difference arises from the different way in which the asymptotically scattered wavepacket is analysed. Guo *et al.* analyse the wavepacket by projecting onto a full three dimensional energy normalized scattering wavefunction, while I utilize the theory of [94] and analyse a cut through the wavepacket in the asymptotic scattering region at each iteration.

5. Summary

Wavepacket methods are becoming increasingly more popular in the calculation of the quantum dynamics of molecular reactive scattering processes. This is due to the fact that as the complexity of a system grows it becomes progressively more difficult to solve the complete set of coupled second order differential equations which arise. Such solutions require repeated matrix-matrix multiplications and scale poorly with increasing dimensionality. For reactive scattering such an approach yields the entire **S** matrix for a particular energy and therefore permits the calculation of all state-to-state cross-sections at this energy. In contrast, wavepacket calculations provide an 'initial value' approach to the problem and focus on the production of all possible product states arising from a well specified initial quantum state. Such calculations provide information on fewer transitions, but they have the advantage of providing this information over a large energy range from a single calculation. Furthermore, as only matrix-vector operations are used in wavepacket based calculations, they scale much more favourably

with increasing dimensionality. In photodissociation wavepacket based theories arise more naturally from a physical perspective, as the molecule normally starts off in a single well defined quantum state which then provides the specification for the initial wavepacket in a very natural way.

This review has attempted to bring together and relate different forms of wavepacket based dynamical theories for reactive scattering and photodissociation. In reactive scattering I have focused on the calculation of the reactive scattering **S** matrix elements. These can provide all possible information about the outcome of a reactive collision [47]. In photodissociation I have discussed both the total integral cross-section, or absorption line shape, and also the partial integral photodissociation cross-section, which measures the probability of producing products in specific quantum states. The mathematical aspects arising in the calculation of partial photodissociation cross-sections are very similar to those arising in the calculation of the reactive scattering **S** matrix elements.

The two main types of dynamics discussed in the review are time-dependent and time-independent formulations. As the quantities of interest are all energy dependent, time only enters as a supplementary variable and all time-dependent quantities are eventually eliminated by a Fourier transform so as to provide the energy dependent quantity of interest. A time-dependent formulation may therefore be transformed into a time-independent one by taking the Fourier transform of the relevant formulae. One of the most efficient ways of performing a time-dependent wavepacket calculation is to expand the time evolution operator in terms of Chebyshev polynomials [13,120,121]. It turns out that it is possible to find an analytic expression for the Fourier transform over time of the time evolution operator when it is expanded in this way. This is the basis of the time-independent wavepacket method [82] which we focus on in this review.

For each case, i.e reactive **S** matrix elements, total integral photodissociation cross section and partial photodissociation cross-section, the review starts with the time-dependent formulation and derives the time-independent formulation from it. The basic theory needed to derive for these relationships is available in the literature [30,82,122–124], but is nowhere clearly laid out or easily accessible. Many of the detailed mathematical derivations needed in the theoretical development of the formulae are presented in the six appendices.

We also discuss the real wavepacket method and its application to both reactive scattering and photodissociation. This method uses only the real part of a complex wavepacket together with a mapped Hamiltonian operator and an iterative equivalent to the time-dependent Schrödinger equation [86]. For reactive scattering I show that this method is identical to the time-independent wavepacket method (except for the fact that in the real wavepacket method there is a saving of about a factor of two arising from the use of only the real part of the wavepacket). For photodissociation theory I present the basic equations needed to apply the real wavepacket approach to such calculations.

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Appendix A: Expansion of the time evolution operator in Chebyshev polynomials

The solution of the time-dependent Schrödinger equation may be written in the form:

$$\Psi(t) = \exp\left[\frac{-i\hat{\mathbf{H}}t}{\hbar}\right]\Psi(t=0) = \hat{\mathbf{U}}(0,t)\Psi(t=0), \tag{73}$$

if the Hamiltonian $\hat{\mathbf{H}}$ does not depend on time.

The operator $\hat{\mathbf{U}}(0,\tau) = \exp[(-i\hat{\mathbf{H}}\tau/\hbar)]$ is the time evolution operator and propagates the wavepacket forward in time from $t=0$ to τ. Expanding the propagator in terms of cosines and sines, we may write:

$$\Psi(t) = \exp\left[\frac{-i\hat{\mathbf{H}}t}{\hbar}\right]\Psi(0) = \cos\left[\frac{\hat{\mathbf{H}}t}{\hbar}\right]\Psi(0) - i\sin\left[\frac{\hat{\mathbf{H}}t}{\hbar}\right]\Psi(0). \tag{74}$$

or

$$\hat{\mathbf{U}}(0,t) = \exp\left[\frac{-i\hat{\mathbf{H}}t}{\hbar}\right] = \cos\left[\frac{\hat{\mathbf{H}}t}{\hbar}\right] - i\sin\left[\frac{\hat{\mathbf{H}}t}{\hbar}\right]. \tag{75}$$

The Chebyshev polynomials are defined as:

$$T_n(x) = \cos(n\arccos x) \quad \text{where } -1 \leq x \leq 1 \tag{76}$$

and the first few polynomials are [125]

$$\begin{aligned} T_0(x) &= 1 \\ T_1(x) &= x \\ T_2(x) &= 2x^2 - 1. \end{aligned} \tag{77}$$

The Chebyshev recursion relationship is [126]

$$T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x). \tag{78}$$

The Chebyshev polynomial orthogonality relationship is (see [126], integral 7.343):

$$\begin{aligned} \int_{-1}^{1} T_n(x)T_m(x)\frac{dx}{\sqrt{1-x^2}} &= 0 \quad \text{if } n \neq m \\ &= \frac{\pi}{2} \quad \text{if } n = m \neq 0 \\ &= \pi \quad \text{if } n = m = 0. \end{aligned} \tag{79}$$

We now write the the time evolution operator, $U(0,t)$, in the form:

$$\hat{\mathbf{U}}(0,t) = \cos\left[\frac{\hat{\mathbf{H}}t}{\hbar}\right] - i\sin\left[\frac{\hat{\mathbf{H}}t}{\hbar}\right]. \tag{80}$$

From Gradshteyn and Ryzhik [126] Equation 7.355 we have:

$$\begin{aligned} \int_0^1 T_{2n+1}(x)\sin ax\,\frac{dx}{\sqrt{1-x^2}} &= (-1)^n \frac{\pi}{2} J_{2n+1}(a) \\ \int_0^1 T_{2n}(x)\cos ax\,\frac{dx}{\sqrt{1-x^2}} &= (-1)^n \frac{\pi}{2} J_{2n}(a) \quad [a > 0]. \end{aligned} \tag{81}$$

As $T_{2n+1}(x)$ is odd with respect to x and $T_{2n}(x)$ is even, the integrands in both the above integrals are even. We can therefore write the slightly more useful equations:

$$\int_{-1}^{1} T_{2n+1}(x) \sin ax \frac{\mathrm{d}x}{\sqrt{1-x^2}} = (-1)^n \pi J_{2n+1}(a)$$

$$\int_{-1}^{1} T_{2n}(x) \cos ax \frac{\mathrm{d}x}{\sqrt{1-x^2}} = (-1)^n \pi J_{2n}(a) \quad [a > 0]. \tag{82}$$

These equations should enable us to find the expansions of $\sin ax$ and $\cos ax$ in terms of Chebyshev polynomials. Now writing $\sin x$ as an expansion in terms of Chebyshev polynomials we have:

$$\sin ax = \sum_{n=0}^{\infty} C_{2n+1}^s(a) T_{2n+1}(x) \tag{83}$$

where, taking account of the non-normalized nature of the Chebyshev polynomials (see Equation 79) we can write:

$$C_{2n+1}^s(a) = \frac{2}{\pi} \int_{-1}^{1} T_{2n+1}(x) \sin ax \frac{\mathrm{d}x}{\sqrt{1-x^2}} = (-1)^n \, 2 \, J_{2n+1}(a). \tag{84}$$

Similarly the expansion of $\cos ax$ becomes:

$$\cos ax = \sum_{n=0}^{\infty} C_{2n}^c(a) T_{2n}(x) \tag{85}$$

where

$$C_0^c(a) = \frac{1}{\pi} \int_{-1}^{1} \cos ax \frac{\mathrm{d}x}{\sqrt{1-x^2}} = J_0(a) \quad \text{for } n = 0 \tag{86}$$

$$C_{2n}^c(a) = \frac{2}{\pi} \int_{-1}^{1} T_{2n}(x) \cos ax \frac{\mathrm{d}x}{\sqrt{1-x^2}} = (-1)^n \, 2 \, J_{2n}(a) \quad \text{for } n > 0. \tag{87}$$

Using the equation:

$$\exp[iax] = \cos ax + i \sin ax \tag{88}$$

we obtain [127]

$$\exp[iax] = \sum_{n=0}^{\infty} C_{2n}^c(a) T_{2n}(x) + i \sum_{n=0}^{\infty} C_{2n+1}^s(a) T_{2n+1}(x)$$

$$= C_0^c(a) T_0(x) + i C_1^s(a) T_1(x) + C_2^c(a) T_2(x) + i C_3^s(a) T_3(x) + C_4^c(a) T_4(x) + i C_5^s(a) T_5(x)$$

$$= J_0(a) T_0(x) + i 2 J_1(a) T_1(x) + (-1) 2 J_2(a) T_2(x) + i(-1) 2 J_3(a) T_3(x)$$

$$\quad + (-1)^2 2 J_4(a) T_4(x) + i(-1)^2 2 J_5(a) T_5(x)$$

$$= \sum_{n=0}^{\infty} (i)^n \, c_n \, J_n(a) \, T_n(x), \tag{89}$$

where

$$c_0 = 1$$
$$c_k = 2 \quad \text{for } n \geq 1. \tag{90}$$

Our objective is to use Equation (89) for the expansion of the time evolution operator, $\hat{U}(0, t) = \exp[(-i\hat{H}t/\hbar)]$. In order to do this we must take account of the requirement that the argument of the Chebyshev polynomial must lie in the interval $[-1, 1]$. The minimum value of the potential energy, V_{min}, is the lowest possible eigenvalue of $\hat{H}$. We denote the highest possible eigenvalue by E_{max} and the range of the possible eigenvalues by; $\Delta E = E_{max} - V_{min}$. With these definitions a shifted and scaled Hamiltonian can be defined as [13]:

$$\hat{H}_s = \frac{\hat{H} - \hat{I}\left(\frac{1}{2}\Delta E + V_{min}\right)}{\frac{1}{2}\Delta E}. \tag{91}$$

The inverse of this equation is:

$$\hat{H} = \frac{1}{2}\Delta E \hat{H}_s + \hat{I}\left(\frac{1}{2}\Delta E + V_{min}\right). \tag{92}$$

The time evolution operator may now be written in terms of $\hat{H}_s$ as:

$$\hat{U}(0, t) = \exp\left[\frac{-i\hat{H}t}{\hbar}\right] = \exp\left[\frac{-i\left\{\frac{1}{2}\Delta E \hat{H}_s + \hat{I}\left(\frac{1}{2}\Delta E + V_{min}\right)\right\}t}{\hbar}\right]$$

$$= \exp\left[\frac{-i\left(\frac{1}{2}\Delta E + V_{min}\right)t}{\hbar}\right] \times \exp\left[-i\left\{\frac{\Delta E t}{2\hbar}\right\}\hat{H}_s\right]. \tag{93}$$

Using the expansion of Equation (89) in Equation (93), and making the assignments $a = (\Delta E t/2\hbar)$ and $x = -\hat{H}_s$ we obtain:

$$\hat{U}(0, t) = \exp\left[\frac{-i\left(\frac{1}{2}\Delta E + V_{min}\right)t}{\hbar}\right] \times \sum_{n=0}^{\infty} (i)^n c_n J_n\left(\frac{\Delta E t}{2\hbar}\right) T_n(-\hat{H}_s). \tag{94}$$

We now follow Tal-Ezer [127] and define the complex Chebyshev polynomials by the relationship:

$$Q_k(\omega) = (i)^k T_k(-i\omega) \qquad \omega \in [-i, i]. \tag{95}$$

By substituting $x = -i\omega$ into Equation (78), it can be shown that these polynomials obey the recursion relationship;

$$Q_{n+1}(\omega) = 2\omega Q_n(\omega) + Q_{n-1}(\omega). \tag{96}$$

By substituting $\omega \rightarrow -iz$ in Equation (95) we obtain:

$$Q_k(-iz) = (i)^k T_k(-z). \tag{97}$$

We can now identify z with $\hat{H}_s$ in Equation (94) and obtain the expression:

$$\hat{U}(0, t) = \exp\left[\frac{-i\left(\frac{1}{2}\Delta E + V_{min}\right)t}{\hbar}\right] \times \sum_{n=0}^{\infty} c_n J_n\left(\frac{\Delta E t}{2\hbar}\right) Q_n(-i\hat{H}_s) \tag{98}$$

where

$$Q_{n+1}(-i\hat{H}_s) = -i2\hat{H}_s Q_n(-i\hat{H}_s) + Q_{n-1}(-i\hat{H}_s) \tag{99}$$

and

$$c_0 = 1$$
$$c_k = 2 \quad \text{for } n \geq 1. \tag{100}$$

Appendix B: Half Fourier transform of the Bessel function coefficients in the Chebyshev expansion of the time evolution operator

In this appendix we discuss the evaluation of the half Fourier transform of the Bessel Function coefficients in the Chebyshev expansion of the time evolution operator. This half Fourier transform arose in Equation (22) from our attempt to derive time-independent equations for the evaluation of the **S** matrix elements from the time-dependent equations by changing the order in which the Fourier transform over time is performed. The equations which result should be identical to those which have been derived by Kouri and co-workers [82–84,96–100,128] and by Taylor and coworkers [51,70,78,85] using a time-independent wavepacket formalism.

The half Fourier transform occurring in Equation (22) is:

$$I_n(E) = \frac{1}{2\pi} \int_0^\infty dt \exp(iEt/\hbar) \exp\left(\frac{-i((\Delta E/2) + V_{\min})t}{\hbar}\right) J_n\left(\frac{\Delta E\, t}{2\hbar}\right). \tag{101}$$

We now simplify the this expression using the definitions:

$$\alpha = \left(\frac{1}{2}\Delta E + V_{\min}\right), \quad \beta = \left\{\frac{\Delta E}{2}\right\} \tag{102}$$

to obtain:

$$I_n(E) = \frac{1}{2\pi} \int_0^\infty dt \exp(i(E - \alpha)t/\hbar) J_n\left(\frac{\beta\, t}{\hbar}\right). \tag{103}$$

This integral may be evaluated using Equations 6.671.1 and 6.671.2 of [126]. These integrals state:

$$\int_0^\infty J_n(ax)\sin bx\, dx = \frac{\sin(n\arcsin(b/a))}{\sqrt{a^2 - b^2}} \quad \text{for } b < a$$
$$\int_0^\infty J_n(ax)\cos bx\, dx = \frac{\cos(n\arcsin(b/a))}{\sqrt{a^2 - b^2}} \quad \text{for } b < a. \tag{104}$$

Using these equations the integral in Equation (103) can be written as:

$$\int_0^\infty dt \exp(i(E - \alpha)t/\hbar) J_n\left(\frac{\beta\, t}{\hbar}\right) = \int_0^\infty dt[\cos((E - \alpha)t/\hbar) + i\sin((E - \alpha)t/\hbar)]J_n\left(\frac{\beta\, t}{\hbar}\right)$$
$$= \int_0^\infty dt\, J_n\left(\frac{\beta\, t}{\hbar}\right)\cos((E - \alpha)t/\hbar) + i \int_0^\infty dt\, J_n\left(\frac{\beta\, t}{\hbar}\right)\sin((E - \alpha)t/\hbar)$$
$$= \frac{\hbar \cos(n\arcsin((E - \alpha)/\beta))}{\beta\sqrt{1 - ((E - \alpha)\beta)^2}} + i\frac{\hbar \sin(n\arcsin((E - \alpha)/\beta))}{\beta\sqrt{1 - ((E - \alpha)\beta)^2}}. \tag{105}$$

We now make the definition:

$$\cos \phi = \frac{E - \alpha}{\beta}. \tag{106}$$

Note also that:

$$\arcsin\left(\frac{E - \alpha}{\beta}\right) = -\phi + \frac{\pi}{2}. \tag{107}$$

Utilizing Equations (106) and (107) in Equation (105) we obtain:

$$\int_0^\infty dt \, \exp(i(E - \alpha)t/\hbar) J_n\left(\frac{\beta t}{\hbar}\right) = \frac{\hbar \cos(n(-\phi + (\pi/2)))}{\beta \sin \phi} + i \frac{\hbar \sin(n(-\phi + (\pi/2)))}{\beta \sin \phi}$$

$$= \frac{\hbar}{\beta \sin \phi} \left\{ \cos\left(n\left(\phi - \frac{\pi}{2}\right)\right) - i \sin\left(n\left(\phi - \frac{\pi}{2}\right)\right) \right\}$$

$$= \frac{\hbar}{\beta \sin \phi} \exp\left[-in\left(\phi - \frac{\pi}{2}\right)\right] = \frac{\hbar}{\beta \sin \phi} i^n \exp[-in\phi]. \tag{108}$$

Equation (108) can now be substituted back into Equation (103) to provide a compact expression for the half Fourier transform occurring in Equation (22) of the text:

$$\frac{1}{2\pi} \int_0^\infty dt \, \exp(iEt/\hbar) \exp\left(\frac{-i((\Delta E/2) + V_{\min})t}{\hbar}\right) J_n\left(\frac{\Delta E \, t}{2\hbar}\right) = \frac{1}{2\pi} \frac{\hbar}{\beta \sin \phi} i^n \exp[-in\phi]. \tag{109}$$

Appendix C: Expansion of $\sqrt{1 - x^2}$ in Chebyshev polynomials

The expansion of $\sqrt{1 - x^2}$ in Chebyshev polynomials may be written in the form:

$$\sqrt{1 - x^2} = \sum_n c_n T_n(x) \tag{110}$$

where $T_n(x)$ is a Chebyshev polynomial.

Multiplying both sides by $T_{m(x)}/\sqrt{1 - x^2}$ and integrating over x we obtain:

$$\int_{-1}^1 T_m(x) dx = c_m \frac{\pi}{2} [1 + \delta_{m,0}] \tag{111}$$

where I have used the Chebyshev polynomial orthogonality condition (see integral 7.343 of [126]):

$$\int_{-1}^1 T_m(x) T_n(x) \frac{dx}{\sqrt{1 - x^2}} = \frac{\pi}{2} \delta_{m,n}[\delta_{n,0} + 1]. \tag{112}$$

For odd values of m the integral in Equation (111) is clearly zero. For even values of $m = 2k$ we have;

$$T_{2k}(x) = \cos(2k \arccos(x)) = \cos^2(k \arccos(x)) - \sin^2(k \arccos(x))$$

$$= 2\cos^2(k \arccos(x)) - 1 = 2 T_k^2(x) - 1. \tag{113}$$

Substituting into Equation (111) and using integral 7.341 of [126] we obtain:

$$\frac{\pi}{2}[1 + \delta_{k,0}]c_{2k} = \int_{-1}^1 T_{2k}(x) dx = \int_{-1}^1 [2 T_k^2(x) - 1] dx$$

$$= 2 \int_{-1}^1 [T_k^2(x)] dx - 2 = 2\left\{1 - \frac{1}{4k^2 - 1}\right\} - 2 = -\frac{2}{4k^2 - 1} \tag{114}$$

or

$$c_0 = \frac{2}{\pi} \qquad c_{2k} = -\frac{2}{\pi}\frac{2}{4k^2 - 1} \quad k \geq 1 \tag{115}$$

finally yielding the expansion:

$$\sqrt{1 - x^2} = \frac{2}{\pi}\left[1 - 2\sum_{n=1}^{\infty}\frac{T_{2n}(x)}{4n^2 - 1}\right]. \tag{116}$$

Appendix D: Derivation of the expression for the integral partial photodissociation cross section from the differential cross section

Throughout this appendix I will use the angular momentum coupling formulae from the book of Edmonds [129].

In Appendix C of [89] the following equation was derived for the differential partial photodissociation cross section:

$$\sigma_{vjm_j}(E; \hat{\mathbf{k}}) = \frac{2\pi^2 v}{c\epsilon_0}\frac{1}{4\pi}\left|\sum_{J=J_i-1}^{J_i+1}\sum_{K=\lambda}^{J}(2J+1)^{1/2}D_{K,M_i+m}^{J}(\phi_k, \theta_k, 0)D_{-K,-m_j}^{j}(\phi_k, \theta_k, 0)\right.$$
$$\left. \times \begin{pmatrix} 1 & J_i & J \\ m & M_i & -m+M_i \end{pmatrix}T_{vj}^{JKp'}\right|^2 \tag{117}$$

where the angles ϕ_k, θ_k refer to the scattering direction of the fragments in a space-fixed reference frame and M_i is the space-fixed z-component of the total angular momentum of the original molecule. $\lambda = (1 - (-1)^{J+p}/2)$ where $p = 1$ for negative parity and $p = 2$ for positive parity [74]. 'm' depends on the polarization of the incident radiation. $m = 0$ corresponds to linearly polarized light with the polarization direction defining the space-fixed z axis, while $m = \pm 1$ corresponds to circularly polarized light [89].

Assuming the incident light to be linearly polarized and setting $m = 0$ we obtain:

$$\sigma_{vjm_j}(E; \hat{\mathbf{k}}) = \frac{2\pi^2 v}{c\epsilon_0}\frac{1}{4\pi}\left|\sum_{J=J_i-1}^{J_i+1}\sum_{K=\lambda}^{J}(2J+1)^{1/2}D_{K,M_i}^{J}(\phi_k, \theta_k, 0)D_{-K,-m_j}^{j}(\phi_k, \theta_k, 0)\right.$$
$$\left. \times \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix}T_{vj}^{JKp'}\right|^2 \tag{118}$$

where I have used the symmetry properties of the 3-*j* symbols (see Edmonds [129], Equation (3.7.5)).

This equation is identical in form to Equation (35) of [130]). It provides an expression for the most detailed possible type of photodissociation cross section. The manipulations used in [130] to derive less detailed or more averaged types of cross-section may now be invoked. First of all we multiply out the square term in the above to obtain:

$$\sigma_{vjm_j}(E; \hat{\mathbf{k}}) = \frac{2\pi^2 v}{c\epsilon_0}\frac{1}{4\pi}\sum_{J=J_i-1}^{J_i+1}\sum_{K=\lambda}^{J}\sum_{J'=J_i-1}^{J_i+1}\sum_{K'=\lambda}^{J'}(2J+1)^{1/2}(2J'+1)^{1/2}$$
$$\times D_{K,M_i}^{J}(\phi_k, \theta_k, 0)D_{-K,-m_j}^{j}(\phi_k, \theta_k, 0)D_{K',M_i}^{J'*}(\phi_k, \theta_k, 0)D_{-K',-m_j}^{j*}(\phi_k, \theta_k, 0)$$
$$\times \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \times \begin{pmatrix} J' & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix}T_{vj}^{JKp'}T_{vj}^{J'K'p'*}. \tag{119}$$

We now integrate over the scattering angles ϕ_k, θ_k to obtain an expression for a detailed integral photodissociation cross section. Let us first consider the integral:

$$I = \int_0^\pi \sin\theta_k \, d\theta_k \int_0^{2\pi} d\phi_k D^J_{K,M_i}(\phi_k,\theta_k,0) D^j_{-K,-m_j}(\phi_k,\theta_k,0) D^{J'*}_{K',M_i}(\phi_k,\theta_k,0) D^{j*}_{-K',-m_j}(\phi_k,\theta_k,0). \quad (120)$$

We now make the following substitutions in Equation (120) (see Edmonds [129] Equation (4.2.7)).

$$D^{J'*}_{K',M_i}(\phi_k,\theta_k,0) = (-1)^{K'-M_i} D^{J'}_{-K',-M_i}(\phi_k,\theta_k,0)$$
$$D^{j*}_{-K',-m_j}(\phi_k,\theta_k,0) = (-1)^{-K'+m_j} D^{j}_{K',m_j}(\phi_k,\theta_k,0) \quad (121)$$

followed by (see Edmonds [129], Equation (4.3.2))

$$D^J_{K,M_i}(\phi_k,\theta_k,0) D^{J'}_{-K',-M_i}(\phi_k,\theta_k,0) = \sum_{Lm}(2L+1)\begin{pmatrix} J & J' & L \\ K & -K' & m \end{pmatrix} D^{L*}_{m,0}(\phi_k,\theta_k,0)\begin{pmatrix} J & J' & L \\ M_i & -M_i & 0 \end{pmatrix}$$

$$D^j_{-K,-m_j}(\phi_k,\theta_k,0) D^{j}_{K',m_j}(\phi_k,\theta_k,0) = \sum_{\ell m'}(2\ell+1)\begin{pmatrix} j & j & \ell \\ -K & K' & m' \end{pmatrix} D^{\ell*}_{m',0}(\phi_k,\theta_k,0)\begin{pmatrix} j & j & \ell \\ -m_j & m_j & 0 \end{pmatrix} \quad (122)$$

and (see Edmonds [129], (Equations (4.6.1) and (4.2.7))

$$\int_0^\pi \sin\theta_k \, d\theta_k \int_0^{2\pi} d\phi_k D^{L*}_{m,0}(\phi_k,\theta_k,0) D^{\ell*}_{m',0}(\phi_k,\theta_k,0)$$

$$= (-1)^{-m'}\int_0^\pi \sin\theta_k \, d\theta_k \int_0^{2\pi} d\phi_k D^{L*}_{m,0}(\phi_k,\theta_k,0) D^{\ell}_{-m',0}(\phi_k,\theta_k,0) = (-1)^{-m'}\delta_{m,-m'}\,\delta_{L\ell}\frac{4\pi}{2L+1} \quad (123)$$

where I have assumed that the m values are integers.

Substituting Equations (121), (122) and (123) into Equation (120) we obtain:

$$I = (-1)^{K'-M_i}(-1)^{-K'+m_j}\sum_{Lm}(2L+1)\begin{pmatrix} J & J' & L \\ K & -K' & m \end{pmatrix}\begin{pmatrix} J & J' & L \\ M_i & -M_i & 0 \end{pmatrix}$$

$$\times \sum_{\ell m'}(2\ell+1)\begin{pmatrix} j & j & \ell \\ -K & K' & m' \end{pmatrix}\begin{pmatrix} j & j & \ell \\ -m_j & m_j & 0 \end{pmatrix}(-1)^{-m'}\delta_{m,-m'}\,\delta_{L\ell}\frac{4\pi}{2L+1}$$

$$= (-1)^{m_j-M_i}4\pi\sum_{LM}(2L+1)(-1)^M\begin{pmatrix} J & J' & L \\ K & -K' & M \end{pmatrix}\begin{pmatrix} J & J' & L \\ M_i & -M_i & 0 \end{pmatrix}$$

$$\times\begin{pmatrix} j & j & L \\ -K & K' & -M \end{pmatrix}\begin{pmatrix} j & j & L \\ -m_j & m_j & 0 \end{pmatrix}. \quad (124)$$

The detailed partial integral photodissociation cross section, which is given by the integral of Equation (119) over all angles is therefore:

$$\sigma_{vjm_j}(E) = \frac{2\pi^2 v}{c\epsilon_0}\sum_{J=J_i-1}^{J_i+1}\sum_{K=\lambda}^{J}\sum_{J'=J_i-1}^{J_i+1}\sum_{K'=\lambda}^{J'}(2J+1)^{1/2}(2J'+1)^{1/2}(-1)^{m_j-M_i}$$

$$\times\sum_{LM}(2L+1)(-1)^M\begin{pmatrix} J & J' & L \\ K & -K' & M \end{pmatrix}\begin{pmatrix} J & J' & L \\ M_i & -M_i & 0 \end{pmatrix}$$

$$\times\begin{pmatrix} j & j & L \\ -K & K' & -M \end{pmatrix}\begin{pmatrix} j & j & L \\ -m_j & m_j & 0 \end{pmatrix}\begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix}$$

$$\times\begin{pmatrix} J' & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix}T^{JKp'}_{vj}T^{J'K'p'*}_{vj}. \quad (125)$$

The partial integral photodissociation cross section summed over all final m_j states is given by:

$$\bar{\sigma}_{vj}(E) = \sum_{m_j} \sigma_{vjm_j}(E)$$

$$= \frac{2\pi^2 v}{c\epsilon_0} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} \sum_{J'=J_i-1}^{J_i+1} \sum_{K'=\lambda}^{J'} (2J+1)^{1/2}(2J'+1)^{1/2}(-1)^{-M_i}$$

$$\times \sum_{LM} (2L+1)(-1)^M \begin{pmatrix} J & J' & L \\ K & -K' & M \end{pmatrix} \begin{pmatrix} J & J' & L \\ M_i & -M_i & 0 \end{pmatrix} \begin{pmatrix} j & j & L \\ -K & K' & -M \end{pmatrix}$$

$$\times \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J' & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} T_{vj}^{JKp'} T_{vj}^{J'K'p'*} \left\{ \sum_{m_j} (-1)^{m_j} \begin{pmatrix} j & j & L \\ -m_j & m_j & 0 \end{pmatrix} \right\}. \quad (126)$$

I now consider the final curly bracket of Equation (126). Edmonds [129], Equation (3.7.8) is:

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = (2j_3+1)^{-1} \delta_{j_3 j_3'} \delta_{m_3 m_3'} \delta(j_1 j_2 j_3). \quad (127)$$

Now let $j_3' = 0$, $m_3' = 0$, $j_1 = j_2 = j$, $m_1 = m_j = -m_2$ and $j_3 = L$ and from Edmonds [129], Equation (3.7.9) we have:

$$\begin{pmatrix} j & j & 0 \\ m_j & -m_j & 0 \end{pmatrix} = (-1)^{j-m_j}(2j+1)^{-(1/2)}. \quad (128)$$

Substituting Equation (128) into Equation (127) now gives:

$$\sum_{m_j} \begin{pmatrix} j & j & L \\ m_j & -m_j & 0 \end{pmatrix} (-1)^{-m_j}(2j+1)^{-(1/2)} = (-1)^j (2L+1)^{-1} \delta_{L0}\, \delta(jjL) \quad (129)$$

or

$$\sum_{m_j} (-1)^{m_j} \begin{pmatrix} j & j & L \\ -m_j & m_j & 0 \end{pmatrix} = (-1)^{j-L}(2L+1)^{-1}(2j+1)^{1/2} \delta_{L0}\, \delta(jjL). \quad (130)$$

Now substituting into Equation (126) we obtain:

$$\bar{\sigma}_{vj}(E) = \frac{2\pi^2 v}{c\epsilon_0} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} \sum_{J'=J_i-1}^{J_i+1} \sum_{K'=\lambda}^{J'} (2J+1)^{1/2}(2J'+1)^{1/2}(2j+1)^{1/2}(-1)^{j-M_i} \begin{pmatrix} J & J' & 0 \\ K & -K' & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} J & J' & 0 \\ M_i & -M_i & 0 \end{pmatrix} \begin{pmatrix} j & j & 0 \\ -K & K' & 0 \end{pmatrix} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J' & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} T_{vj}^{JKp'} T_{vj}^{J'K'p'*}. \quad (131)$$

Noting that a 3-j symbol of the type

$$\begin{pmatrix} J & J' & 0 \\ K & -K' & 0 \end{pmatrix}$$

is zero unless $J = J'$ and $K = K'$ and also making use again of Edmonds [129], Equation (3.7.9) (see Equation (128)) we obtain:

$$\bar{\sigma}_{vj}(E) = \frac{2\pi^2 v}{c\epsilon_0} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} \left| \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} T_{vj}^{JKp'} \right|^2. \quad (132)$$

Finally we can average the partial integral cross section over all possible orientations of the initial total angular momentum:

$$
\bar{\bar{\sigma}}_{vj}(E) = \frac{1}{2J_i + 1} \sum_{M_i} \bar{\sigma}_{vj}(E)
$$

$$
= \frac{2\pi^2 v}{c\epsilon_0} \frac{1}{2J_i + 1} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} \left\{ \sum_{M_i} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \right\} T_{vj}^{JKp'} T_{vj}^{JKp'*}. \tag{133}
$$

Using Edmonds [129], Equation (3.7.8) the term in curly brackets can be shown to be equal to $\frac{1}{3}$. Equation (133) therefore becomes:

$$
\bar{\bar{\sigma}}_{vj}(E) = \frac{2\pi^2 v}{3c\epsilon_0} \frac{1}{2J_i + 1} \sum_{J=J_i-1}^{J_i+1} \sum_{K=\lambda}^{J} \left| T_{vj}^{JKp'} \right|^2. \tag{134}
$$

Appendix E: Half Fourier transform over time occurring in the expression for the partial photodissociation cross section

The Fourier transform over time occurring in the expression for the partial photodissociation cross section (see Equation (58)) is:

$$
I = \frac{1}{2\pi} \int_{t=0}^{\infty} \exp(iEt/\hbar) \langle \chi_{v'j'K'}(\mathbf{r}) | \Phi^{JK'}(\mathbf{r}, R = R_\infty, t) \rangle dt. \tag{135}
$$

We first introduce a Dirac delta function $\delta(R - R_\infty)$ so as to obtain the full time-dependent wavepacket in the integral:

$$
I = \int_0^\infty dR \delta(R - R_\infty) \left\{ \frac{1}{2\pi} \int_{t=0}^\infty \exp(iEt/\hbar) \langle \chi_{v'j'K'}(\mathbf{r}) | \Phi^{JK'}(\mathbf{r}, R, t) \rangle dt \right\}. \tag{136}
$$

We now substitute in the Chebyshev expansion of the time-dependent wavepacket from Equation (14):

$$
I = \int_0^\infty dR \delta(R - R_\infty) \sum_{n=0}^{N} (2 - \delta_{no})
$$
$$
\times \left\{ \frac{1}{2\pi} \int_{t=0}^\infty dt \exp(iEt/\hbar) \exp\left(\frac{-i((\Delta E/2) + V_{\min})t}{\hbar} \right) J_n\left(\frac{\Delta E t}{2\hbar} \right) \right\} \langle \chi_{v'j'K'}(\mathbf{r}) | \Phi_n^{JK'} \rangle \tag{137}
$$

where (see also Equations (12) and (13) and Appendix A)

$$
\Phi_n^{JK'} = Q_n(-i\hat{\mathbf{H}}_s) \Phi^{JK'}(\mathbf{r}, R, t = 0). \tag{138}
$$

The integral in curly brackets in Equation (137) is discussed in Appendix B. Using Equation (109) of Appendix B to substitute for the integral in curly brackets in Equation (137) we obtain:

$$
I = \frac{\hbar}{\pi \Delta E \sin\phi} \sum_{n=0}^{N} (2 - \delta_{no}) i^n \exp[-in\phi] \langle \chi_{v'j'K'}(\mathbf{r}) | \Phi_n^{JK'}(R = R_\infty) \rangle \tag{139}
$$

where ϕ depends on the energy and is defined in Equations (25) and (26) and also in Appendix B. In analogy with the treatment of the reactive scattering $\mathbf{S}$ matrix elements we now incorporate an extra 'i' into the definition of the wavepacket iterates (see Equations (27) and (29)):

$$
\eta_n^{JK'} = i^n \Phi_n^{JK'}. \tag{140}
$$

Substituting this into Equation (139) we obtain:

$$\frac{1}{2\pi} \int_{t=0}^{\infty} \exp(iEt/\hbar) \langle \chi_{\upsilon'j'K'}(\mathbf{r}) | \Phi^{JK'}(\mathbf{r}, R = R_{\infty}, t) \rangle \mathrm{d}t$$

$$= \frac{\hbar}{\pi \Delta E \sin \phi} \sum_{n=0}^{N} (2 - \delta_{no}) \exp[-in\phi] \langle \chi_{\upsilon'j'K'}(\mathbf{r}) | \eta_n^{JK'}(R = R_{\infty}) \rangle. \tag{141}$$

Appendix F: Use of only the real part of the time-dependent wavepacket in the evaluation of the total integral photodissociation cross section

In this Appendix I use the same logic as was used in Appendix A of [86]. The equation for the total integral photodissociation cross section is (Equation (47)):

$$\sigma_{\text{tot}}(E) = \frac{2\pi\nu}{c\epsilon_0\hbar} \int_0^{\infty} \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) | \Phi(\mathbf{r}, \mathbf{R}, t) \rangle. \tag{142}$$

We now consider the integral on the right hand side of the equation, but replace the time-dependent wavepacket by its real part. Notice that the initial wavepacket, $\Phi(\mathbf{r}, \mathbf{R}, t = 0)$, is real. This will be useful to us in the execution of the real wavepacket method.

$$I = \int_0^{\infty} \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \left\langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) \left| \frac{1}{2} \{ \Phi(\mathbf{r}, \mathbf{R}, t) + \Phi^*(\mathbf{r}, \mathbf{R}, t) \} \right. \right\rangle$$

$$= \frac{1}{2} \int_0^{\infty} \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) | \Phi(\mathbf{r}, \mathbf{R}, t) \rangle + \frac{1}{2} \int_0^{\infty} \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) | \Phi^*(\mathbf{r}, \mathbf{R}, t) \rangle$$

$$= \frac{1}{2} \int_0^{\infty} \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \left\langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) \left| \exp\left[\frac{-i\hat{\mathbf{H}}t}{\hbar}\right] \Phi(\mathbf{r}, \mathbf{R}, t = 0) \right. \right\rangle$$

$$+ \frac{1}{2} \int_0^{\infty} \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \left\langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) \left| \left\{ \exp\left[\frac{-i\hat{\mathbf{H}}t}{\hbar}\right] \Phi(\mathbf{r}, \mathbf{R}, t = 0) \right\}^* \right. \right\rangle. \tag{143}$$

The identity operator, $\hat{I}$, for scattering states may be expanded in a complete set of continuum wavefunctions [86]

$$\hat{I} = \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F |\psi_F^-(E')\rangle \langle \psi_F^-(E')|. \tag{144}$$

We now insert this expansion to the left of the wavepackets $\Phi(\mathbf{r}, \mathbf{R}, t = 0)$ in Equation (143):

$$I = \frac{1}{2} \int_0^{\infty} \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \left\langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) \left| \exp\left[\frac{-i\hat{\mathbf{H}}t}{\hbar}\right] \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F |\psi_F^-(E')\rangle \langle \psi_F^-(E') | \Phi(\mathbf{r}, \mathbf{R}, t = 0) \right. \right\rangle$$

$$+ \frac{1}{2} \int_0^{\infty} \mathrm{d}t \exp\left[\frac{iEt}{\hbar}\right] \left\langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) \left| \left\{ \exp\left[\frac{-i\hat{\mathbf{H}}t}{\hbar}\right] \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F |\psi_F^-(E')\rangle \langle \psi_F^-(E') | \Phi(\mathbf{r}, \mathbf{R}, t = 0) \right\}^* \right. \right\rangle$$

$$= \frac{1}{2} \int_0^{\infty} \mathrm{d}t \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F \exp\left[\frac{iEt}{\hbar}\right] \left\langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) \left| \exp\left[\frac{-iE't}{\hbar}\right] | \psi_F^-(E')\rangle \langle \psi_F^-(E') | \Phi(\mathbf{r}, \mathbf{R}, t = 0) \right. \right\rangle$$

$$+ \frac{1}{2} \int_0^{\infty} \mathrm{d}t \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F \exp\left[\frac{iEt}{\hbar}\right] \left\langle \Phi(\mathbf{r}, \mathbf{R}, t = 0) \left| \left\{ \exp\left[\frac{-iE't}{\hbar}\right] | \psi_F^-(E')\rangle \langle \psi_F^-(E') | \Phi(\mathbf{r}, \mathbf{R}, t = 0) \right\}^* \right. \right\rangle$$

$$= \frac{1}{2} \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F \left\{ \int_0^{\infty} \mathrm{d}t \exp\left[\frac{i(E-E')t}{\hbar}\right] \right\} \langle \Phi(\mathbf{r},\mathbf{R},t=0) | \psi_F^-(E') \rangle \langle \psi_F^-(E') | \Phi(\mathbf{r},\mathbf{R},t=0) \rangle$$

$$+ \frac{1}{2} \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F \left\{ \int_0^{\infty} \mathrm{d}t \exp\left[\frac{i(E+E')t}{\hbar}\right] \right\} \langle \Phi(\mathbf{r},\mathbf{R},t=0) | \{ | \psi_F^-(E') \rangle \langle \psi_F^-(E') | \Phi(\mathbf{r},\mathbf{R},t=0) \}^* \rangle \quad (145)$$

but

$$\int_0^{\infty} \mathrm{d}t \exp\left[\frac{i(E-E')t}{\hbar}\right] = 2\pi\hbar\delta(E-E') \quad (146)$$

therefore

$$I = \frac{1}{2} \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F 2\pi\hbar\delta(E-E') \langle \Phi(\mathbf{r},\mathbf{R},t=0) | \psi_F^-(E') \rangle \langle \psi_F^-(E') | \Phi(\mathbf{r},\mathbf{R},t=0) \rangle$$

$$+ \frac{1}{2} \int_{-\infty}^{\infty} \mathrm{d}E' \sum_F 2\pi\hbar\delta(E+E') \langle \Phi(\mathbf{r},\mathbf{R},t=0) | \{ | \psi_F^-(E') \rangle \langle \psi_F^-(E') | \Phi(\mathbf{r},\mathbf{R},t=0) \}^* \rangle$$

$$= \frac{1}{2} \left\{ 2\pi\hbar \sum_F \langle \Phi(\mathbf{r},\mathbf{R},t=0) | \psi_F^-(E) \rangle \langle \psi_F^-(E) | \Phi(\mathbf{r},\mathbf{R},t=0) \rangle \right.$$

$$\left. \times + 2\pi\hbar \sum_F \langle \Phi(\mathbf{r},\mathbf{R},t=0) | \{ | \psi_F^-(-E) \rangle \langle \psi_F^-(-E) | \Phi(\mathbf{r},\mathbf{R},t=0) \}^* \rangle \right\}. \quad (147)$$

We choose our zero of energy to lie at the onset of the scattering continuum. The second term in Equation (147) gives non-zero contributions only for negative energies. These energies do not lie in the continuum and do not contribute to the photodissociation of the molecule. At the energies of interest only the first term in the expression for the above integral contributes. If we had not taken the real part of the wavepacket in Equation (143) we would have obtained exactly the same expression except that the factor of $\frac{1}{2}$ in the front and the second term would have been absent. We conclude that we may use only the real part of the time-dependent wavepacket to obtain the total integral cross section, but that we must then multiply the result by 2.