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State-to-State Reactive Scattering

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1. INTRODUCTION

The field of quantum reactive scattering theory has progressed a great deal since the mid 1970s. The earliest exact three-dimensional quantum reactive scattering calculations were performed for the prototypical $\text{H}+\text{H}_2 \rightleftharpoons \text{H}_2+\text{H}$ exchange reaction by Kuppermann and Schatz¹ in 1975. More recently, the development of new computational methods and more powerful computers has enabled equally detailed state-to-state calculations to be performed on

a variety of more “chemical” reactions such as $F+H_2 \rightleftharpoons HF+H$.² Approximate state-to-state calculations have also been performed on a whole host of reactions, including some four-atom reactions such as $OH+H_2 \rightleftharpoons H+H_2O$ in which all six internal degrees of freedom have been treated exactly and only the overall rotational motion has been approximated.³ In many cases, the results of these calculations have been invaluable in helping us to interpret the results of modern reaction dynamics experiments and to assess the role of quantum mechanical effects in chemical reaction dynamics. This is likely to become even more the case in the future as the available electronic potential energy surfaces for chemical reactions continue to improve (see *Ab Initio Potential Energy Surfaces for Chemical Reaction Dynamics*).

The central quantity in the quantum theory of chemical reactions is the quantum mechanical probability amplitude or *scattering matrix element*, $S_{\mathbf{p}\mathbf{r}}(E)$, for a transition from an initial channel \mathbf{r} of the reactants to a final channel \mathbf{p} of the products as a function of the scattering energy E (and also implicitly of the conserved total angular momentum quantum number J). Once this quantity is known at sufficiently many values of E (and J) and for sufficiently many reactant and product channels, *all* observable consequences of the reaction can be extracted from it using straightforward and well-established formulae.^{1(b),4} The observables in question range from highly detailed quantities such as state-to-state differential cross sections and rotational polarisations⁴ through to highly averaged quantities such as total reaction cross sections and thermal rate constants,^{1(b)} although these more averaged quantities can also be computed more directly without first calculating all of the detailed state-to-state information⁵ (see *Chemical Reaction Rates*). The reactive scattering matrix elements $S_{\mathbf{p}\mathbf{r}}(E)$ thus contain everything there is to know about a chemical reaction, and the central task of state-to-state reactive scattering theory is to compute them as efficiently as possible.

The fact that this is not an easy task is what makes reactive scattering theory interesting. The fundamental difficulty is the so-called *coordinate problem*: the coordinates which best describe the products of a chemical reaction are not the same as those which best describe the reactants, and this leads to technical difficulties in quantum mechanics where all regions of coordinate space have to be treated simultaneously. The same difficulty does not arise in classical mechanics, where there is nothing to prevent one from running a classical trajectory in whatever set of coordinates one chooses

and simply monitoring whether or not it reacts. Neither is the coordinate problem an issue for other molecular collision processes such as inelastic energy transfer, in which the optimum reactant and product coordinates are the same. The coordinate problem is thus a unique and complicating feature of quantum mechanical reactive scattering (or “rearrangement”) theory.

As a result of this complication, an extraordinarily diverse variety of methods have been suggested over the years for calculating the reactive scattering matrix elements $S_{\text{pr}}(E)$. In order to give the reader a broad overview of these methods, we shall confine our attention in this article to the simple collinear model for an $A+BC \rightleftharpoons AB+C$ reaction and describe how each method applies to this model in turn. The collinear model itself is introduced in Section 2, where the reactive scattering problem is defined in terms of the optimum (mass-scaled Jacobi) coordinates of the reactant and product arrangements. Following this, four different approaches to solving the reactive scattering problem are described in Sections 3 to 6. The first two of these approaches attack the problem by introducing new coordinates which swing smoothly from reactants to products, whereas the second two approaches attack the problem by introducing new expressions for the reactive scattering matrix elements $S_{\text{pr}}(E)$. Section 7 concludes by summarising the advantages and disadvantages of the various approaches to the reactive scattering problem that are discussed in the preceding four sections of the article.

2. COLLINEAR REACTIVE SCATTERING

The coordinate problem becomes apparent as soon as one considers even the simplest models for chemical reactions, such as the collinear model for an atom-diatom reaction



The natural coordinates to use to describe the reactants of this reaction are the distance R_A between A and the centre-of-mass of BC and the distance r_{BC} between B and C, since these coordinates describe respectively the relative translational motion of A towards BC and the vibrational motion of the reactant diatomic. Similarly, the natural coordinates to use to describe the products are the distance R_C between C and the centre-of-mass of AB and

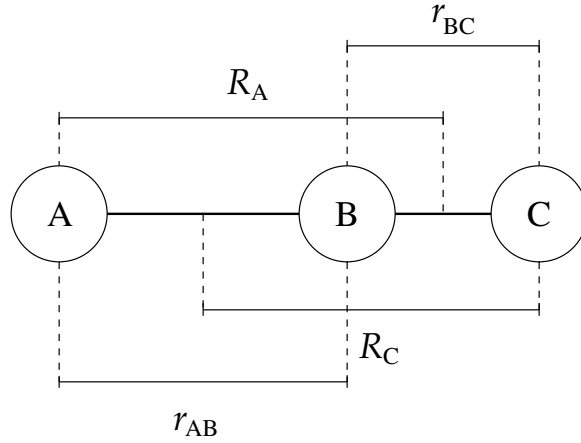


Figure 1: The coordinate problem for a collinear A+BC reaction

the distance r_{AB} between A and B, which are clearly very different from the reactant coordinates (see Figure 1).

Instead of working directly with these coordinates, it is more convenient to work with the *mass-scaled Jacobi coordinates* R_a and r_a of the reactants:

$$R_a = \lambda_a R_A, \quad (2)$$

and

$$r_a = \lambda_a^{-1} r_{BC}, \quad (3)$$

where

$$\lambda_a = \left(\frac{m_A m_{BC}^2}{m_B m_C m_{ABC}} \right)^{\frac{1}{4}}, \quad (4)$$

and with the analogous coordinates R_c and r_c of the products:

$$R_c = \lambda_c R_C, \quad (5)$$

and

$$r_c = \lambda_c^{-1} r_{AB}, \quad (6)$$

where

$$\lambda_c = \left(\frac{m_C m_{AB}^2}{m_A m_B m_{ABC}} \right)^{\frac{1}{4}}. \quad (7)$$

The reason for this is that the collinear reactive scattering Hamiltonian can be written equivalently in terms of the mass-scaled Jacobi coordinates of either arrangement $\alpha = a$ or c as

$$H = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R_\alpha^2} + \frac{\partial^2}{\partial r_\alpha^2} \right) + V(R_\alpha, r_\alpha), \quad (8)$$

where the reduced mass μ is the same in both cases:

$$\mu = \left(\frac{m_A m_B m_C}{m_{ABC}} \right)^{\frac{1}{2}}. \quad (9)$$

Indeed the (collinear) mass-scaled Jacobi coordinates of the two arrangements are related by the orthogonal transformation

$$\begin{pmatrix} R_c \\ r_c \end{pmatrix} = \begin{pmatrix} \cos \Theta & \sin \Theta \\ \sin \Theta & -\cos \Theta \end{pmatrix} \begin{pmatrix} R_a \\ r_a \end{pmatrix}, \quad (10)$$

where Θ is the *skewing angle* between the arrangements:

$$\Theta = \arctan \left(\frac{m_B}{\mu} \right). \quad (11)$$

This transformation is illustrated in Figure 2, which shows a typical potential energy surface $V(R_\alpha, r_\alpha)$ for a collinear $A+BC \rightleftharpoons AB+C$ reaction as a contour plot in mass-scaled Jacobi coordinates. Notice in particular that the presence of a single reduced mass μ in Eq. (8) means that there is no preferred direction in these coordinates and that Figure 2 therefore provides a kinematically democratic picture of the reaction.

The scattering matrix elements for this collinear model can be defined by noting that the reactive scattering Hamiltonian H in Eq. (8) separates at large R_α into the sum of a translational kinetic energy operator and a vibrational Hamiltonian H_α :

$$H \xrightarrow{R_\alpha \rightarrow \infty} -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R_\alpha^2} + H_\alpha, \quad (12)$$

where

$$H_\alpha = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r_\alpha^2} + V_\alpha(r_\alpha), \quad (13)$$

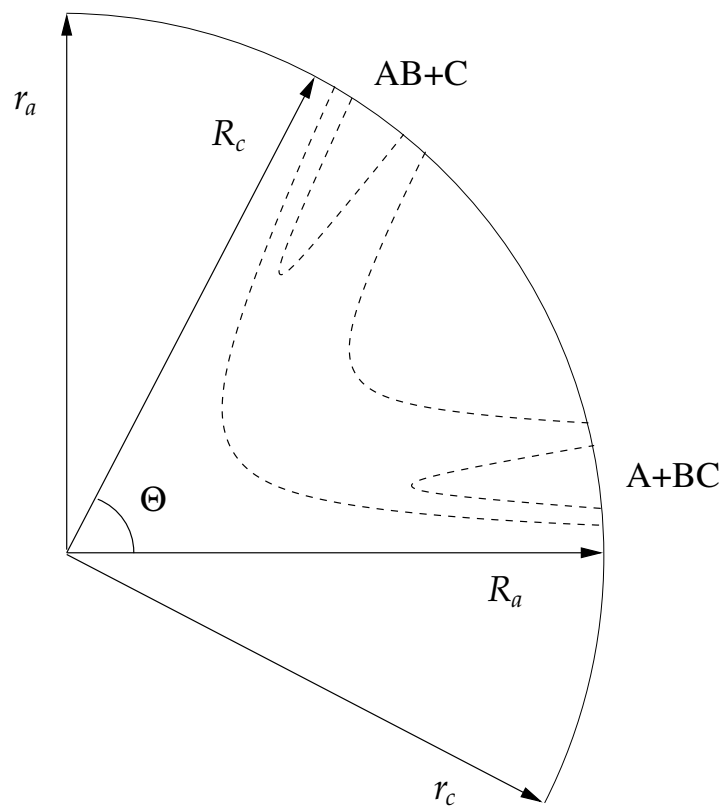


Figure 2: Mass-scaled Jacobi coordinates for a collinear A+BC reaction. The sector labelled A+BC corresponds to the reactant arrangement and the sector labelled AB+C to the product arrangement.

with

$$V_\alpha(r_\alpha) = \lim_{R_\alpha \rightarrow \infty} V(R_\alpha, r_\alpha). \quad (14)$$

As a result of this separation, the asymptotic solutions of the Schrödinger equation in each arrangement must be linear combinations of incoming (−) and outgoing (+) wavefunctions of the form

$$\phi_{E\alpha\nu}^\pm(R_\alpha, r_\alpha) = v_{\alpha\nu}^{-\frac{1}{2}} e^{\pm ik_{\alpha\nu} R_\alpha} \phi_{\alpha\nu}(r_\alpha), \quad (15)$$

where $\phi_{\alpha\nu}(r_\alpha)$ is an eigenstate of the vibrational Hamiltonian

$$H_\alpha \phi_{\alpha\nu}(r_\alpha) = \epsilon_{\alpha\nu} \phi_{\alpha\nu}(r_\alpha), \quad (16)$$

and $k_{\alpha\nu} = \sqrt{2\mu(E - \epsilon_{\alpha\nu})}/\hbar$ and $v_{\alpha\nu} = \hbar k_{\alpha\nu}/\mu$ in Eq. (15) are respectively the asymptotic wavenumber and velocity in channel $\alpha\nu$.

The particular reactive scattering wavefunctions that define the scattering matrix are the solutions $\psi_{E\alpha\nu}$ of the Schrödinger equation

$$H \psi_{E\alpha\nu} = E \psi_{E\alpha\nu} \quad (17)$$

subject to the following asymptotic boundary condition in each arrangement $\alpha' = a$ and $\alpha' = c$:

$$\psi_{E\alpha\nu} \stackrel{R_{\alpha'} \rightarrow \infty}{\sim} \phi_{E\alpha\nu}^-(R_\alpha, r_\alpha) \delta_{\alpha\alpha'} - \sum_{\nu'} \phi_{E\alpha'\nu'}^+(R_{\alpha'}, r_{\alpha'}) S_{\alpha'\nu',\alpha\nu}(E). \quad (18)$$

Note that this boundary condition is simply a linear combination of functions of the form given in Eq. (15), as required by the above separation argument, and that it corresponds to the physical situation of an incoming wave in channel $\alpha\nu$ and outgoing scattered waves in all energetically accessible channels $\alpha'\nu'$ at energy E . The coefficients of the scattered waves are the scattering matrix elements $S_{\alpha'\nu',\alpha\nu}(E)$, which include reactive scattering matrix elements of the form $S_{c\nu',av}(E)$, inelastic scattering matrix elements of the form $S_{a\nu',av}(E)$, and elastic scattering matrix elements of the form $S_{a\nu,av}(E)$.

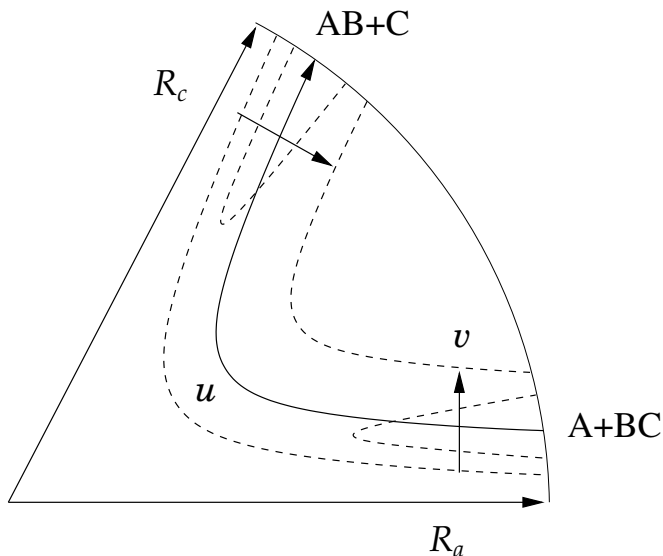


Figure 3: The natural collision coordinates u and v

3. NATURAL COLLISION COORDINATES

The first solution to the reactive scattering problem we shall consider is the oldest and the most intuitive.⁶ It recognises that R_a and r_a are the ideal coordinates to use to describe the reactants and R_c and r_c are the ideal coordinates to use to describe the products, and simply “matches” these two coordinate systems together in the intervening interaction region. The matching is accomplished by constructing a translational *reaction coordinate*, u , which approximates the minimum energy path between reactants and products and is defined such that u is proportional to $-R_a$ in the limit as $u \rightarrow -\infty$ and to $+R_c$ in the limit as $u \rightarrow \infty$. The remaining coordinate is then a vibrational coordinate v orthogonal to u which is parallel to r_a as $u \rightarrow -\infty$ and to r_c as $u \rightarrow \infty$, as shown in Figure 3.

Since the motion in v is a bound vibrational motion at each value of u , the reactive scattering wavefunction $\psi_{E\alpha\nu}$ can be expanded in a basis set of vibrational wavefunctions $\phi_n(v)$ in this coordinate with u -dependent

expansion coefficients $\psi_{n,E\alpha\nu}(u)$:

$$\psi_{E\alpha\nu}(u, v) = \sum_n \psi_{n,E\alpha\nu}(u) \phi_n(v). \quad (19)$$

Substitution of this expansion into the Schrödinger equation $H\psi_{E\alpha\nu} = E\psi_{E\alpha\nu}$ then leads to a set of coupled second-order linear differential equations for the translational wavefunctions $\psi_{n,E\alpha\nu}(u)$ which can be solved using standard close-coupling techniques⁷ (see *Close-Coupling Calculations for Molecular Collision Processes*). This is essentially how Kuppermann and Schatz performed their $\text{H}+\text{H}_2 \rightleftharpoons \text{H}_2+\text{H}$ reactive scattering calculations in 1975,¹ although the three-dimensional problem they studied was of course considerably more complicated than the simple collinear model we are describing here.

The natural collision coordinates u and v in Figure 3 are intuitively appealing because they swing naturally from reactants to products in such a way that u remains a translational coordinate and v remains a vibrational coordinate throughout the course of the reaction. The price that has to be paid for this, however, is that the kinetic energy operator and volume element in natural collision coordinates are rather awkward,⁶ and this in turn complicates the calculation. Moreover the problem is compounded in the three-dimensional case by the fact that a general atom+diatom reaction has three different chemical arrangements (A+BC, B+CA and C+AB), so there are in general three different reaction coordinates u between the various possible reactants and products. Because of these and other difficulties, natural collision coordinates have now given way to newer and better solutions to the quantum reactive scattering problem and are simply of historical interest.

4. HYPERSPHERICAL COORDINATES

The basic idea behind hyperspherical coordinates is the same as the idea behind natural collision coordinates: to find a single set of coordinates that swings naturally from reactants to products. In this case, however, the idea is implemented in a way that is motivated more by mathematical considerations than by physical intuition, with the consequence that hyperspherical coordinate methods currently provide one of the most reliable and widely-used solutions to the quantum mechanical reactive scattering problem.

The hyperspherical coordinates for a collinear $A+BC \rightleftharpoons AB+C$ reaction are simply the polar coordinates

$$\rho = (R_\alpha^2 + r_\alpha^2)^{\frac{1}{2}}, \quad (20)$$

and

$$\theta_\alpha = \arctan\left(\frac{r_\alpha}{R_\alpha}\right). \quad (21)$$

Note that the *hyperradius* ρ is independent of the arrangement label α by virtue of the orthogonal transformation in Eq. (10) and that the *hyperangles* θ_a and θ_c of the two arrangements are obliged by this transformation to sum to the skewing angle Θ :

$$\theta_a + \theta_c = \Theta. \quad (22)$$

The hyperspherical coordinates ρ , θ_a and θ_c are shown in Figure 4. Although they do not bear any resemblance to the mass-scaled Jacobi coordinates at small ρ , it is clear from this figure that the hyperangle θ_α will become parallel to the vibrational coordinate r_α and the hyperradius ρ will become parallel to the translational coordinate R_α within each arrangement in the limit of sufficiently large ρ . In this sense, therefore, the hyperspherical coordinates swing smoothly from reactants to products like the natural collision coordinates in Figure 3.

The main advantage that hyperspherical coordinates have over natural collision coordinates is that the kinetic energy operator and volume element are far simpler in hyperspherical coordinates. The collinear reactive scattering Hamiltonian can be written in terms of ρ and θ_a , for example, as

$$H = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial}{\partial \theta_a^2} \right) + V(\rho, \theta_a), \quad (23)$$

which is not a great deal more complicated than the mass-scaled Jacobi coordinate Hamiltonian in Eq. (8), and the integral over collinear coordinate space of a general function $f(\rho, \theta_a)$ is simply

$$\int_{2D} f(\tau) d\tau = \int_0^\infty \int_0^\Theta f(\rho, \theta_a) \rho d\rho d\theta_a. \quad (24)$$

More importantly, in contrast to the situation described above for natural collision coordinates, comparatively simple Hamiltonians and volume integrals

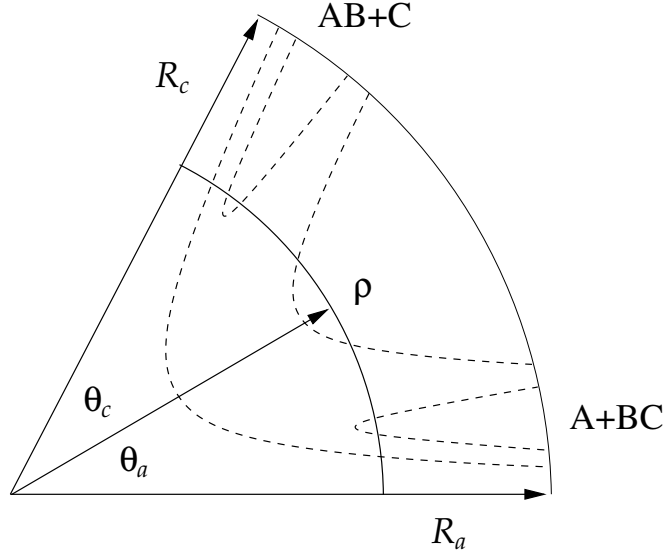


Figure 4: The hyperspherical coordinates ρ , θ_a and θ_c

are also obtained for a variety of triatomic⁸ and tetratomic⁹ hyperspherical coordinate systems in three-dimensional space.

The reactive scattering problem in hyperspherical coordinates can in principle be solved in the same way as in the natural collision coordinate case by expanding the wavefunction $\psi_{E\alpha\nu}$ in a set of orthonormal basis functions $\phi_n(\theta_a)$ in the bound “vibrational” coordinate θ_a with ρ -dependent expansion coefficients $\psi_{n,E\alpha\nu}(\rho)$:

$$\psi_{E\alpha\nu}(\rho, \theta_a) = \rho^{-\frac{1}{2}} \sum_n \psi_{n,E\alpha\nu}(\rho) \phi_n(\theta_a). \quad (25)$$

Substituting this expansion into the Schrödinger equation $H\psi_{E\alpha\nu} = E\psi_{E\alpha\nu}$ then leads to a set of *close-coupled equations* for the translational wavefunctions $\psi_{n,E\alpha\nu}(\rho)$ which can be solved using standard techniques:⁷

$$\frac{d^2}{d\rho^2} \psi_{n,E\alpha\nu}(\rho) = \sum_{n'} W_{nn'}(\rho) \psi_{n',E\alpha\nu}(\rho), \quad (26)$$

where

$$W_{nn'}(\rho) = \frac{2\mu}{\hbar^2} \int_0^\Theta \phi_n(\theta_a)^* [H(\rho) - E] \phi_{n'}(\theta_a) d\theta_a, \quad (27)$$

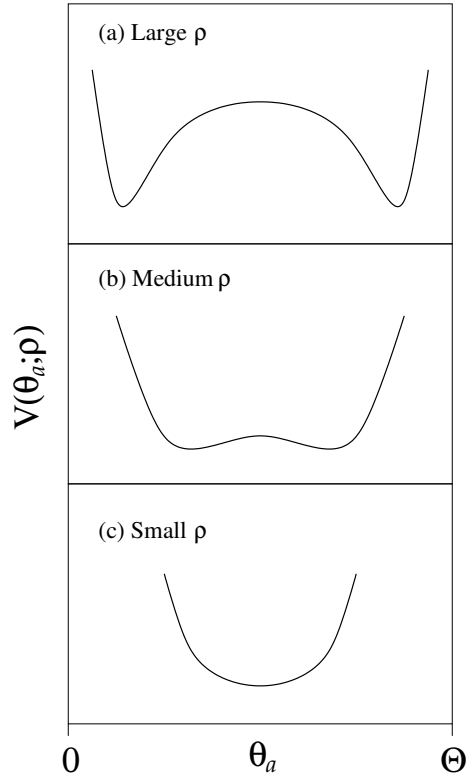


Figure 5: Typical potential energy profiles in the hyperangular coordinate θ_a as a function of the hyperradius ρ

with

$$H(\rho) = -\frac{\hbar^2}{2\mu\rho^2} \left(\frac{d^2}{d\theta_a^2} + \frac{1}{4} \right) + V(\rho, \theta_a). \quad (28)$$

However, whereas the natural collision coordinate v is a simple vibrational coordinate with a Morse oscillator-like potential energy curve throughout the course of the reaction, as can be seen by inspection of Figure 3, the hyperangular coordinate θ_a is subject to a more complicated potential energy profile that changes very dramatically as a function of ρ (see Figures 4 and 5).

Because of this more complicated potential energy behaviour, it is in-

efficient to use a fixed hyperangular basis set $\phi_n(\theta_a)$ to describe the entire course of the reaction as in Eq. (25), and a lot of work has consequently gone in to finding better ways to represent the wavefunction in hyperspherical coordinates. The most widely adopted solution to this problem is to use a sector-by-sector adiabatic method in which the hyperangular basis functions $\phi_n(\theta_a)$ are replaced by the local eigenfunctions $\phi_n(\theta_a; \rho^k)$ of the hyperspherical coordinate *surface eigenvalue problem* at the centre ρ^k of each consecutive sector k in the hyperradius ρ :

$$H(\rho^k) \phi_n(\theta_a; \rho^k) = \epsilon_n(\rho^k) \phi_n(\theta_a; \rho^k). \quad (29)$$

Although substantial progress has already been made in this direction, the development of new methods for solving the full three-dimensional version of this eigenvalue problem in a way that works equally well for the entire range of potential energy profiles that are encountered at different values of ρ^k is still a very active area of quantum reactive scattering theory research.¹⁰

5. TIME-INDEPENDENT VARIATIONAL METHODS

We now come on to a more global approach to the reactive scattering problem in which the reactive scattering matrix elements $S_{\alpha'\nu',\alpha\nu}(E)$ are emphasised as the goal of the calculation and the coordinate problem is addressed merely as an afterthought. Rather than trying to find a new set of coordinates that swing smoothly from reactants to products, as in the natural collision coordinate and hyperspherical coordinate methods described above, the thrust of the methods to be described here and in the following section is thus to find new expressions for the scattering matrix elements that can be implemented in a more generic (and in particular a less coordinate-specific) way.

An abundant source of such expressions is provided by the time-independent variational principles that became popular in reactive scattering theory in the late 1980s. There are at least three different scattering variational principles, associated with the names of Kohn,¹¹ Schwinger,¹² and Newton,¹³ each of which can be combined with a variety of different scattering boundary conditions.^{14,15} However, for purposes of illustration, we shall concentrate in this section on one particularly straightforward variational method known as the S-matrix version of the Kohn variational principle.¹⁴ Furthermore, in

order to describe this method as simply as possible, we shall begin (following Zhang, Chu and Miller¹⁴) with a discussion of potential scattering before considering the added complications that arise for reactions.

5.1 Variational Theory

The potential scattering Schrödinger equation $H\psi_E = E\psi_E$ can be written in the coordinate representation as

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V(R)\right)\psi_E(R) = E\psi_E(R), \quad (30)$$

where the potential $V(R)$ vanishes as $R \rightarrow \infty$. As in Eq. (18), the boundary conditions on the wavefunction $\psi_E(R)$ are that it must be regular at the origin and tend to a linear combination of incoming and outgoing waves at infinity:

$$\psi_E(R \rightarrow 0) \sim 0, \quad (31)$$

and

$$\psi_E(R \rightarrow \infty) \sim \phi_E^-(R) - \phi_E^+(R) S(E), \quad (32)$$

where

$$\phi_E^\pm(R) = v^{-\frac{1}{2}} e^{\pm ikR}, \quad (33)$$

with $k = \sqrt{2\mu E}/\hbar$ and $v = \hbar k/\mu$. The boundary condition in Eq. (32) defines the scattering “matrix” $S(E)$, which in this case is simply a complex scalar of modulus one and is the goal of the potential scattering calculation.

In terms of these definitions, the S-matrix version of the Kohn variational principle is embodied in the variational functional

$$S[\tilde{\psi}_E] = \tilde{S}(E) + \frac{i}{\hbar} \langle \tilde{\psi}_E^* | H - E | \tilde{\psi}_E \rangle, \quad (34)$$

where $\tilde{\psi}_E(R)$ can be any trial wavefunction satisfying both

$$\tilde{\psi}_E(R \rightarrow 0) \sim 0, \quad (35)$$

and

$$\tilde{\psi}_E(R \rightarrow \infty) \sim \phi_E^-(R) - \phi_E^+(R) \tilde{S}(E). \quad (36)$$

Clearly, since the exact wavefunction $\psi_E(R)$ satisfies the Schrödinger equation $H\psi_E = E\psi_E$, the corresponding functional $S[\psi_E]$ is equal to the exact

scattering matrix $S(E)$. Moreover it is straightforward to show using integration by parts that the first variation of $S[\psi_E]$ is

$$\delta S[\psi_E] = \delta S(E) + \frac{i}{\hbar} \langle \psi_E^* | H - E | \delta \psi_E \rangle = 0, \quad (37)$$

and therefore that the functional $S[\tilde{\psi}_E]$ is stationary with respect to variations $\delta \psi_E(R)$ in the trial wavefunction $\tilde{\psi}_E(R) = \psi_E(R) + \delta \psi_E(R)$.

The utility of this result lies in the fact that one can use it to optimise any parameters in the trial wavefunction in the same way as in a variational bound state calculation. For instance the trial wavefunction $\tilde{\psi}_E(R)$ can be expanded in a basis set of translational wavefunctions $u_\tau(R)$ as

$$\tilde{\psi}_E(R) = u_0(R) - \sum_{\tau=1}^{N_\tau} u_\tau(R) c_\tau, \quad (38)$$

in which the basis functions $u_\tau(R)$ with $\tau > 1$ are required to vanish as $R \rightarrow 0$ and $R \rightarrow \infty$ and the remaining two basis functions $u_0(R)$ and $u_1(R)$ are chosen so as to impose the boundary conditions in Eqs. (35) and (36) (with $\tilde{S}(E) = c_1$ as yet undetermined):

$$u_0(R) = f(R) \phi_E^-(R), \quad (39)$$

and

$$u_1(R) = f(R) \phi_E^+(R), \quad (40)$$

where $f(R \rightarrow 0) \sim 0$ and $f(R \rightarrow \infty) \sim 1$.

Substituting this expansion into Eq. (34) and requiring

$$\frac{\partial S[\tilde{\psi}_E]}{\partial c_\tau} = 0 \quad (41)$$

for each coefficient c_τ in turn leads to a system of linear equations for the optimum expansion coefficients which can be substituted back into Eq. (34) to give the following optimum (variational) approximation to the scattering matrix:¹⁴

$$S(E) \simeq \frac{i}{\hbar} \left(M_{00} - M_{10}^T M_{11}^{-1} M_{10} \right), \quad (42)$$

where

$$M_{00} = \langle u_0^* | H - E | u_0 \rangle, \quad (43)$$

and

$$(M_{10})_\tau = \langle u_\tau^* | H - E | u_0 \rangle, \quad (44)$$

and

$$(M_{11})_{\tau'\tau} = \langle u_{\tau'}^* | H - E | u_\tau \rangle. \quad (45)$$

In this method, and indeed also in all of the other variational methods that have been used for reactive scattering,¹⁵ the calculation of the scattering matrix $S(E)$ is thus reduced to a standard quantum chemistry calculation involving basis sets, matrix elements, and linear algebra.¹⁴

5.2 Implementation

The Kohn variational method described above for potential scattering extends in a straightforward way to the collinear reactive scattering problem described in Section 2 *without* the need to introduce any special coordinates (i.e., one can continue to work with the optimum mass-scaled Jacobi coordinates of the reactant and product arrangements). Moreover the extensions that are required are comparatively minor, and the overall structure of the method remains the same.

In terms of the definitions in Section 2, and noting in particular that the vibrational eigenfunctions $\phi_{\alpha\nu}(r_\alpha)$ in Eq. (16) can be chosen to be purely real (so it is immaterial whether or not they are complex conjugated in bras), the reactive scattering version of the variational functional in Eq. (34) for a general scattering matrix element $S_{\alpha'\nu',\alpha\nu}(E)$ becomes¹⁴

$$S[\tilde{\psi}_{E\alpha'\nu'}, \tilde{\psi}_{E\alpha\nu}] = \tilde{S}_{\alpha'\nu',\alpha\nu}(E) + \frac{i}{\hbar} \langle \tilde{\psi}_{E\alpha'\nu'}^* | H - E | \tilde{\psi}_{E\alpha\nu} \rangle, \quad (46)$$

where the trial wavefunctions $\tilde{\psi}_{E\alpha\nu}$ and $\tilde{\psi}_{E\alpha'\nu'}$ are both regular at the origin and satisfy the following asymptotic boundary conditions in arrangement α'' [cf. Eq. (18)]:

$$\tilde{\psi}_{E\alpha\nu} \stackrel{R_{\alpha''} \rightarrow \infty}{\sim} \phi_{E\alpha\nu}^-(R_\alpha, r_\alpha) \delta_{\alpha\alpha''} - \sum_{\nu''} \phi_{E\alpha''\nu''}^+(R_{\alpha''}, r_{\alpha''}) \tilde{S}_{\alpha''\nu'',\alpha\nu}(E), \quad (47)$$

and

$$\tilde{\psi}_{E\alpha'\nu'} \stackrel{R_{\alpha''} \rightarrow \infty}{\sim} \phi_{E\alpha'\nu'}^-(R_{\alpha'}, r_{\alpha'}) \delta_{\alpha'\alpha''} - \sum_{\nu''} \phi_{E\alpha''\nu''}^+(R_{\alpha''}, r_{\alpha''}) \tilde{S}_{\alpha''\nu'',\alpha'\nu'}(E). \quad (48)$$

Once again, since the exact wavefunction $\psi_{E\alpha\nu}$ satisfies the Schrödinger equation $H\psi_{E\alpha\nu} = E\psi_{E\alpha\nu}$, the functional $S[\psi_{E\alpha'\nu'}, \psi_{E\alpha\nu}]$ is clearly equal to the exact scattering matrix element $S_{\alpha'\nu',\alpha\nu}(E)$. Moreover one can show explicitly by considering the first variation of $S[\psi_{E\alpha'\nu'}, \psi_{E\alpha\nu}]$ that the stationary property of Eq. (34) also carries over to Eq. (46).¹⁴

As in the potential scattering case, this stationary property can be exploited by using a basis set expansion of the trial wavefunctions $\tilde{\psi}_{E\alpha\nu}$ and $\tilde{\psi}_{E\alpha'\nu'}$. However, in view of the boundary conditions in Eqs. (47) and (48), the natural expansion of each trial function is now a *multiple-arrangement* expansion of the form

$$\tilde{\psi}_{E\alpha\nu} = u_{\alpha 0\nu}(R_\alpha) \phi_{\alpha\nu}(r_\alpha) - \sum_{\alpha''\tau''\nu''} u_{\alpha''\tau''\nu''}(R_{\alpha''}) \phi_{\alpha''\nu''}(r_{\alpha''}) c_{\alpha''\tau''\nu'',E\alpha\nu}, \quad (49)$$

and

$$\tilde{\psi}_{E\alpha'\nu'} = u_{\alpha' 0\nu'}(R_{\alpha'}) \phi_{\alpha'\nu'}(r_{\alpha'}) - \sum_{\alpha''\tau''\nu''} u_{\alpha''\tau''\nu''}(R_{\alpha''}) \phi_{\alpha''\nu''}(r_{\alpha''}) c_{\alpha''\tau''\nu'',E\alpha'\nu'}, \quad (50)$$

where the translational basis functions $u_{\alpha\tau\nu}(R_\alpha)$ are defined in the same way as before (except that they are now also labelled by the arrangement index α and the vibrational quantum number ν so that the k and v of potential scattering can be replaced by the $k_{\alpha\nu}$ and $v_{\alpha\nu}$ of reactive scattering in the asymptotic forms of $u_{\alpha 0\nu}(R_\alpha)$ and $u_{\alpha 1\nu}(R_\alpha)$). In particular, the coefficient $c_{\alpha''\tau''\nu'',E\alpha\nu}$ in Eq. (49) can be identified with the quantity $\tilde{S}_{\alpha''\nu'',\alpha\nu}(E)$ in Eq. (47), and the coefficient $c_{\alpha''\tau''\nu'',E\alpha'\nu'}$ in Eq. (50) with the quantity $\tilde{S}_{\alpha''\nu'',\alpha'\nu'}(E)$ in Eq. (48).

Substituting Eqs. (49) and (50) into Eq. (46) and performing the variational calculation

$$\frac{\partial S[\tilde{\psi}_{E\alpha'\nu'}, \tilde{\psi}_{E\alpha\nu}]}{\partial c_{\alpha''\tau''\nu'',E\alpha'\nu'}} = \frac{\partial S[\tilde{\psi}_{E\alpha'\nu'}, \tilde{\psi}_{E\alpha\nu}]}{\partial c_{\alpha''\tau''\nu'',E\alpha\nu}} = 0 \quad (51)$$

for each expansion coefficient $c_{\alpha''\tau''\nu'',E\alpha\nu}$ and $c_{\alpha''\tau''\nu'',E\alpha'\nu'}$ in turn leads directly to a matrix generalisation of Eq. (42),

$$S(E) = \frac{i}{\hbar} \left(M_{00} - M_{10}^T M_{11}^{-1} M_{10} \right), \quad (52)$$

where now

$$(M_{00})_{\alpha'\nu',\alpha\nu} = \langle u_{\alpha' 0\nu'}^* \phi_{\alpha'\nu'} | H - E | u_{\alpha 0\nu} \phi_{\alpha\nu} \rangle, \quad (53)$$

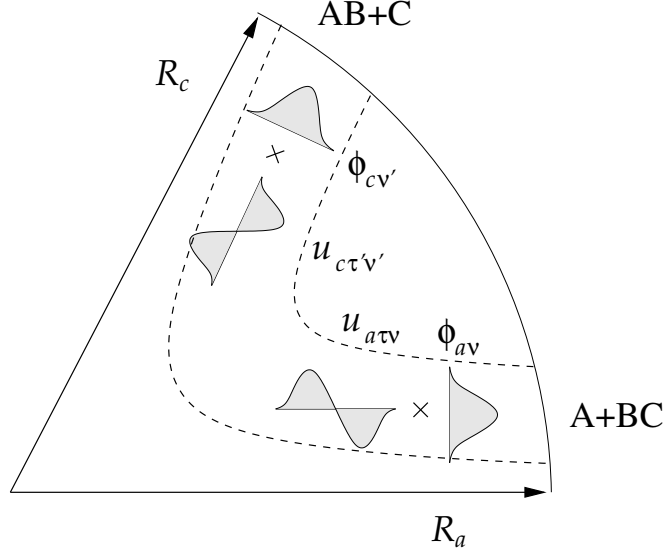


Figure 6: Typical basis functions in the multiple-arrangement expansion used in variational methods

and

$$(M_{10})_{\alpha'\tau'\nu',\alpha\nu} = \langle u_{\alpha'\tau'\nu'}^* \phi_{\alpha'\nu'} | H - E | u_{\alpha 0\nu} \phi_{\alpha\nu} \rangle, \quad (54)$$

and

$$(M_{11})_{\alpha'\tau'\nu',\alpha\tau\nu} = \langle u_{\alpha'\tau'\nu'}^* \phi_{\alpha'\nu'} | H - E | u_{\alpha\tau\nu} \phi_{\alpha\nu} \rangle. \quad (55)$$

Thus the calculation of the reactive scattering matrix $S(E)$ again boils down to a standard quantum chemistry calculation involving basis sets, matrix elements, and linear algebra.

The only really new complication in the reactive scattering case that did not arise for potential scattering comes from the multiple-arrangement expansions in Eqs. (49) and (50) (see also Figure 6). As a result of these expansions, the Hamiltonian and overlap matrix elements that are required in Eqs. (53) to (55) include both direct matrix elements between basis functions in the same arrangement,

$$\int \int u_{\alpha\tau'\nu'}(R_\alpha) \phi_{\alpha\nu'}(r_\alpha) [H - E] u_{\alpha\tau\nu}(R_\alpha) \phi_{\alpha\nu}(r_\alpha) dR_\alpha dr_\alpha, \quad (56)$$

and more complicated *exchange* matrix elements between basis functions in different arrangements:

$$\int \int u_{\alpha'\tau'\nu'}(R_{\alpha'})\phi_{\alpha'\nu'}(r_{\alpha'}) [H - E] u_{\alpha\tau\nu}(R_{\alpha})\phi_{\alpha\nu}(r_{\alpha}) dR_{\alpha}dr_{\alpha}. \quad (57)$$

In order to evaluate these exchange matrix elements, one clearly has to perform the coordinate transformation in Eq. (10) so that $u_{\alpha'\tau'\nu'}(R_{\alpha'})$ and $\phi_{\alpha'\nu'}(r_{\alpha'})$ can be evaluated as functions of R_{α} and r_{α} . This is not however particularly difficult, and even with the coordinate transformation the evaluation of the required matrix elements is generally only a small part of the calculation when compared with the linear algebraic construction of the matrix $M_{11}^{-1}M_{10}$ in Eq. (52).

Finally, while we have confined our attention here to one particular variational method, it should be stressed that all of the other variational methods that can be used for quantum reactive scattering calculations involve the same basic ingredients of basis set definition, matrix element evaluation, and linear algebra.¹⁵ At the level of this article, the differences between the various possible time-independent variational methods will therefore simply be glossed over, although these differences can actually be quite important for large-scale quantum reactive scattering calculations. The interested reader is referred to two earlier reviews of quantum reactive scattering theory for more details,¹⁶ both of which were written at the end of the 1980s when variational methods were at the height of their popularity.

6. THE TIME-DEPENDENT WAVEPACKET METHOD

The final solution to the quantum reactive scattering problem we shall consider is the time-dependent wavepacket method¹⁷ (see *Wave Packets*). This is one of the simplest ways to solve the Schrödinger equation for a chemical reaction, and it is also rapidly emerging as one of the most powerful.³ Moreover it has the great advantage that its numerical implementation via the techniques described elsewhere in this volume is only a small step away from its theoretical formulation, which makes the method especially easy to justify and explain.

The time-dependent wavepacket method for state-to-state reactive scattering is based on the following remarkable expression for the reactive scat-

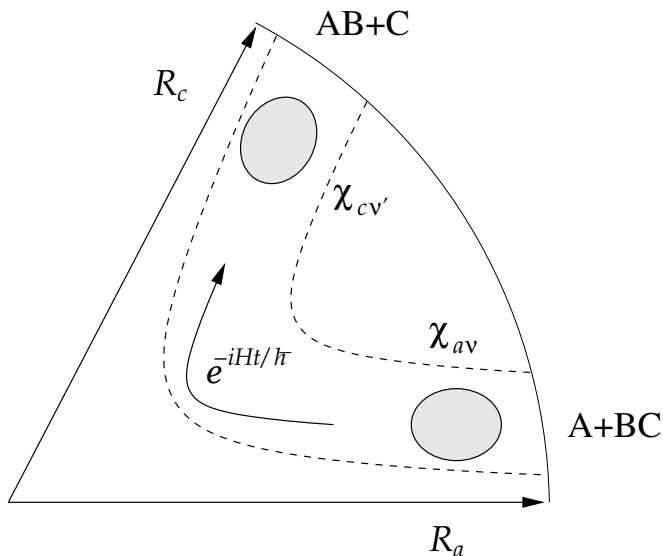


Figure 7: Schematic illustration of the time-dependent wavepacket method for state-to-state reactive scattering

tering matrix element $S_{cv',av}(E)$ involving the Fourier transform of a correlation function $C_{cv',av}(t)$ between an initial reactant wavepacket χ_{av} and a final product wavepacket $\chi_{cv'}$ (see Figure 7):

$$S_{cv',av}(E) = -\frac{1}{\langle \chi_{cv'} | \phi_{Ecv'}^+ \rangle \langle \phi_{Eav}^- | \chi_{av} \rangle} \int_0^\infty e^{+iEt/\hbar} C_{cv',av}(t) dt, \quad (58)$$

where

$$C_{cv',av}(t) = \langle \chi_{cv'} | e^{-iHt/\hbar} | \chi_{av} \rangle. \quad (59)$$

A number of different derivations of this expression have been given in the last few years, ranging from the straightforward derivation given by Dai and Zhang¹⁸ to the more formal derivation given by Tannor and Weeks.¹⁹ However, nearly all of these derivations have considered the case where the lower limit of the time integral in Eq. (58) is replaced by minus infinity, which places unnecessary restrictions on the initial wavepacket χ_{av} . (One of the few notable exceptions²⁰ to this is the variational derivation of Kouri and coworkers,^{20(a)} which arrives at Eqs. (58) and (59) in the equivalent

time-independent form

$$S_{cv',a\nu}(E) = -i\hbar \frac{\langle \chi_{cv'} | G^+(E) | \chi_{a\nu} \rangle}{\langle \chi_{cv'} | \phi_{Ecv'}^+ \rangle \langle \phi_{Ea\nu}^- | \chi_{a\nu} \rangle}, \quad (60)$$

where

$$G^+(E) = \lim_{\epsilon \rightarrow 0} \frac{1}{i\hbar} \int_0^\infty e^{+i(E+i\epsilon-H)t/\hbar} dt. \quad (61)$$

In order to clarify this point, and at the same time justify the time-dependent wavepacket method, we shall now describe how Eq. (58) can be obtained in a way that highlights the implications of its causal ($t \geq 0$) time integral.

6.1 Wavepacket Theory

The first observation that is needed to obtain Eq. (58) is the fact that the orthonormality of the vibrational eigenfunctions $\phi_{\alpha'\nu'}(r_{\alpha'})$ can be used to rewrite the boundary condition in Eq. (18) as

$$\langle \chi_{\alpha'\nu'} | \psi_{E\alpha\nu} \rangle = \langle \chi_{\alpha'\nu'} | \phi_{E\alpha'\nu'}^- \rangle \delta_{\alpha'\alpha} \delta_{\nu',\nu} - \langle \chi_{\alpha'\nu'} | \phi_{E\alpha'\nu'}^+ \rangle S_{\alpha'\nu',\alpha\nu}(E), \quad (62)$$

where $\chi_{\alpha'\nu'}$ can be any localised wavepacket in the asymptotic region of channel α' (i.e., any wavepacket of the form

$$\chi_{\alpha'\nu'}(R_{\alpha'}, r_{\alpha'}) = g_{\alpha'\nu'}(R_{\alpha'}) \phi_{\alpha'\nu'}(r_{\alpha'}) \quad (63)$$

in which the translational component $g_{\alpha'\nu'}(R_{\alpha'})$ is localised at sufficiently large $R_{\alpha'}$). Indeed specialising Eq. (62) to the case where $\alpha' = c$ and $\alpha = a$ immediately gives

$$\langle \chi_{cv'} | \psi_{Ea\nu} \rangle = -\langle \chi_{cv'} | \phi_{Ecv'}^+ \rangle S_{cv',a\nu}(E), \quad (64)$$

and hence the required reactive scattering matrix element $S_{cv',a\nu}(E)$ as

$$S_{cv',a\nu}(E) = -\frac{\langle \chi_{cv'} | \psi_{Ea\nu} \rangle}{\langle \chi_{cv'} | \phi_{Ecv'}^+ \rangle}. \quad (65)$$

The next task is to eliminate the scattering eigenstate $\psi_{Ea\nu}$ from Eq. (65). The easiest way to do this (at least formally) is to use the fact that the microcanonical density operator $\delta(E - H)$ can be written in terms of the complete set of scattering eigenstates $\psi_{E\alpha\nu}$ as

$$\delta(E - H) = \frac{1}{2\pi\hbar} \sum_{\alpha\nu} |\psi_{E\alpha\nu}\rangle \langle \psi_{E\alpha\nu}|, \quad (66)$$

where the factor of $1/(2\pi\hbar)$ comes from the normalisation of the incoming and outgoing wavefunctions $\phi_{E\alpha\nu}^\pm$ in Eq. (15).²¹ Combining this with Eq. (62), it follows that the effect of operating with $2\pi\hbar\delta(E-H)$ on a general asymptotic wavepacket $\chi_{\alpha'\nu'}$ of the form in Eq. (63) is

$$2\pi\hbar\delta(E-H)|\chi_{\alpha'\nu'}\rangle = |\psi_{E\alpha'\nu'}\rangle\langle\phi_{E\alpha'\nu'}^-|\chi_{\alpha'\nu'}\rangle - \sum_{\alpha\nu}|\psi_{E\alpha\nu}\rangle\langle\phi_{E\alpha'\nu'}^+|\chi_{\alpha'\nu'}\rangle S_{\alpha'\nu',\alpha\nu}(E)^*, \quad (67)$$

and hence that the effect of $2\pi\hbar\delta(E-H)$ on a purely incoming wavepacket $\chi_{\alpha'\nu'}$ (i.e., a wavepacket that satisfies $\langle\phi_{E\alpha'\nu'}^+|\chi_{\alpha'\nu'}\rangle=0$) is simply

$$2\pi\hbar\delta(E-H)|\chi_{\alpha'\nu'}\rangle = |\psi_{E\alpha'\nu'}\rangle\langle\phi_{E\alpha'\nu'}^-|\chi_{\alpha'\nu'}\rangle. \quad (68)$$

The scattering eigenstate $\psi_{E\alpha\nu}$ in Eq. (65) can therefore be calculated as

$$|\psi_{E\alpha\nu}\rangle = 2\pi\hbar\frac{\delta(E-H)|\chi_{\alpha\nu}\rangle}{\langle\phi_{E\alpha\nu}^-|\chi_{\alpha\nu}\rangle}, \quad (69)$$

to give

$$S_{c\nu',\alpha\nu}(E) = -2\pi\hbar\frac{\langle\chi_{c\nu'}|\delta(E-H)|\chi_{\alpha\nu}\rangle}{\langle\chi_{c\nu'}|\phi_{E c\nu'}^+\rangle\langle\phi_{E\alpha\nu}^-|\chi_{\alpha\nu}\rangle}, \quad (70)$$

where we have assumed that the reactant wavepacket $\chi_{\alpha\nu}$ contains only incoming waves.

The third and final stage of the argument is simply to replace the delta function $\delta(E-H)$ in Eq. (70) with its Fourier representation

$$\delta(E-H) = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}e^{+i(E-H)t/\hbar}dt, \quad (71)$$

to obtain

$$S_{c\nu',\alpha\nu}(E) = -\frac{1}{\langle\chi_{c\nu'}|\phi_{E c\nu'}^+\rangle\langle\phi_{E\alpha\nu}^-|\chi_{\alpha\nu}\rangle}\int_{-\infty}^{\infty}e^{-iEt/\hbar}C_{c\nu',\alpha\nu}(t)dt, \quad (72)$$

where $C_{c\nu',\alpha\nu}(t)$ is defined as in Eq. (59). Now although Eq. (72) looks very similar to Eq. (58), except for the lower limit on the time integral, the difference between the two equations is actually quite remarkable. It is clear from the above derivation that Eq. (72) will only give the correct result if

the reactant wavepacket $\chi_{a\nu}$ is composed purely of incoming waves, for otherwise Eq. (69) for $\psi_{E_{a\nu}}$ will be incorrect. The remarkable thing is that simply replacing the lower limit of the time integral with zero makes the equation correct more generally, as explained in the following section.

6.2 Causality

Clearly, since the reactant wavepacket $\chi_{a\nu}$ is assumed in Eq. (72) to be both purely incoming and localised in the asymptotic region of channel $a\nu$, its entire history $\chi_{a\nu}(t) = e^{-iHt/\hbar}\chi_{a\nu}$ with $t \leq 0$ will also be confined to the asymptotic region of the reactant channel by virtue of the separation of the Hamiltonian H in Eq. (12). This history will therefore have zero overlap with $\chi_{c\nu'}$, and the correlation function $C_{c\nu',a\nu}(t) = \langle \chi_{c\nu'} | \chi_{a\nu}(t) \rangle$ will be zero for all $t \leq 0$. Thus negative times will not contribute to the time integral in Eq. (72), which can therefore be replaced by Eq. (58). However, this still leaves the restriction that $\chi_{a\nu}$ must be composed solely of incoming waves.

In order to remove this restriction, we can now turn the argument on its head and use the fact that the lower limit of the time integral in Eq. (58) is zero rather than minus infinity. In particular, since we have established that Eq. (58) is correct for a purely incoming reactant wavepacket, let us consider what happens to this equation when we add an arbitrary outgoing component $\delta\chi_{a\nu}$ to $\chi_{a\nu}$ that is also localised in the asymptotic region of channel $a\nu$:

$$\chi'_{a\nu}(R_a, r_a) = \chi_{a\nu}(R_a, r_a) + \delta\chi_{a\nu}(R_a, r_a). \quad (73)$$

Since the correction $\delta\chi_{a\nu}$ is assumed to be purely outgoing we immediately have $\langle \phi_{E_{a\nu}}^- | \delta\chi_{a\nu} \rangle = 0$, which shows that the addition of an outgoing component to $\chi_{a\nu}$ will not change the denominator of Eq. (58). Furthermore, since $\delta\chi_{a\nu}$ is assumed to be purely outgoing and localised in the asymptotic region of channel $a\nu$, its entire future $\delta\chi_{a\nu}(t) = e^{-iHt/\hbar}\delta\chi_{a\nu}$ with $t \geq 0$ will remain in the asymptotic region of the reactant channel and therefore have zero overlap with $\chi_{c\nu'}$. Thus the addition of an outgoing component to $\chi_{a\nu}$ will not change either the numerator or the denominator of Eq. (58), and we have shown that this equation applies equally well to $\chi'_{a\nu}$ as it does to $\chi_{a\nu}$.

Changing the notation back from $\chi'_{a\nu}$ to $\chi_{a\nu}$ therefore confirms that Eq. (58) is valid for *any* reactant and product wavepackets of the form in Eq. (63), provided simply that the denominator in Eq. (58) does not vanish (i.e., provided the reactant wavepacket $\chi_{a\nu}$ has a non-zero incoming com-

ponent and the product wavepacket $\chi_{c\nu'}$, a non-zero outgoing component at energy E).

6.3 Implementation

The practical application of the time-dependent wavepacket method to a collinear state-to-state reactive scattering problem simply involves the straightforward numerical implementation of Eqs. (58) and (59). For instance one can represent the Hamiltonian H and the initial and final wavepackets χ_{av} and $\chi_{c\nu'}$ using a standard discrete variable representation in the reactant mass-scaled Jacobi coordinates R_a and r_a (see *Discrete Variable Basis Sets*), thereby eliminating the need for any special coordinates that swing smoothly from reactants to products, and one can perform the time-evolution in Eq. (59) using any one of a variety of standard wavepacket propagation techniques²² (see *Time Dependent Quantum Methods*). Moreover a similar approach can also be used for both triatomic¹⁸ and tetratomic³ reactions in three-dimensional space.

There is however one important difficulty which makes this approach significantly less straightforward than it sounds. In order to use a finite rather than an infinite grid, one must absorb the wavepacket $\chi_{av}(t) = e^{-iHt/\hbar}\chi_{av}$ as it approaches the grid boundary so as to avoid any unphysical reflections. The standard way to do this is to employ a negative imaginary absorbing potential $-i\epsilon(R_\alpha, r_\alpha)$ at the edge of the grid.^{3,18} However, one then has to ensure that the parameters in this absorbing potential give complete (or nearly complete) absorption of the wavepacket, and this is not possible for the low translational energy components of the wavepacket unless one uses a very large absorbing region (and therefore also a very large grid). It follows from the analyses of Neuhauser and Baer²³ and Child,²⁴ for example, that the width of the absorbing region for a linear negative imaginary absorbing potential must be at least as large as the de Broglie wavelength $\lambda = h/(2\mu E_t)^{1/2}$ at translational energy E_t , and Seideman and Miller have obtained the same result semiclassically for a more general class of negative imaginary absorbing potentials.²⁵ Clearly, therefore, the required width of the absorbing region becomes infinite as the translational energy goes to zero.

As a result of this difficulty, and also the simple fact that the lower the average translational energy of the reactant wavepacket the longer it will take to react (and therefore also the larger the number of iterations that will be required in the wavepacket propagation algorithm), the time-dependent

wavepacket method is at its best in situations where low reactant and product translational energies are comparatively unimportant (for example in the study of reactions with significant activation barriers). In such situations, and also in photodissociation theory where high photofragment translational energies are the norm (see *Photodissociation*), the time-dependent wavepacket method can however be *extremely* effective.³

7. CLOSING REMARKS

In this article, we have considered four very different methods for solving the state-to-state reactive scattering problem in the simple (but nonetheless typical) context of a collinear $A+BC \rightleftharpoons AB+C$ reaction. Of these four methods, the natural collision coordinates described in Section 3 are now simply of historical interest, but the remaining three methods are all still widely used in quantum reactive scattering calculations. The very fact that this is the case shows that all three methods have their advantages and disadvantages, and that no one method has yet been discovered that is ideal for every reaction. In order to emphasise this fact, we shall now close with a few comparative remarks on the merits of each method in turn.

The hyperspherical coordinate method described in Section 4 is characterised more by its generality and reliability than by its simplicity or computational efficiency. It is equally applicable to both triatomic⁸ and tetratomic⁹ reactions, and it has also been used in conjunction with reduced dimensionality approximations to study even larger polyatomic reactions²⁶ (see *Reactive Scattering of Polyatomic Molecules*). However, it is considerably more difficult to implement for three-dimensional reactions than either of the other two methods, largely because of the difficulties posed by the hyperspherical coordinate surface eigenvalue problem (see Eq. (29)), and the fact that it involves solving a system of close-coupled equations at each energy (see Eq. (26)) can make it significantly less efficient than the time-dependent wavepacket method if results are required at many energies.

The time-independent variational methods described in Section 5 are equally reliable and general as the hyperspherical coordinate method, although it is probably fair to say that they have not yet been used to study quite such a diverse variety of chemical reactions. Their main advantage lies

in their simplicity, and indeed their implementation boils down to performing little more than a standard computational quantum chemistry calculation involving basis sets, matrix elements, and linear algebra.¹⁴ The cost of this simplicity, however, is that the size of the matrices involved in these methods is one full dimension (ρ) larger than the size of the matrices that arise in the hyperspherical coordinate method, and it can rapidly become difficult to fit them into computer memory.

Finally, the time-dependent wavepacket method described in Section 6 is both extremely simple and highly efficient, but falls down in terms of its reliability at low translational energies. Its efficiency derives from the fact that the entire range of energies required in the calculation can be extracted from the propagation of a single wavepacket for each reactant quantum state, rather than having to repeat the calculation at each separate energy.^{3,18} The price that has to be paid for this, however, is that the reliability of the wavepacket method is questionable near channel thresholds because it approximates the scattering boundary conditions with an empirical absorbing potential rather than applying them correctly at each energy.

8. RELATED ARTICLES

Ab Initio Potential Energy Surfaces for Chemical Reaction Dynamics; Chemical Reaction Rates; Close-Coupling Calculations for Molecular Collision Processes; Wave Packets; Time Dependent Quantum Methods; Discrete Variable Basis Sets; Photodissociation; Reactive Scattering of Polyatomic Molecules.

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