R-matrix Theory of Electron Molecule Scattering

P.G. Burke[†] and J. Tennyson[*]
[†] Department of Applied Mathematics and Theoretical Physics,
Queen's University Belfast, BT7 1NN
[*] Department of Physics and Astronomy, University College London,
London WC1E 6BT

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1 Introduction

Electron molecule scattering processes are important in all cold plasmas such as those found in planetary ionospheres, astrophysics, at the edge of fusion reactors and in chemical processing, as well as discharges such as those that drive lasers. Radiation damage in living systems arise primarily from the interaction of low energy secondary electrons through dissociative interactions with components of DNA or the water around them [1]. R-matrix calculations have been performed to aid the understanding of most of these processes.

Most astronomical plasmas, such as those found in the interstellar medium, are both cold and diffuse. This means that for molecules possessing a permanent dipole moment, collisional excitation is usually followed by radiative emission back to the ground state. Knowledge of the collisional excitation rates is therefore essential to interpret any observed emissions. Molecular ions have very large electron impact excitation cross sections and electrons are thought to be the primary collision partner for ions such as CH^+, CO^+ and HCO^+ whose emission spectra are well known from regions such as planetary nebulae.

The processes that occur in the scattering of electrons by molecules are considerably more challenging than those that arise in electron scattering by atoms and atomic ions because of the possibility of exciting degrees of freedom associated with the motion of the nuclei. Thus as well as electronic excitation and ionization, which also occur in electron atom scattering, additional processes that now take place include rotational and vibrational excitation, dissociation and dissociative attachment or recombination.

In this paper we present an overview of R-matrix theory of electron molecule scattering which enables these processes to be accurately calculated. We commence in Section 2 by considering the fixed-nuclei approximation where the electronic degrees of freedom of the molecule are first calculated in the molecular or body-fixed frame of reference in which the nuclei are held fixed in space. The molecular rotational, vibrational and dissociative motion is then included in a second stage of the calculation which we will discuss in Sections 3 and 4. This procedure owes its validity to the large ratio of the nuclear mass to the electronic mass which is the basis of the Born-Oppenheimer separation of the electronic and nuclear motion made in molecular structure calculations. Finally, in Section 5 we present a selection of some illustrative results from recent calculations for molecules of importance in applications.

2 Fixed-Nuclei Approximation

The fixed-nuclei approximation was first used to describe low-energy electron scattering by diatomic molecules by Stier [2], Fisk [3] and Massey and Ridley [4]. In

recent years it has been widely used as the basis of *ab initio* computational methods that are yielding the most accurate cross sections for electron scattering by diatomic and polyatomic molecules. These methods include the complex Kohn variational method [5], the Schwinger variational method [6] and the R-matrix method [7, 8] which we consider in this paper.

The R-matrix method,first used to describe low-energy electron atom scattering by Burke *et al* [9], was extended to treat electron scattering by diatomic molecules by Schneider [10], [11], Schneider and Hay [12] and Burke *et al* [13]. In order to formulate the electron molecule scattering process in the fixed-nuclei approximation we adopt a frame of reference which is rigidly attached to the molecule, where the centre of gravity of the molecule is chosen as the origin of coordinates. In the case of diatomic molecules, which we will use as an examplar of the general case in the following discussion, we introduce a molecular frame of reference where the z-axis is convenently chosen to lie along the internuclear axis, as illustrated in Figure 1. Also in this figure G is the centre of gravity of the two nuclei labelled A and B, $R = R_A + R_B$ is the distance between the nuclei and the vector distances between

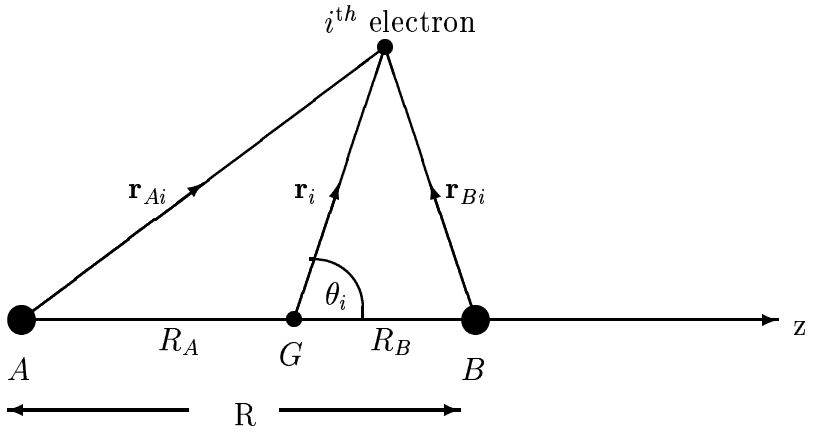

Figure 1: Molecular frame for electron diatomic molecule scattering

A, B and G and the ith electron are $\mathbf{r}_{Ai}$, $\mathbf{r}_{Bi}$ and $\mathbf{r}_i$ respectively. We consider first the scattering process represented by the equation

$$\mathrm{e}^- + AB_i \rightarrow AB_j + \mathrm{e}^- \tag{1}$$

where AB_i and AB_j are the initial and final electronic bound states of the target, which we assume has N electrons, and where the nuclear charge numbers corresponding to A and B are Z_A and Z_B. Also as discussed above, we assume that A and B are fixed in space. We reserve a discussion of the rotational and vibrational degrees of freedom to Sections 3 and 4.

We assume that the target nuclei are light so that relativistic effects can be neglected for low-energy electron scattering. The scattering process is then described by the time-independent Schrödinger equation

$$H_{N+1}\Psi = E\Psi, \tag{2}$$

where H_{N+1} is the non-relativistic Hamiltonian defined in atomic units by

$$H_{N+1} = \sum_{i=1}^{N+1}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z_A}{r_{Ai}} - \frac{Z_B}{r_{Bi}}\right) + \sum_{i>j=1}^{N+1}\frac{1}{r_{ij}} + \frac{Z_A Z_B}{R}. \tag{3}$$

In order to solve eq. (2) using R-matrix theory we proceed by partitioning configuration space into an internal region, an external region and an asymptotic region as illustrated in Figure 2.

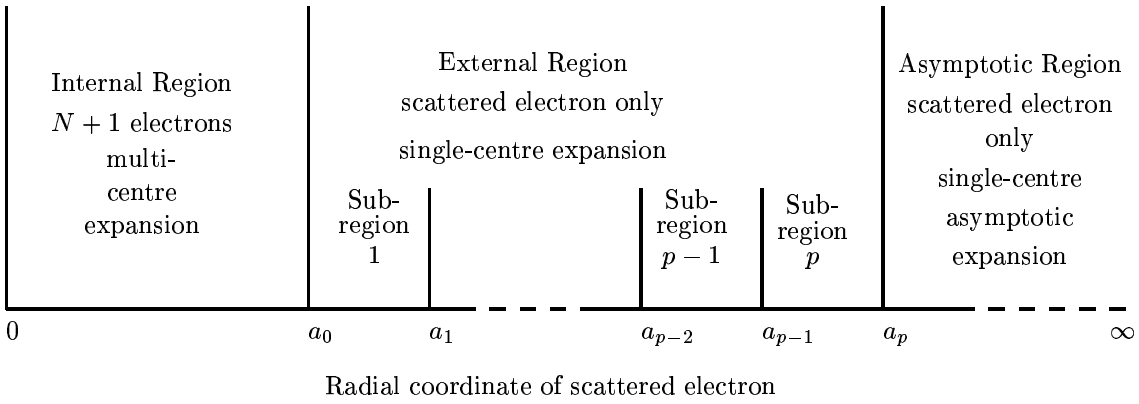

Figure 2: Partitioning of configuration space in R-matrix theory of electron molecule scattering.

In the internal region $0 \leq r \leq a_0$, where r is the radial coordinate of the scattered electron relative to the centre of gravity G of the target nuclei, electron exchange and electron-electron correlation effects between the scattered electron and the N electrons of the target are important and the $(N+1)$-electron collision complex behaves in a similar way to a bound state. Consequently a configuration interaction expansion of this complex similar to that used for molecular bound state calculations is used. Recent work has produced both a diatomic molecule code, based on Slater Type Orbitals (STOs), and a polyatomic molecule code, based on Gaussian Type Orbitals (GTOs) [7, 8]. In each case these functions are centred on the nuclei and are combined with a continuum basis centred on the centre of gravity.

The solution of eq. (2) in the internal region takes the following form

$$\Psi = \sum_k \psi_k A_{Ek}, \tag{4}$$

where the ψ_k are energy-independent basis functions which are expanded as an antisymmetrised summation as follows

$$\psi_k^{\Delta}(\mathbf{X}_{N+1},R) = \mathcal{A}\sum_{i=1}^{n}\sum_{j=1}^{n_c}\overline{\Phi}_i^{\Delta}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})r_{N+1}^{-1}u_{ij}^0(r_{N+1})a_{ijk}^{\Delta} + \sum_{i=1}^{m}\chi_i^{\Delta}(\mathbf{X}_{N+1})b_{ik}^{\Delta}, \quad k=1,\ldots,n_t, \tag{5}$$

for each fixed internuclear separation R, where $n_t = nn_c+m$ is the number of linearly independent basis functions and $\mathbf{X}_{N+1} \equiv \mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{N+1}$ with $\mathbf{x}_i \equiv \mathbf{r}_i\sigma_i$, represents the space and spin coordinates of the $N+1$ electrons. The channel functions $\overline{\Phi}_i^{\Delta}$, the continuum orbitals u_{ij}^0 and the quadratically integrable functions χ_i^{Δ} depend parametrically on R. Also Δ represents the conserved quantum numbers which correspond to the irreducible representation of the symmetry group of the molecule under consideration.

The channel functions $\overline{\Phi}_i^{\Delta}$, which are formed by coupling the target physical states and possibly pseudo-states to the angular and spin functions of the scattered electron, and the quadratically integrable functions χ_i^{Δ} are constructed from STOs or GTOs centred on the nuclei. The radius a_0 is chosen so that these orbitals vanish by the boundary of the internal region. On the other hand the continuum basis orbitals u_{ij}^0, which represent the scattered electron, are non-vanishing on this boundary and are used to construct the R-matrix linking the internal and external regions. These continuum orbitals can be formed from STOs for the diatomic code. However difficulties have been experienced at higher incident electron energies due to linear dependence of these orbitals [14]. Hence they are more usually generated numerically as solutions of a zero-order second-order differential equation [15] for the diatomic code and are based on expansions of GTOs for the polyatomic code[16, 17]. Finally, the coefficients a_{ijk}^{Δ} and b_{ik}^{Δ} in eq. (5) are obtained by diagonalizing the operator $H_{N+1}+\mathcal{L}_{N+1}$ for fixed R in the basis ψ_k^{Δ} over the internal region as follows

$$\langle\psi_k^{\Delta}|H_{N+1}+\mathcal{L}_{N+1}|\psi_{k'}^{\Delta}\rangle_{\rm int} = E_k^{\Delta}\delta_{kk'}, \quad k,k'=1,\ldots,n_t, \tag{6}$$

where $\mathcal{L}_{N+1}$ is the Bloch operator [20]

$$\mathcal{L}_{N+1} = \sum_{i=1}^{N+1}\frac{1}{2}\delta(r_i-a_0)\left(\frac{d}{dr_i}-\frac{b_0-1}{r_i}\right), \tag{7}$$

where b_o is an arbitrary constant. We can then show that $H_{N+1}+\mathcal{L}_{N+1}$ is hermitian in the basis of quadratically integrable functions satisfying arbitrary boundary conditions at $r=a_0$. The Hamiltonian matrix elements in eq. (6) can be calculated using standard molecular structure packages, modified to carry out the radial integrals over a finite range and to treat continuum orbitals as well as STOs or GTOs.

However it is possible to exploit the structure of the wavefunction given by eq. (5) to greatly enhance the efficiency of the calculation.[18]

Eq. (2) is solved in the internal region for each fixed internuclear separation R and for each set of conserved quantum numbers denoted by Δ, by rewriting it as follows

$$(H_{N+1} + \mathcal{L}_{N+1} - E)\,\Psi^{\Delta} = \mathcal{L}_{N+1}\Psi^{\Delta}, \tag{8}$$

which has the formal solution

$$\Psi^{\Delta} = (H_{N+1} + \mathcal{L}_{N+1} - E)^{-1}\,\mathcal{L}_{N+1}\Psi^{\Delta}. \tag{9}$$

We expand the inverse operator in this equation in terms of the basis defined by eqs. (5) and (6), project the equation onto the channel functions $\overline{\Phi}_i^{\Delta}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1})$, and evaluate it on the boundary of the internal region $r_{N+1} = a_0$. We then obtain

$$F_i^{\Delta}(a_0) = \sum_{j=1}^{n} R_{ij}^{\Delta}(E) \left(a_0 \frac{dF_j^{\Delta}}{dr} - b_0 F_j^{\Delta} \right)_{r=a_0}, \quad i = 1, \ldots, n, \tag{10}$$

where the R-matrix $R_{ij}^{\Delta}(E)$ is defined by

$$R_{ij}^{\Delta}(E) = \frac{1}{2a_0} \sum_{k=1}^{n_t} \frac{w_{ik}^{\Delta} w_{jk}^{\Delta}}{E_k^{\Delta} - E}, \quad i, j = 1, \ldots, n; \tag{11}$$

where the sum runs over the solutions of the Hamiltonian. Recent developments have shown how this sum can be drastically reduced without significantly compromising the accuracy of the calculation [19].

To construct eq. (11) it is necessary to define the reduced radial wave functions $F_i^{\Delta}(r)$ which is given by

$$F_i^{\Delta}(r_{N+1}) = \langle \overline{\Phi}_i^{\Delta} r_{N+1}^{-1} | \Psi^{\Delta} \rangle' \quad i = 1, \ldots, n, \tag{12}$$

and the surface amplitudes w_{ik}^{Δ} are given by

$$w_{ik}^{\Delta} = \langle \overline{\Phi}_i^{\Delta} r_{N+1}^{-1} | \psi_k^{\Delta} \rangle'_{r_{N+1}=a_0} = \sum_{j=1}^{n_c} u_{ij}^{0}(a_0) a_{ijk}^{\Delta}, \quad i = 1, \ldots, n, k = 1, \ldots, n_t. \tag{13}$$

The primes on the Dirac brackets in eqs. (12) and (13) mean that the integrations are carried out over all $N+1$ electronic space and spin coordinates in the internal region except the radial coordinates r_{N+1} of the scattered electron. These are the basic equations which describe the scattering of electrons by molecules in the internal region for fixed internuclear separation.

In the external region, defined in Figure 2, a_0 is chosen so that electron exchange and electron-electron correlation effects between the scattered electron and

the target electrons vanish. The total wave function can then be expanded in the form

$$\Psi^{\Delta}(\mathbf{X}_{N+1}) = \sum_{i=1}^{n} \overline{\Phi}_i^{\Delta}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} F_i^{\Delta}(r_{N+1}), \quad r_{N+1} \geq a_0. \tag{14}$$

In this expansion the multicentre channel functions $\overline{\Phi}_i^{\Delta}$ are the same as those retained in the internal region expansion (5). However we now no longer include the antisymmetrization operator, since the scattered electron and the target electrons occupy different regions of space. Also the multicentre quadratically integrable functions χ_i^{Δ} vanish in the external region and the scattered electron is represented by the single-centre reduced radial functions $F_i^{\Delta}(r)$.

Substituting eq. (14) into the Schrödinger equation (2) and projecting onto the channel functions $\overline{\Phi}_i^{\Delta}$ then yields the following set of coupled second-order differential equations satisfied by the reduced radial functions

$$\left(\frac{d^2}{dr^2} - \frac{\ell_i(\ell_i+1)}{r^2} + \frac{2(Z_A+Z_B-N)}{r} + k_i^2\right) F_i^{\Delta}(r) = 2\sum_{j=1}^{n} V_{ij}^{\Delta}(r) F_j^{\Delta}(r),$$
$$i = 1, \ldots, n, \; r \geq a_0. \tag{15}$$

In these equations

$$k_i^2 = 2(E - E_i), \quad i = 1, \ldots, n, \tag{16}$$

where the energy E_i defined by

$$E_i = \langle \overline{\Phi}_i^{\Delta}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} | H_N | \overline{\Phi}_i^{\Delta}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} \rangle, \quad i = 1, \ldots, n, \tag{17}$$

H_N being the target molecule Hamiltonian. Also the potential matrix V_{ij}^{Δ} in eqs. (15) is defined by

$$V_{ij}^{\Delta}(r_{N+1}) = \langle \overline{\Phi}_i^{\Delta}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} \left| \sum_{k=1}^{N} \frac{1}{r_{kN+1}} - \frac{Z_A}{r_{AN+1}} - \frac{Z_B}{r_{BN+1}} \right.$$
$$\left. + \frac{Z_A+Z_B-N}{r_{N+1}} \right| \overline{\Phi}_j^{\Delta}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} \rangle', \quad i,j = 1, \ldots, n, \tag{18}$$

which can be written as a summation over inverse powers of r as follows

$$V_{ij}^{\Delta}(r) = \sum_{\lambda=1}^{\infty} a_{ij\lambda}^{\Delta} r^{-\lambda-1}, \quad i,j = 1, \ldots, n, \quad r \geq a_0, \tag{19}$$

where the long-range potential coefficients $a_{ij\lambda}^{\Delta}$ can be determined by carrying out the multicentre integrals in eq. (18).

The solution of eqs. (15) can be obtained, using a standard method for solving a set of linear coupled second-order differential equations enabling the R-matrix at $r = a_p$ in Figure 2 to be expressed in terms of the R-matrix at $r = a_0$.

In the asymptotic region, defined in Figure 2, an asymptotic solution of eqs. (15) is determined and the solution satisfying the asymptotic boundary conditions

$$\mathbf{F}^{\Delta}(r) \underset{r\to\infty}{\sim} \mathbf{k}^{-\frac{1}{2}}(\sin\boldsymbol{\theta} + \cos\boldsymbol{\theta}\mathbf{K}^{\Delta}), \tag{20}$$

is obtained where $\boldsymbol{\theta}$ is a diagonal matrix with elements

$$\theta_i = k_i r - \frac{1}{2}\ell_i\pi - \eta_i \ln 2k_i r + \sigma_{\ell_i}, \tag{21}$$

with

$$\eta_i = -\frac{Z_A + Z_B - N}{k_i}, \tag{22}$$

and

$$\sigma_{\ell_i} = \arg\Gamma(\ell_i + 1 + \mathrm{i}\eta_i). \tag{23}$$

In this way the $n_a \times n_a$ dimensional K-matrix $\mathbf{K}^{\Delta}$ is determined in terms of the $n \times n$ dimensional R-matrix at $r = a_p$, where n_a is the number of open channels at the incident electron energy under consideration. The corresponding S-matrix is then defined by

$$\mathbf{S}^{\Delta} = \frac{\mathbf{I} + \mathrm{i}\mathbf{K}^{\Delta}}{\mathbf{I} - \mathrm{i}\mathbf{K}^{\Delta}}. \tag{24}$$

The cross section in the molecular fixed frame can then be expressed in terms of the S-matrix.

3 Inclusion of Nuclear Motion

In this and the following section we review how processes involving the nuclear motion such as rotational and vibrational excitation, as well as dissociative processes can be represented in the theory.

One of the most widely used approaches for including the nuclear motion is the adiabatic-nuclei approximation which was introduced by Drozdov [21, 22] and Chase [23] for problems involving vibration and rotation, and has been extended to also treat dissociation [24]. In the case of diatomic molecules in a $^1\Sigma$ state the scattering amplitude for a transition between electronic, vibrational and rotational states defined by the quantum numbers $ivjm_j$ and $i'v'j'm_{j'}$ is given by

$$f_{i'v'j'm_{j'},ivjm_j}(\mathbf{k}.\hat{\mathbf{r}}) = \langle \chi_{i'v'}(R) Y_{j'm_{j'}}(\hat{\mathbf{R}}) | f_{i'i}(\mathbf{k}.\hat{\mathbf{r}};\mathbf{R}) | \chi_{iv}(R) Y_{jm_j}(\hat{\mathbf{R}}) \rangle. \tag{25}$$

where $f_{i'i}(\mathbf{k}.\hat{\mathbf{r}};\mathbf{R})$ is the fixed-nuclei scattering amplitude, which depends parametricaly on the inter-nuclear coordinate $\mathbf{R}$, and χ_{iv} and Y_{jm_j} are the molecular vibrational and rotational eigenfunctions respectively. This approximation is valid

provided that the collision time is short compared with the vibration and rotation times. Hence it can be accurately applied in non-resonant regions.

The adiabatic-nuclei approximation breaks down in the neighbourhood of narrow resonances or close to thresholds. This is because the scattered electron then spends an appreciable time in the neighbourhood of the molecule allowing it to transfer energy to the nuclear motion with high probability. One procedure for overcoming these difficulties is to carry out the calculation in the laboratory frame of reference including the nuclear motion explicitly. The time-independent Schrödinger equation (2) is then replaced by

$$(H_{N+1} + T_{\mathbf{R}})\Psi(\mathbf{X}_{N+1}; \mathbf{R}) = E\Psi(\mathbf{X}_{N+1}; \mathbf{R}), \tag{26}$$

where $T_{\mathbf{R}}$ is the kinetic energy operator of nuclear motion which includes both rotational and vibrational terms and where $\mathbf{R}$ represents the coordinates of the nuclei. The corresponding expansion of the total wave function which replaces eqs. (5) and (14) is then

$$\Psi^{\Delta}(\mathbf{X}_{N+1}; \mathbf{R}) = \mathcal{A}\sum_{i=1}^{n} \overline{\Phi}_i^{\Delta}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}; \mathbf{R}) r_{N+1}^{-1} F_i^{\Delta}(r_{N+1}) + \sum_{j=1}^{m} \chi_i^{\Delta}(\mathbf{X}_{N+1}; \mathbf{R}) b_j^{\Delta}, \tag{27}$$

where the summations over i and j now go over the rotational and vibrational states as well as the electronic states of the molecule and Δ again represents the conserved quantum numbers.

We obtain coupled integro-differential equations for the reduced radial wave functions F_i^{Δ} representing the scattered electron, by substituting eq. (27) into eq. (26) and projecting on to the channel functions $\overline{\Phi}_i^{\Delta}$ and on to the square integrable functions χ_i^{Δ}. After eliminating the b_j^{Δ} coefficients, these equations take the form

$$\left(\frac{d^2}{dr^2} + k_i^2\right) F_i^{\Delta}(r) = 2\sum_{j=1}^{n}(V_{ij}^{\Delta} + W_{ij}^{\Delta} + X_{ij}^{\Delta})F_j^{\Delta}(r), \quad i = 1, \ldots n, \tag{28}$$

where V_{ij}^{Δ}, W_{ij}^{Δ} and X_{ij}^{Δ} are local, non-local exchange and non-local correlation potentials and where we have included the diagonal angular momentum and nuclear Coulomb terms in V_{ij}^{Δ} for notational simplicity.

Coupled equations of this type have been studied by many workers. For example, Arthurs and Dalgarno [25] first obtained coupled equations describing the scattering of an electron by a rigid rotator which have been widely applied. Also Chandra and Temkin [26, 27] used a hybrid theory, in a study of electron scattering by N_2 molecules in the neighbourhood of the $^2\Pi_g$ resonance, which included a summation over vibrational states in eq. (27), but treated the rotational motion adiabatically.

However, in general the number of channels that have to be included in the expansion using this approach becomes prohibitively large for polyatomic molecules when ro-vibrational transitions are treated non-adiabatically.

Finally in discussing the need for laboratory-frame calculations, we mention the frame-transformation theory of Chang and Fano [28] which has been influential in electron atom as well as in electron molecule scattering. Chang and Fano pointed out that the interaction between the electron and the molecule exhibits qualitatively different features when their distance coordinate lies in different regions as illustrated in Figure 3. In the core region electron exchange and correlation effects are dominant

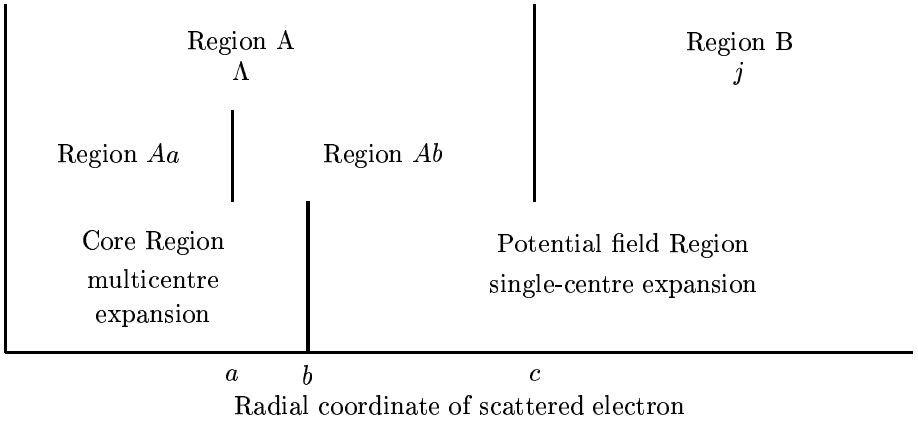

Figure 3: Partitioning of configuration space in frame-transformation theory.

and the molecular frame of reference is appropriate. In the potential field region exchange can be neglected but only in region A can the molecular frame still be used. At large distances, in region B, the coupling of the electron angular momentum to the molecular axis is no longer strong and the laboratory frame of reference is appropriate. Finally if vibrational motion is being considered, region A must be partitioned. In region Aa, a Born-Oppenheimer separation of the nuclear and electronic motion is appropriate and the problem can be solved as a function of the internuclear separation. On the other hand in region Ab, the vibrational motion must be included non-adiabatically in the description of the collision.

In comparing the frame-transformation picture given by Figure 3 with the R-matrix picture given by Figure 2 we see that the core region in frame-transformation theory corresponds to the internal R-matrix region. However in the neighbourhood of narrow resonances or close to thresholds the radius a of region Aa may be less than the radius b of the core region. That is the Born-Oppenheimer separation of vibrational and electronic motion is only applicable in the outer part of the internal region in Figure 2. Since representing electron exchange by the usual antisymmetrization operator requires that the whole of the internal region is treated uniformly, then the vibrational motion must be included explicitly in the whole of the internal region as

discussed in Section 4 below.

4 R-matrix Theory of Nuclear Motion

In this section we describe a non-adiabatic R-matrix theory developed by Schneider *et al* [29] which enables vibrational excitation as well as dissociative attachment and dissociative ionization to be calculated. The theory enables the following processes to be studied:

$$\begin{array}{rcll} & & AB_{i'v'} + \mathrm{e}^- & \text{vibronic excitation} \\ & \nearrow & & \\ \mathrm{e}^- + AB_{iv} & \rightarrow & A_j + B^-_{j'} & \text{dissociative attachment/recombination} \\ & \searrow & & \\ & & A_j + B_{j'} + \mathrm{e}^- & \text{dissociation} \end{array} \tag{29}$$

where i, i', j and j' label the electronic states and v and v' label the vibrational states. We now have to solve the following time-independent Schrödinger equation

$$(H_{N+1} + T_R)\Psi(\mathbf{X}_{N+1}; R) = E\Psi(\mathbf{X}_{N+1}; R), \tag{30}$$

where we consider as an example electron scattering by a diatomic molecule, illustrated in Figure 1. In eq. (30), $\Psi(\mathbf{X}_{N+1}; R)$ is the total wave function describing the processes defined by eq. (29) H_{N+1} is the fixed-nuclei Hamiltonian defined by eq. (3) and T_R is the nuclear kinetic energy operator

$$T_R = -\frac{1}{2\mu}\frac{d^2}{dR^2}, \tag{31}$$

where μ is the reduced mass of the two nuclei and R is the internuclear distance. Also the z-axis is chosen to lie along the internuclear axis where we assume that the molecule does not rotate appreciably during the collision and hence the rotational motion can be treated adiabatically.

In Figure 4 we illustrate the partitioning of configuration space used to solve eq. (30). The internal region is taken to be a rectangle defined by $0 \leq r \leq a_0$ and $A_i \leq R \leq A_0$ where a_0 is defined in the same way as in the fixed-nuclei theory given in Section 2, A_i is chosen to exclude the nuclear Coulomb repulsion singularity at $R = 0$, where the wave function describing the nuclear motion is negligible, and A_0 is chosen so that the target vibrational states of interest in the calculation have negligible amplitude for $R > A_0$. For $r > a_0$ the molecule separates into an electron plus residual molecule which may be vibrationally and electronically excited, as discussed in the fixed-nuclei theory given in Section 2. For $R > A_0$ the molecule separates into an atom plus a negative ion or into two atoms corresponding to dissociative attachment or dissociation.

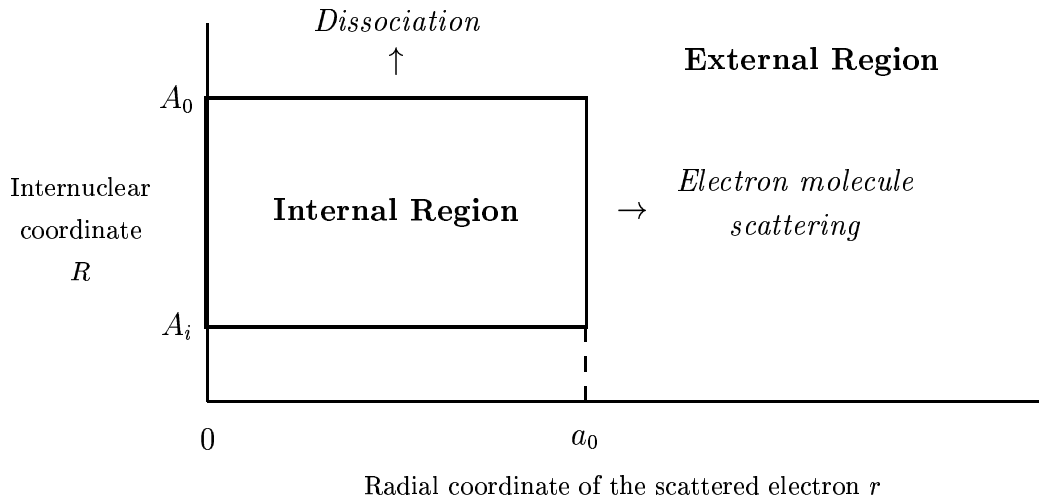

Figure 4: Partitioning of configuration space in non-adiabatic R-matrix theory.

In order to solve eq. (30) in the internal region, for each set of conserved quantum numbers Δ, we write it in the following form.

$$(H_{N+1} + T_R + \mathcal{L}_{N+1} + \mathcal{L}_R - E)\Psi^\Delta = (\mathcal{L}_{N+1} + \mathcal{L}_R)\Psi^\Delta, \tag{32}$$

where the Bloch operators $\mathcal{L}_{N+1}$ and $\mathcal{L}_R$ are introduced so that $H_{N+1}+T_R+\mathcal{L}_{N+1}+\mathcal{L}_R$ is hermitian in the basis of quadratically integrable functions defined over the internal region in Figure 4 and satisfying arbitrary boundary conditions on the boundary of this region. We have already defined $\mathcal{L}_{N+1}$ by eq. (7) such that $H_{N+1}+\mathcal{L}_{N+1}$ is hermitian for fixed internuclear separation R. The Bloch operator $\mathcal{L}_R$, which is defined by

$$\mathcal{L}_R = \frac{1}{2\mu}\left[\delta(R-A_0)\left(\frac{d}{dR} - \frac{B_0}{R}\right) - \delta(R-A_i)\left(\frac{d}{dR} - \frac{B_i}{R}\right)\right], \tag{33}$$

where B_0 and B_i are arbitrary constants, is such that $T_R + \mathcal{L}_R$ is hermitian over the range $A_i \le R \le A_0$. It follows that $H_{N+1} + T_R + \mathcal{L}_{N+1} + \mathcal{L}_R$ is hermitian as required. We can then rewrite eq. (32) as

$$\Psi^\Delta = (H_{N+1} + T_R + \mathcal{L}_{N+1} + \mathcal{L}_R - E)^{-1}(\mathcal{L}_{N+1} + \mathcal{L}_R)\Psi^\Delta, \tag{34}$$

which is a formal solution of eq. (30) in the internal region. In order to provide a representation for the inverse operator in eq. (34) we introduce the following basis in the internal region

$$\Theta_i^\Delta(\mathbf{X}_{N+1}; R) = \sum_{kj} \psi_k^\Delta(\mathbf{X}_{N+1}; R)\zeta_j(R)c_{kji}^\Delta. \tag{35}$$

The ψ_k^Δ in this equation are the fixed-nuclei R-matrix electronic basis functions defined by eqs. (5) and (6) which are solved for a mesh of fixed internuclear values of R spanning the range $A_i \leq R \leq A_0$, and the $\zeta_j(R)$ are basis functions representing the nuclear motion, which are orthonormal over this range. In practise shifted Legendre polynomials are often used for the ζ_j. The coefficients c_{kji}^Δ are obtained by diagonalizing the operator $H_{N+1} + T_R + \mathcal{L}_{N+1} + \mathcal{L}_R$ in this basis. In this diagonalization we assume, in accordance with the Born-Oppenheimer (BO) approximation, that the contributions from the nuclear kinetic energy operator T_R acting on the electronic basis functions ψ_k^Δ is small and can usually be neglected. This assumption can be understood, following the discussion by Schneider [30], by noting that while the adiabatic nuclei theory breaks down for low-energy electron collisions, which led to the "hybrid" theory of Chandra and Temkin [26, 27] discussed in Section 3, this does not mean that the electronic and vibrational degrees of freedom cannot be separated as in the BO approximation. The appropriate expansion of the total wave function for the BO approximation to be valid is in terms of electronic states of the compound $(N+1)$-electron system. In R-matrix theory these compound states are the fixed-nuclei $(N+1)$-electronic basis functions ψ_k^Δ in expansion (35). Hence, using the BO approximation we can write

$$\begin{aligned}
&\langle \Theta_i^\Delta | H_{N+1} + T_R + \mathcal{L}_{N+1} + \mathcal{L}_R | \Theta_{i'}^\Delta \rangle_{\rm int} \\
&\quad = \sum_{kj} \sum_{k'j'} \langle \psi_k^\Delta \zeta_j | H_{N+1} + T_R + \mathcal{L}_{N+1} + \mathcal{L}_R | \psi_{k'}^\Delta \zeta_{j'} \rangle_{\rm int} c_{kji}^\Delta c_{k'j'i'}^\Delta \\
&\quad = \langle \xi_{kl}^\Delta | T_R + E_k^\Delta(R) + \mathcal{L}_R | \xi_{k'l'}^\Delta \rangle_{\rm int} \delta_{kk'} \\
&\quad = \epsilon_{kl} \delta_{kk'} \delta_{ll'}, \qquad (36)
\end{aligned}$$

where we have used eq. (6), remembering that the energy E_k^Δ is a function of R. Also in eq. (36) we have introduced the vibrational functions ξ_{kl}^Δ representing the nuclear motion in the kth electronic state ψ_k^Δ, which are determined by diagonalizing the operator $T_R + E_k^\Delta(R) + \mathcal{L}_R$ for each k in the zero-order basis ζ_j. Hence we have written

$$\xi_{kl}^\Delta(R) = \sum_j \zeta_j(R) c_{kji}^\Delta, \qquad (37)$$

where the subscript l goes over the range 1 to n_v for each k, where n_v is the number of zero-order basis functions ζ_j retained in expansion (35). Hence l can be defined in terms of i and k by the equation

$$l = i - (k-1) n_v. \qquad (38)$$

It follows that the inverse operator in eq. (34) can be written as

$$(H_{N+1} + T_R + \mathcal{L}_{N+1} + \mathcal{L}_R - E)^{-1} = \sum_{kl} \frac{|\psi_k^\Delta \xi_{kl}^\Delta\rangle \langle \psi_k^\Delta \xi_{kl}^\Delta|}{\epsilon_{kl} - E}. \qquad (39)$$

Also we introduce the channel functions θ_{iv}^{Δ} corresponding to electron molecule scattering and the channel functions ϕ_j^{Δ} corresponding to dissociation. These are defined by

$$\theta_{iv}^{\Delta}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1};R) = \overline{\Phi}_i^{\Delta}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\eta_{iv}(R), \tag{40}$$

and

$$\phi_j^{\Delta}(\mathbf{X}_{N+1}) = [\psi_{Aj}(\mathbf{X}_A)\otimes\psi_{Bj}(\mathbf{X}_B)]_j^{\Delta}\,. \tag{41}$$

In eq. (40), $\overline{\Phi}_i^{\Delta}$ are the fixed-nuclei channel functions introduced in eq. (5), which depend on R, and η_{iv} are the vibrational wave functions for the molecule in the ith electronic state. In eq. 41), ψ_{Aj} and ψ_{Bj} are the wave function of the dissociating atoms, with electronic space and spin coordinates denoted by $\mathbf{X}_A$ and $\mathbf{X}_B$ respectively, which are coupled to give eigenstates labelled j belonging to the conserved quantum numbers Δ.

We then determine the R-matrix on the boundaries of the internal region by substituting the representation for $(H_{N+1}+T_R+\mathcal{L}_{N+1}+\mathcal{L}_R-E)^{-1}$ given by eq. (39) into eq. (34), projecting onto the channel functions θ_{iv}^{Δ} and ϕ_j^{Δ} and evaluating the projected equations at $r=a_0$ and $R=A_0$. We obtain

$$\begin{aligned} F_{iv}^{\Delta}(a_0) = &\sum_{i'v'} R_{ivi'v'}^{\Delta}(E)\left(a_0\frac{dF_{i'v'}^{\Delta}}{dr} - b_0F_{i'v'}^{\Delta}\right)_{r=a_0} \\ &+\sum_j R_{ivj}^{\Delta}(E)\left(A_0\frac{dG_j^{\Delta}}{dR} - B_0G_j^{\Delta}\right)_{R=A_0}, \end{aligned} \tag{42}$$

and

$$\begin{aligned} G_j^{\Delta}(A_0) = &\sum_{iv} R_{jiv}^{\Delta}(E)\left(a_0\frac{dF_{iv}^{\Delta}}{dr} - b_0F_{iv}^{\Delta}\right)_{r=a_0} \\ &+\sum_{j'} R_{jj'}^{\Delta}(E)\left(A_0\frac{dG_{j'}^{\Delta}}{dR} - B_0G_{j'}^{\Delta}\right)_{R=A_0}, \end{aligned} \tag{43}$$

where the second term in the Bloch operator $\mathcal{L}_R$ defined by eq. (33) does not contribute since A_i is chosen so that the wave function describing the vibrational motion of the nuclei and their derivatives vanish for $R \le A_i$.

The radial wave functions F_{iv}^{Δ} and G_j^{Δ} describing the motion of the scattered electron and the dissociating atoms in eqs. (42) and (43) are defined by projecting the total wave function Ψ^{Δ} onto the channel functions as follows

$$F_{iv}^{\Delta}(r_{N+1}) = \langle\theta_{iv}^{\Delta}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1};R)r_{N+1}^{-1}|\Psi^{\Delta}(\mathbf{X}_{N+1};R)\rangle', \tag{44}$$

and

$$G_j^{\Delta}(R) = \langle\phi_j^{\Delta}(\mathbf{X}_{N+1})|\Psi^{\Delta}(\mathbf{X}_{N+1};R)\rangle'. \tag{45}$$

The primes on the Dirac brackets mean that the integrations are carried out over all coordinates except r_{N+1} in eq. (44) and except R in eq. (45). Also the R-matrices in eqs. (42) and (43) are defined by

$$R^{\Delta}_{ivi'v'}(E) = \frac{1}{2a_0}\sum_{kl}\frac{w^{\Delta}_{ivkl}w^{\Delta}_{i'v'kl}}{\epsilon_{kl}-E}, \tag{46}$$

$$R^{\Delta}_{ivj}(E) = \frac{1}{2\mu A_0}\sum_{kl}\frac{w^{\Delta}_{ivkl}w^{\Delta}_{jkl}}{\epsilon_{kl}-E}, \tag{47}$$

$$R^{\Delta}_{jiv}(E) = \frac{1}{2a_0}\sum_{kl}\frac{w^{\Delta}_{jkl}w^{\Delta}_{ivkl}}{\epsilon_{kl}-E}, \tag{48}$$

$$R^{\Delta}_{jj'}(E) = \frac{1}{2\mu A_0}\sum_{kl}\frac{w^{\Delta}_{jkl}w^{\Delta}_{j'kl}}{\epsilon_{kl}-E}. \tag{49}$$

Finally, the surface amplitudes in eqs. (46) to (49) are defined by

$$w^{\Delta}_{ivkl} = \langle\theta^{\Delta}_{iv}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1});R)r^{-1}_{N+1}|\psi^{\Delta}_k(\mathbf{X}_{N+1};R)\xi_{kl}(R)\rangle'_{r_{N+1}=a_0}, \tag{50}$$

$$w^{\Delta}_{jkl} = \langle\phi^{\Delta}_j(\mathbf{X}_{N+1})|\psi^{\Delta}_k(\mathbf{X}_{N+1};R)\xi_{kl}(R)\rangle'_{R=A_0}. \tag{51}$$

Substituting the expressions for the R-matrices given by eqs. (46) to (49) into eqs. (42) and (43) provides the boundary conditions satisfied by the solution of eq. (30) in the external region considered below.

The above procedure for calculating the R-matrices has proved to be satisfactory in most applications. However, Gillan *et al* [31] pointed out that this procedure must be modified in situations where there are strongly avoided crossings between the eigenvalues E^{Δ}_k in eq. (6) as a function of R. In this situation the Born-Oppenheimer separation of the electronic and nuclear motion is not valid in the neighbourhood of these avoided crossings and as a result the effect of the nuclear kinetic energy operator T_R acting on the electronic basis functions ψ^{Δ}_k in eq. (36) is no longer negligible. In principle this effect, which couples the electronic states involved in the avoided crossings, can be calculated. However, an alternative procedure, which is straightforward to apply, was proposed by Gillan *et al*. They replaced the expansion basis defined by eq. (35) by a modified expansion given by

$$\Theta^{\Delta}_i(\mathbf{X}_{N+1};R) = \sum_{kj}\psi^{\Delta}_k(\mathbf{X}_{N+1};R_0)\zeta_j(R)\gamma^{\Delta}_{kji}, \tag{52}$$

where the electronic basis functions ψ^{Δ}_k in this expansion are defined for a given fixed internuclear separation R_0 and are thus independent of R. The diagonalization of the Hamiltonian $H_{N+1}+T_R+\mathcal{L}_{N+1}+\mathcal{L}_R$ is then more difficult to apply than that given by eq. (36) since the electronic basis functions no longer diagonalize the electronic part of the Hamiltonian except at $R = R_0$. However a practical procedure for treating

this problem was described by Gillan *et al* which was used in a study of electron scattering by nitrogen molecules. This work has been extended to molecular ions, for which large numbers of resonances occur, and used to study both vibrational excitation [32] and dissociative recombination [33].

In the external sub-region corresponding to electron molecule scattering in Figure 4, we expand the total wave function in terms of the channel functions, defined by eq. (40) as follows

$$\Psi^{\Delta}(\mathbf{X}_{N+1};R)=\sum_{iv}\theta_{iv}^{\Delta}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1};R)r_{N+1}^{-1}F_{iv}^{\Delta}(r_{N+1}). \tag{53}$$

We substitute this expansion into the Schrödinger equation (30) and project it onto the channel functions θ_{iv}^{Δ}. This yields the following set of coupled second-order differential equations satisfied by the reduced radial functions $F_{iv}^{\Delta}(r)$

$$\left(\frac{d^2}{dr^2}-\frac{\ell_i(\ell_i+1)}{r^2}+\frac{2(Z_A+Z_B-N)}{r}+k_{iv}^2\right)F_{iv}^{\Delta}(r)=2\sum_{i'=1}^{n}\sum_{v'=1}^{n_v}V_{ivi'v'}^{\Delta}(r)F_{i'v'}^{\Delta}(r),$$
$$i=1,\ldots,n,v=1,\ldots,n_v,\ r\geq a_0, \tag{54}$$

where we assume that n electronic channels each with n_v vibrational states have been retained in expansion (53). Also in eq. (54)

$$k_{iv}^2=2(E-E_{iv}), \tag{55}$$

where E_{iv} is the energy of the vth vibrational state in the ith electronic channel which is defined by

$$E_{iv}=\langle\eta_{iv}(R)|E_i(R)|\eta_{iv}(R)\rangle\quad i=1,\ldots,n,v=1,\ldots,n_v. \tag{56}$$

The energies $E_i(R)$ in this equation, which are defined by eq. (17) in the fixed-nuclei approximation, are functions of R. Finally, the potential matrix in eq. (54) is defined by

$$V_{ivi'v'}^{\Delta}(r)=\langle\eta_{iv}(R)|V_{ii'}^{\Delta}(r)|\eta_{i'v'}(R)\rangle, \tag{57}$$

which can be written as a summation over inverse powers of r as follows

$$V_{ivi'v'}^{\Delta}(r)=\sum_{\lambda=1}^{\infty}a_{ivi'v'\lambda}^{\Delta}r^{-\lambda-1},\quad i,i'=1,\ldots,n;v,v'=1,\ldots,n_v,\ r\geq a_0, \tag{58}$$

where $V_{ii'}^{\Delta}(r)$ is defined by eq. (18) in the fixed nuclei approximation.

In the external sub-region corresponding to dissociation in Figure 4, we expand the total wave function in terms of the channel functions, defined by eq. (41) as follows

$$\Psi^{\Delta}(\mathbf{X}_{N+1};R)=\sum_{j}\phi_j^{\Delta}(\mathbf{X}_{N+1})G_j^{\Delta}(R). \tag{59}$$

In order to derive coupled second-order differential equations satisfied by the reduced radial functions $G_j^{\Delta}(R)$ we rewrite the Hamiltonian H_{N+1} in eq. (30) in the following alternative form

$$H_{N+1} = H_A + H_B + U_{AB}, \tag{60}$$

where H_A and H_B are the Hamiltonian operators corresponding to the dissociating atoms A and B, which we assume contain N_A and N_B electrons respectively, and U_{AB} is the long-range Coulomb interaction between these atoms. We now substitute expansion (59) into the Schrödinger equation (30) and project it onto the channel functions ϕ_j^{Δ}. This yields the following set of coupled second-order differential equations satisfied by the reduced radial functions $G_j^{\Delta}(r)$

$$\left(\frac{d^2}{dR^2} - \frac{2\mu(Z_A - N_A)(Z_B - N_B)}{R} + k_j^2\right) G_j^{\Delta}(R) = 2\mu \sum_{j'=1}^{m} U_{jj'}^{\Delta}(R) G_{j'}^{\Delta}(R),$$
$$j = 1, \ldots, m, \ R \geq A_0, \tag{61}$$

where we assume that m dissociation channels have been retained in expansion (59). Also in eq. (61) we have defined

$$k_j^2 = 2\mu(E - E_{A_j} - E_{B_j}), \tag{62}$$

where the energies E_{A_j} and E_{B_j} are the energies of the atomic states defined by

$$\langle \psi_{A_j}(\mathbf{X}_A) | H_A | \psi_{A_j}(\mathbf{X}_A) \rangle = E_{A_j}, \tag{63}$$

and

$$\langle \psi_{B_j}(\mathbf{X}_B) | H_B | \psi_{B_j}(\mathbf{X}_B) \rangle = E_{B_j}. \tag{64}$$

Finally, the potential matrix $U_{jj'}^{\Delta}(R)$ in eq. (61) is defined in terms of the Coulomb interaction term U_{AB}. On carrying out the integrals in this equation we find that $U_{jj'}^{\Delta}(R)$ can be written as a summation over inverse powers of R as follows

$$U_{jj'}^{\Delta}(R) = \sum_{\lambda=1}^{\infty} A_{jj'\lambda}^{\Delta} R^{-\lambda-1}, \quad j, j' = 1, \ldots, m, \quad R \geq A_0. \tag{65}$$

As in the fixed-nuclei approximation, eqs. (54) and (61) can be integrated outwards from $r = a_0$ to a_p and from $R = A_0$ to A_q respectively, enabling the R-matrix at $r = a_p$ and $R = A_q$ to be expressed in terms of the R-matrix defined by eqs. (46) to (49). The K-matrix and hence the S-matrix can then be determined in terms of the asymptotic solution in the regions $r \geq a_p$ and $R \geq A_q$. The cross sections corresponding to the processes defined by eq. (29) can then be obtained.

5 Results and Discussions

Electron collisions with water are important for many applications. However the large dipole moment of this system makes even the elastic cross section hard to determine experimentally, due to the very strong forward peak in the differential cross section. Figure 5 compares a recent R-matrix calculation [35] with the differential cross sections measured by Cho *et al* [34]. The R-matrix calculations are rotationally summed elastic cross sections since the experiments do not have rotational resolution. Cho *et al* used a novel technique which allowed them to determine this cross section over a wide range of angles, even at 180^o. Experiment and theory agree well for the angles for which differential measurements have been performed. Despite this there is not good agreement for the total cross section as it is not possible to estimate the magnitude of the forward scattering from the experimental data. Conversely the momentum transfer cross section is insensitive to forward scattering and there is very good agreement between the R-matrix calculations and Cho *et al*'s determination for this quantity, see [35].

There are few laboratory measurements for electron impact rotational excitation of any molecule and none for any molecular ions. This meant that observations rely on theory which until recently performed using a dipole Coulomb-Born model. This leads to the firm prediction that only $J = 1 - 0$ rotational transitions should be observed in these diffuse environments.[36] R-matrix calculations have shown that, particularly for molecular ions which do not have large dipole moments, higher rotational states will be excited by electron collisions leading to emissions from higher states of the molecule.[37] An interesting example is the important CH^+ ion for which transitions as high as $J = 6 - 5$ have been observed [38], a result rationalised by R-matrix calculations which explicitly considered the contribution the short range interactions to the rotational excitation process.[39]

Electron collisions with atmospherically important species are important for determining the ionisation balance in the Earth's ionosphere as dissociative recombination of molecular ions is the dominant neutralisation process. A combined R-matrix – MultiChannel Quantum Defect Theory (MCQDT) study of dissociative recombination of NO^+ [40] gave unprecedent agreement with experiment for this process. Similarly a study of electron collisions with the atmospheric trace species OClO [41] gave excellent agreement with one of the few experiments to get absolute cross sections for electron collisions with an open shell and unstable molecule [42].

These calculations laid the foundation for a series of studies on electron collisions with CF_x, $x = 1, 2, 3$, radicals.[43, 44, 45, 46] These fluorocarbon species are an important constituent of many industrial plasmas used for etching. The calculations on CF_3 represent the largest system for which R-matrix electron collision calculations have been performed. The difficulty with this system is not its physical size but the fact that CF_3 contains 25 electrons in $n = 2$ orbitals all of which might be considered

to be active as far as the scattering process is concerned. In practice such calculations could only be performed with 17 active electrons. An interesting and potentially important result of these studies is that while CF and CF_2 both have low-lying resonances, which can provide a route to dissociative electron attachment, CF_3 does not. This suggests that the concentration of negative ions, particularly F^-, in fluorocarbon plasmas will depend on which radical is dominant. The concentration of radicals can be controlled by choice of the feedstock gas: C_2F_4 yields large CF_2 while CF_3I breaks up to give largely CF_3 for example.

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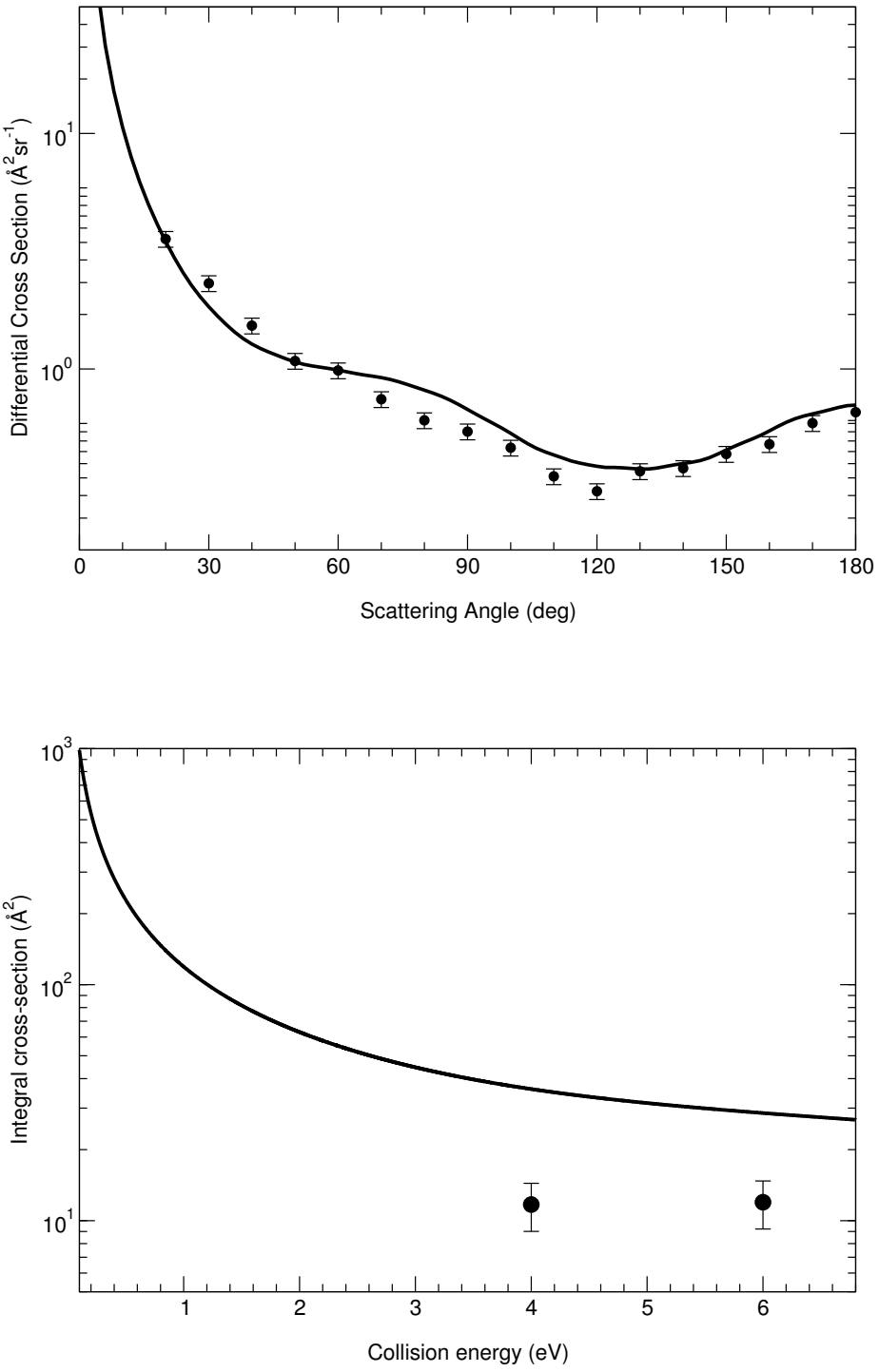

Figure 5: Elastic (rotationally summed) cross sections for electron collisions with water: upper figure differential cross section at 4 eV; lower figure: integral cross section. Curve: R-matrix calculation of Faure *et al* [35]; circles: measurements of Cho *et al.*