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Abstract.
   This review surveys the different theoretical approaches, used to describe inelastic and rearrangement processes in collisions involving atoms and ions. For a range of energies from a few meV up to about 1 keV, the adiabatic representation is expected to be valid and under these conditions, inelastic and rearrangement processes take place via a network of avoided crossings of the potential energy curves of the collision system. In general, such avoided crossings are finite in number. The non-adiabatic coupling, due to the breakdown of the Born-Oppenheimer separation of the electronic and nuclear variables, depends on the ratio of the electron mass to the nuclear mass terms in the total Hamiltonian. By limiting terms in the total Hamiltonian correct to first order in the electron to nuclear mass ratio, a system of reaction coordinates is found which allows for a correct description of both inelastic channels. The connection between the use of reaction coordinates in the quantum description and the electron translation factors of the impact parameter approach is established. A major result is that only when reaction coordinates are used, is it possible to introduce the notion of a minimal basis set. Such a set must include all avoided crossings including both radial coupling and long range Coriolis coupling. But, only when reactive coordinates are used, can such a basis set be considered as complete. In particular when the centre of nuclear mass is used as centre of coordinates, rather than the correct reaction coordinates, it is shown that erroneous results are obtained. A few results to illustrate this important point are presented: one concerning a simple two-state Landau-Zener type avoided crossing, the other concerning a network of multiple crossings in a typical electron capture process involving a highly charged ion with a neutral atom.

1. Introduction

Ever since the early days of quantum mechanics, it has been known that an adiabatic representation of the transition state complex formed in the collision of two atomic systems provides an excellent framework for the description of inelastic and rearrangement processes when the relative kinetic energy of the collision partners is lower than a few keV/amu. In this picture, collision processes leading to an electronic transition occur via the non-adiabatic coupling between those adiabatic states correlated to the the entry and exit channels. Non-adiabatic couplings are important not only in the vicinity of avoided crossings involving states of the same symmetry but also in the asymptotic region where states of different symmetry become degenerate. As a general rule only a few states are strongly coupled. This leads to a high degree of state selection, which greatly reduces the number of adiabatic reaction channels required to describe the collision process. For many systems, a two state adiabatic representation often gives a satisfactory description of the dominant reaction channel. Indeed the simple Landau-Stuckelberg-Zener model [1, 2, 3] based on a knowledge of the minimum energy separation at the avoided crossing, proved to be successful in providing reasonable estimates of electron capture cross sections in low energy ion-atom collisions. But more generally, when a multi-state basis is required, the number of interacting states rarely exceeds more than 5 or 6.

Unfortunately, in spite of the attractive features of the adiabatic representation in a qualitative understanding of the collision mechanisms, quantitative applications encounter severe problems. Non-adiabatic couplings depend on the choice of coordinates used to separate the adiabatic variables. For example, in an adiabatic representation of the 3-body problem consisting of 2 nuclei and an electron e, a common choice is to use as independent variables, the vector **R** connecting the 2 nuclei and the vector **r** connecting the centre of mass of the nuclei (CMN) with the electron. In this coordinate system, the kinetic energy operator of the system contains cross-derivative terms with respect to r and R, which leads to the intertwining of a large number of basis functions leading to a slow convergence of the basis set and in some cases to the existence of non-vanishing asymptotic matrix elements, which make it rigorously impossible to extract a scattering matrix from the dynamical equations.

So it was not surprising that the first attempt by Bates et al. [4] to develop a theoretical model using an adiabatic basis, inspired by the perturbed stationary state (PSS) method proposed by Mott [5], ran into severe difficulties. In particular, the use of Jacobi coordinates, used to describe the adiabatic state, made it impossible to satisfy the correct asymptotic conditions necessary for the extraction of the scattering amplitudes and the cross sections. However, it was realised that a considerable simplification could be achieved in the case where the collision energy was much greater than the energy of the bound electrons involved in the excitation or rearrangement process. Typically, at the time, most experimental measurements concerned ions with energies greater than 100 eV for which the scattering angles were less than a few degrees ($< 3°$). On the other

hand, for ion energies up to a few keV, the collision velocity was sufficiently small to utilize an adiabatic representation of the collision system. It was legitimate to assume a classical rectilinear trajectory for the nuclear motion, thereby transforming the original stationary state Schrödinger equation to a time-dependent problem for a given classical impact parameter‡. (In this respect, it should be observed that the impact parameter method is not strictly equivalent to a semi-classical method). But while the impact parameter approach did indeed simplify some aspects of the collision process, it did not solve the problem of representing rearrangement collisions (such as charge exchange), in an adiabatic representation, since then, the results are not invariant with respect to the time origin. To overcome this problem, it proved necessary to introduce the notion of electron translation factors (ETF) [7]. However, apart from constraints on their asymptotic form, there was no unique way to define such ETF in any rigorous way and over the course of the following two decades, many variants of ETF were investigated. As originally formulated, the inclusion of state dependent ETF proved to be unworkable with no guarantee of success. The first breakthrough came by the introduction of state independent factors depending on a switching function [8], chosen to be such that the required asymptotic conditions were respected. The optimal form of the switching function designated as a common translation factor (CTF), first introduced by Errea et al. [9], proved to be the most efficient form of translation factor and has been used extensively with success ever since in calculations based on the impact parameter approach. However, the development of theoretical investigations of translation factors is now mainly of historical interest and the reader is referred to a more detailed discussion given in the book by Bransden and McDowell [10]. See also a more recent review by Errea et al. [11].

In retrospect, it seems surprising that the problem associated with the impact parameter method has taken so long to be resolved. Recently, Solovev [12] pointed out that the solution of the time-dependent impact parameter equation involves the superposition of nuclear motions of different channels with significantly different momenta. In consequence, a unique time for all channels does not exist. For this reason the notion of a single classical trajectory fails to describe correctly the collision process without the empirical introduction of translation factors. It is also worth stressing the principal characteristics of impact parameter methods. Their most notable property is that the total cross section, which depends only on the amplitude of the probabilities scales with the collision velocity. So if the velocity dependence of the cross sections is known for one isotopic species, it can be deduced for all isotopes. For this reason, impact parameter methods are efficient for the calculation of total cross sections. On the other hand, the differential cross section depends also on the phase of the transition probabilities and so depends on the isotopic mass. Therefore when differential cross sections are required, it is more practical to use a quantum mechanical formulation [13].

Prior to the 1980s, most atomic collision experiments were primarily concerned with

‡ For an exhaustive to the impact parameter method see the review of Solovev [6]

the processes of excitation, ionization and charge transfer occurring in the interaction of ion beams with atoms in the energy range of a few hundred eV to a few keV. In this energy range, both the impact parameter method and an adiabatic basis are appropriate. So it was not very surprising that little attempt was made before the late 1970s to develop a consistent quantum mechanical formulation of the collision process, which would have avoided the necessity of introducing what appears as the notion of arbitrary electron translation factors inherent to the impact parameter method. However, in the late 1970s, new experimental techniques using ion-sources allowing for the production of slow multiply charged ion on a variety of atomic and molecular targets, opened up new fields relevant to the study of astrophysical and high temperature fusion plasmas. A little later, the development of techniques using merged ion beams made it possible to study very low energy collisions with a precision allowing for a sensitive test of the theoretical models. So it became imperative to develop a purely quantum mechanical approach.

The first successful formulation was given by Thorson and Delos [14]. See also the exhaustive review of Delos [15]. This involved the introduction of reaction coordinates, originally proposed by Mittleman [16], which are defined in such a way that these new coordinates become the appropriate atomic frame coordinates in each asymptotic channel, while in the strong interaction region provide a coordinate system locally adapted to the molecular region. This approach is fully quantum-mechanical and no reference to electron translation factors is required. In their work, Thorson and Delos had in mind a typical isotopic system such as the charge exchange reaction $H^+ + D \rightarrow H + D^+$, a system which is electrically symmetric, for which the molecular electronic states are parity eigen-functions, just like those of H_2^+, since the electronic Hamiltonian is symmetric. The small isotopic difference in D and H binding energies can be assumed to be negligible. But Thorson and Delos pointed out that when the centre of mass of the nuclei is chosen as origin of coordinates, the mass asymmetry parameter of the reaction would lead to a non-adiabatic coupling. This is clearly incorrect.

In this review, a simplified presentation of the approach used by Thorson and Delos [14] is given, based on a coordinate system of Eckart-type coordinates [17] which is correct to first order of the ratio of the electron-nuclear mass ratio. The main advantage of this procedure is that it preserves the use of an adiabatic basis set with a relatively simple modification of the non-adiabatic coupling operators. However, In spite of the concordance of the quantum mechanical formulation (with the appropriate reaction coordinates) and the impact parameter method (using the corresponding translation factors), there still remained the problem of the completeness of the basis set. It was clear from the early calculations using either the impact parameter with inappropriate translation factors or quantum calculations with the standard Born-Oppenheimer conditions that the basis set was incomplete. But, a direct test of the convergence of the basis set is not simple since an infinite number of bound and continuum adiabatic states may be needed to represent the asymptotic conditions correctly. Comparison with experiment is, of course helpful, but the precision of experimental cross section

measurements is rarely sufficient to make a critical comparison of theory and experiment.

To test the convergence of the basis set, one way to proceed is via a standard unitary transformation, of the kind introduced by Smith [20] to eliminate the cross diagonal terms of the kinetic energy operator from the coupled equations. This procedure is often referred to as an adiabatic/diabatic transformation. Although such a diabatic basis has no very precise physical meaning, it does have the practical advantage of simpifying the numerical solution of the differential equations. However, for such a basis set to be meaningful, the non-adiabatic coupling to states outside the minimal basis must be negligible. This procedure was adopted in the work of Rabli and McCarroll [19] concerning the C^{4+}/H system, where the main objective was to demonstrate that the notion of a minimal basis set is valid when reaction coordinates are used. Their results indicated that indeed all of the spurious asymptotic couplings which arise in the case of a Jacobi coordinates are indeed removed, but only when the correct reaction coordinates are used. And it was found that when the appropriate reaction coordinates were not used, the basis set was not complete. This result explained why even for a simple Landau-Zener avoided crossing, the choice of the appropriate reaction coordinates in a quantum calculation (or the equivalent CTF in an impact parameter method) is essential to obtain a meaningful result.

Prior to these considerations related to the necessity of ensuring a complete basis set, there had been for some considerable time a general consensus on the precaution to be taken in the calculation of crosss-sections of inelastic and rearrangement processes in ion-atom collisions using an adiabatic basis: either a fully quantum mechanical approach,using the reaction coordinates [14], involving a sum over all angular momenta, or a semi-classical approach with common translation factors involving an integration over all impact parameters. Two comprehensive reviews of the state-of-the art methods at that time were published , one by McCarroll [21] on the quantum mechanical methods, the other by Errea et al [11] on impact parameter methods, indicated that both approaches were valid and in good agreement with experimental measurements. But at the time, the notion of a minimal basis set had not been evoked. And it was only in 2005 that a way of testing the adequacy of the basis set was achieved.

The aim of this review is primarily to highlight the necessity of using correct reaction coordinates even for the simplest of collision processes involving non-adiabatic coupling and to show that only under these conditions can the completeness of the basis set be guaranteed. For that reason, it did not appear neccessary to include material which had already been treated adequately either in earlier reviews [21] [11]or developed in the book of Bransden & McDowell [10].

Atomic units will be used, except where otherwise stated.

2. Theory

The notion of reaction coordinates (and/or translation factors) arises from the need to modify the adiabatic basis set in order to describe the kinematics of the reactants

and the dissociation products correctly. The problem is of particular importance in rearrangement processes involving the electron capture in ion-atom collisions with an ion, but it is present even for inelastic processes when an adiabatic representation is used to describe a many-body collision complex. First of all, we recall briefly how the reaction coordinates used in this work have been constructed.

Let us consider a system of two ionic cores A and B of masses m_a and m_b and an electron of mass m_e (=1 in atomic units). After separation of the center of mass motion, the kinetic energy operator takes its simplest form in one of the three Jacobi coordinates, $(\mathbf{r}, \mathbf{R}), (\mathbf{r_a}, \mathbf{R_a}), (\mathbf{r_b}, \mathbf{R_b})$ where $\mathbf{r_a}, \mathbf{r_b}, \mathbf{r}$ are respectively the position vectors of the electron relative to A, B and CMN (the center of mass of nuclear cores A and B) while $\mathbf{R}, \mathbf{R_a}, \mathbf{R_b}$ are respectively the position vectors of B relative to A, of A relative to the center of mass of (B+e) and of B relative to the center of mass of (A+e). No single Jacobi system can adequately describe collision processes involving the transfer of an electron in a state bound initially to A to a state bound finally to B. The initial state is described by coordinate system $(\mathbf{r_a}, \mathbf{R_a})$ while the final state is described by the coordinate system $(\mathbf{r_b}, \mathbf{R_b})$.

On the other hand, the adiabatic states are defined by a clamped nuclei approximation (with R fixed), the most natural choice of Jacobi coordinates is $(\mathbf{r}, \mathbf{R})$, which was the choice in the original Born-Oppenheimer separation of the rotation, vibrational and electronic motion in stable molecules. The total Hamiltonian for the system can then be written in the form

$$H = -\frac{1}{2M}\Delta_{\mathbf{R}} - \frac{1}{2m_{ab,e}}\Delta_{\mathbf{r}} + V_{int}(\mathbf{r}, \mathbf{R}), \tag{1}$$

where the operator $V_{int}(\mathbf{r}, \mathbf{R})$ contains all interactions between particles and

$$M = \frac{m_a m_b}{m_a + m_b}, \tag{2a}$$

$$m_{ab,e} = \frac{m_a + m_b}{m_a + m_b + 1} \simeq 1. \tag{2b}$$

The adiabatic basis set is generated by the Hamiltonian in the clamped nuclei limit, that is to say, by the electronic Hamiltonian H_e (with no nuclear kinetic terms)

$$H_e = -\frac{1}{2m_{ab,e}}\Delta_{\mathbf{r}} + V_{int}(\mathbf{r}, \mathbf{R}), \tag{3}$$

whose eigen functions $\mid \chi_j(\mathbf{r}, R)\rangle$ and eigenvalues $\epsilon_j(R)$ are defined by

$$H_e \mid \chi_j(\mathbf{r}, R)\rangle = \epsilon_j(R) \mid \chi_j(\mathbf{r}, R)\rangle. \tag{4}$$

We may observe that by convention the Oz axis of the reference frame is taken to be in the direction of $\mathbf{R}$.

The standard treatment of the problem is to expand the total wave-function of the system $\Psi(\mathbf{r}, \mathbf{R})$ by an expansion in the form:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_n F_n(R)\chi_n(\mathbf{r}, R). \tag{5}$$

However, such an expansion, while satisfactory for a description of the system in the strong interaction region, does not allow for a correct description of either the entry or exit channel. The defects of the expansion (5) have been discussed at length in many previous studies [10, 21, 22, 23] and will not be elaborated upon here. But rather than abandon the notion of an adiabatic basis, a compromise solution is to replace the Jacobi coordinates $(\mathbf{r}, \mathbf{R})$ by some appropriate reaction coordinates $(\mathbf{r}', \mathbf{R}')$ which do allow for a correct description of both the entry and exit channels. Of course, there is no unique coordinate system and in this work, we adopt Eckart-type coordinates [17, 18], which are convenient when, as is the case here, one of the three particles is much lighter than the other two. Based on Eckart-type coordinates, and which has been used successfully in many subsequent applications [22, 21].

$$\mathbf{R}' = \mathbf{R}cos\phi + \frac{1}{\sqrt{M}}\mathbf{r}sin\phi, \tag{6a}$$

$$\mathbf{r}' = \mathbf{r}cos\phi + \sqrt{M}\mathbf{R}sin\phi, \tag{6b}$$

where ϕ denotes the angle characterizing the 2×2 rotation matrix which diagonalizes the Gram matrix:

$$\begin{pmatrix} MR^2 & \sqrt{M}\mathbf{R}.\mathbf{r} \\ \sqrt{M}\mathbf{R}.\mathbf{r} & r^2 \end{pmatrix} \tag{7}$$

is given by

$$tan2\phi = \frac{2\sqrt{M}\mathbf{r}.\mathbf{R}}{MR^2 - r^2}. \tag{8}$$

Except for very small R, $sin\phi$ and $cos\phi$ may, to a good approximation, be written as:

$$sin\phi \simeq \frac{\mathbf{r}.\mathbf{R}}{\sqrt{M}R^2}, \tag{9a}$$

$$cos\phi \simeq 1 - \frac{1}{2M}(\frac{\mathbf{r}.\mathbf{R}}{R^2})^2. \tag{9b}$$

Then we have

$$\mathbf{R}' = \mathbf{R} + \frac{1}{M}\mathbf{s}, \tag{10a}$$

$$\mathbf{r}' = \mathbf{r} - \frac{\mathbf{r}.\mathbf{R}}{R^2}\mathbf{R}, \tag{10b}$$

where

$$\mathbf{s} = \frac{\mathbf{r}.\mathbf{R}}{R^2}\mathbf{r} - \frac{1}{2}(\frac{\mathbf{r}.\mathbf{R}}{R^2})^2\mathbf{R}. \tag{11}$$

It is easily verified that these coordinates allow for a correct description of the asymptotic states. The coordinates defined by the relations (2-11) are identical to those proposed by Thorson and Delos [14].

While the introduction of the $(\mathbf{r}', \mathbf{R}')$ coordinates involves in principle a modification of the original adiabatic basis, there is no need to explicitly define the modified basis functions since, as pointed out in [14], they only differ from the original adiabatic basis

functions by variations of the order of $1/M$. For this reason it is sufficient to treat $\mathbf{R}'$ as the adiabatic coordinate, and replace the expansion (5) by

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_n F_n(\mathbf{R}')\chi_n(\mathbf{r}', R'). \tag{12}$$

This form of expansion has the required flexibility to represent correctly the asymptotic conditions of both the entry and exit channels of the collision complex.

The coupled differential equations for the functions $F_n(\mathbf{R}')$, can be obtained in the usual way by calculating the action of the total Hamiltonian operator (1) on the total wave function (12). Of course care must then be taken in calculating $\nabla_{\mathbf{R}}F(\mathbf{R}')$ and $\nabla_{\mathbf{r}}F(\mathbf{R}')$. Retaining only the leading term in a $1/M$ expansion, it is easily established that:

$$\nabla_{\mathbf{R}}F(\mathbf{R}') \simeq \nabla_{\mathbf{R}}F(\mathbf{R}), \tag{13a}$$

$$\nabla_{\mathbf{R}}\chi(\mathbf{r}, \mathbf{R}') \simeq \nabla_{\mathbf{R}}\chi(\mathbf{r}, \mathbf{R}), \tag{13b}$$

$$\nabla_r F(\mathbf{R}') = \frac{1}{M}\nabla_{\mathbf{R}}F(\mathbf{R}).\nabla_{\mathbf{r}}\mathbf{s}, \tag{14a}$$

$$\nabla_{\mathbf{r}}^2 F(\mathbf{R}') = \frac{1}{M}\nabla_{\mathbf{R}}F(\mathbf{R}).\nabla_{\mathbf{r}}^2\mathbf{s}, \tag{14b}$$

and

$$\nabla_{\mathbf{r}}\chi(\mathbf{r}', \mathbf{R}') = \tag{15}$$

$$(\nabla_{\mathbf{r}} + \frac{1}{M}\nabla_{\mathbf{R}}.\nabla_{\mathbf{r}}\mathbf{s})\chi(\mathbf{r}, \mathbf{R})\nabla_{\mathbf{r}}^2\chi(\mathbf{r}', \mathbf{R}') =$$

$$[\nabla_{\mathbf{r}}^2 + \frac{2}{M}A.\nabla_{\mathbf{R}} + \frac{1}{M}(\nabla_{\mathbf{R}}.A)]\chi(\mathbf{r}, \mathbf{R}),$$

where

$$\mathbf{A} = (\nabla_{\mathbf{r}}.\mathbf{s}).\nabla_{\mathbf{r}} + \frac{1}{2}(\nabla_{\mathbf{r}}^2\mathbf{s}). \tag{16}$$

It should be remarked that the expansion (12) constitutes the essential difference from the standard adiabatic basis. It leads to the existence of several additional non-adiabatic coupling terms, which correct for the basic defects the standard adiabatic separation using Jacobi coordinates. Using (2) and (2), we then have:

$$-\frac{1}{2M}\nabla_{\mathbf{R}}^2 F_n(\mathbf{R})\chi_n(\mathbf{r}, R) = \frac{1}{2M}[\nabla_{\mathbf{R}}^2 F_n(\mathbf{R}) + 2\nabla_{\mathbf{R}}F_n(\mathbf{R}).\nabla_{\mathbf{R}} + F_n(\mathbf{R})\nabla_{\mathbf{R}}^2]\chi_n(\mathbf{r}, R). \tag{17}$$

$$-\frac{1}{2M}\nabla_{\mathbf{r}}^2 F_n(\mathbf{R}')\chi_n(\mathbf{r}, R') = \tag{18}$$

$$-\frac{1}{2}F_n(R)[\nabla_r^2 + \frac{1}{M}\nabla_R.\mathbf{A}]\chi_n(\mathbf{r}, R) - \frac{1}{M}[\nabla_{\mathbf{R}}F_n(\mathbf{R})]\mathbf{A}\chi_n(\mathbf{r}, R).$$

Combining (16) and (17), and using the fact that $\mid \chi_n\rangle$ is an eigen function of H_e with eigen value $\epsilon_n(R)$, we obtain:

$$[\nabla_{\mathbf{R}}^2 + 2M\{E - \epsilon_n(R)\}]F_n(\mathbf{R}) + 2\sum_m[P_{nm} + A_{nm}]\nabla_{\mathbf{R}}F_m(\mathbf{R}) + \sum_m B_{nm}F_m(\mathbf{R}) = 0, \tag{19}$$

where E is the total energy and the matrix elements P_{nm}, A_{nm} and B_{nm} are defined as

$$\mathbf{P}_{nm} = \langle \chi_n \mid \nabla_{\mathbf{R}} \mid \chi_m \rangle, \tag{20}$$

$$\mathbf{A}_{nm} = \langle \chi_n \mid \mathbf{A} \mid \chi_m \rangle = (\epsilon_n - \epsilon_m)\langle \chi_n \mid \mathbf{s} \mid \chi_m \rangle, \tag{21}$$

$$\mathbf{B}_{nm} = \langle \chi_n \mid \nabla_{\mathbf{R}}^2 + \mathbf{A}.\nabla_{\mathbf{R}} + \nabla_{\mathbf{R}}.\mathbf{A} \mid \chi_m \rangle = \langle \chi_n \mid (\nabla_{\mathbf{R}} + \mathbf{A})^2 \mid \chi_m \rangle - \langle \chi_n \mid \mathbf{A}^2 \mid \chi_m \rangle. \tag{22}$$

In (22), the term involving $\mathbf{B}_{nm}$ is often neglected because of the mass factor. But it is known to give a small contribution to some resonance phenomena in photo dissociation cross sections [24],since it can attain an appreciable size in the vicinity of an avoided curve crossing. It has therefore been retained in the present work. On the other hand, the term involving $\mathbf{A}^2$ in (22) can be neglected, since it only represents corrections to the binding energy of the bound electron due to isotopic effects. The equation 19 may be expressed in matrix form as:

$$\{\nabla_{\mathbf{R}}^2 + 2M[E + \epsilon(R)]\}F(\mathbf{R}) + 2(P + A).\nabla_{\mathbf{R}}F(\mathbf{R}) + BF(\mathbf{R}) = 0. \tag{23}$$

In the case of multiply coupled channels, where the adiabatic functions are defined in the body-fixed frame with Oz in the direction of the internuclear axis $\mathbf{R}$, care must be taken in computing the gradient and Laplacian operators $\nabla_{\mathbf{R}}$ and $\nabla_{\mathbf{R}}^2$. However, in the case of a two-state basis; where the states are of the same molecular symmetry Λ, the Coriolis type coupling arising from the electron angular momentum coupling terms vanishes and only the radial coupling component of $\mathbf{P}_{nm} + \mathbf{A}_{nm}$ contributes to the non adiabatic coupling. Then, decomposing the functions $F_n(\mathbf{R})$ on a basis set of symmetric top functions $D^K_{\Lambda,M}(\Theta, \Phi)$ according to:

$$F_n(\mathbf{R}) = \sum_{K,M}(-)^K\sqrt{\frac{2K+1}{4\pi}}D^K_{\Lambda,M}(\Theta, \Phi)\frac{1}{R}f_n^{(K)}(R), \tag{24}$$

where Θ and Φ are the polar angles of the internuclear axis, we obtain a set of coupled differential equations for the radial functions $f_n^{(K)}(R)$ of the form:

$$[\frac{d^2}{dR^2} + 2M\{E - \epsilon_n(R)\}]f_n^{(K)}(R) + \tag{25}$$

$$2\sum_m\langle \chi_m \mid U \mid \chi_n \rangle\frac{d}{dR}f_n^{(K)}(R) + \sum_m\langle \chi_m \mid U^2 \mid \chi_n \rangle f_n^{(K)}(R) = 0,$$

where

$$U = \frac{\partial}{\partial R} + \frac{z}{R}\frac{\partial}{\partial z}. \tag{26}$$

3. Adiabatic-Diabatic transformation

The matrix element of $\mathbf{U}$ which controls the charge transfer process is highly peaked at the avoided crossing and a direct numerical solution of the coupled differential equations (25) is not a recommended procedure. It is preferable to make a unitary transformation

of the adiabatic basis functions to a new basis, usually called a diabatic basis in which the off diagonal non-adiabatic matrix elements are smoothly varying or zero. But the notion of smoothness is rather arbitrary and precludes a precise physical significance of a diabatic state. However, the notion of a diabatic matrix does provide an interesting connection with the Landau-Zener model and the 2-state adiabatic representation.

The diabatic basis is defined by a unitary transformation of the adiabatic basis. If $\mathbf{C}(R)$ denotes the transformation matrix, we then have

$$\chi_j^d(\mathbf{r}, \mathbf{R}) = \sum_{\mathbf{k}} \chi_{\mathbf{k}}(\mathbf{r}, \mathbf{R})\mathbf{C_{k,j}}(\mathbf{R}). \tag{27}$$

In this diabatic basis $\mid \chi^d \rangle$, the matrix $\mathbf{U}$ is transformed according to the relation

$$\mathbf{U^d} = \mathbf{C^{-1}UC} + \mathbf{C^{-1}}\frac{\mathbf{d}}{\mathbf{dR}}\mathbf{C}. \tag{28}$$

To specify the transformation matrix $\mathbf{C}$, it is necessary to impose some constraint on the matrix elements of $\mathbf{U}^d$, The simplest constraint, first proposed by Smith [20], is that the matrix elements of $\mathbf{U}^d$ should vanish. This condition is achieved if $\mathbf{C}$ satisfies the equation:

$$\mathbf{UC} + \frac{\mathbf{dC}}{\mathbf{dR}} = \mathbf{0}, \tag{29}$$

with the boundary condition that $C(R) \rightarrow \mathbb{1}$ as R$\rightarrow \infty$. This definition avoids the necessity of introducing the concept of smoothness. And as a general rule, it is found in practice that it does indeed result in a transformed Hamiltonian matrix which is smooth in the crossing region.

Let us now consider how the matrix $\mathbf{B}$ transforms under a diabatic transformation. The matrix elements of the transformed matrix $\mathbf{B}^d$ may be written in the form

$$\mathbf{B^d} = \mathbf{C^{-1}BC} + 2\mathbf{C^{-1}U}\frac{d}{dR}\mathbf{C} + \mathbf{C^{-1}}\frac{d^2}{dR^2}\mathbf{C} \tag{30}$$

Taking equation (29) and its derivative, we obtain:

$$\frac{d\mathbf{C}}{dR} = -\mathbf{UC} \tag{31}$$

$$\frac{d^2\mathbf{C}}{dR^2} = -\mathbf{U}\frac{d\mathbf{C}}{dR} - \frac{d\mathbf{U}}{dR}\mathbf{C}, \tag{32}$$

from which we may deduce that:

$$\mathbf{B}^d = \mathbf{C^{-1}BC} + \mathbf{C^{-1}U}\frac{d}{dR}\mathbf{C} - \mathbf{C^{-1}}\frac{d\mathbf{U}}{dR}\mathbf{C} = \mathbf{C^{-1}}(\mathbf{B} - \mathbf{U^2} - \frac{d\mathbf{U}}{dR})\mathbf{C}. \tag{33}$$

Taking the derivative of $\mathbf{U}$ with respect to R, it follows that

$$\frac{d\mathbf{U_{ij}}}{dR} = \langle \frac{\partial \chi_i}{\partial R} \mid U \mid \chi_j \rangle + \langle \chi_i \mid \frac{dU}{dR} \mid \chi_j \rangle + \langle \chi_i \mid U \mid \frac{\partial \chi_j}{\partial R} \rangle. \tag{34}$$

Writing the sum of the last two terms that appear in previous equation in the form:

$$\langle \chi_i \mid \frac{dU}{dR} \mid \chi_j \rangle + \langle \chi_i \mid U \mid \frac{\partial \chi_j}{\partial R} \rangle = \langle \chi_i \mid \frac{\partial}{\partial R}U \mid \chi_j \rangle = \tag{35}$$

$$\langle \chi_i \mid U^2 \mid \chi_j \rangle - \langle \chi_i \mid \frac{z}{R}\frac{\partial}{\partial z}U \mid \chi_j \rangle,$$

it is easy to show that

$$\frac{d\mathbf{U_{ij}}}{dR} = \langle \frac{\partial \chi_i}{\partial R} \mid \frac{\partial}{\partial R} + \frac{z}{R}\frac{\partial}{\partial z} \mid \chi_j \rangle - \langle \chi_i \mid \frac{\partial}{\partial R} + \frac{z}{R}\frac{\partial}{\partial z} \mid \chi_j \rangle = \tag{36}$$

$$B_{ij} + \langle \chi_i \mid \frac{\partial}{\partial R} + \frac{z}{R}\frac{\partial}{\partial z} \mid \frac{\partial}{\partial R} + \frac{z}{R}\frac{\partial}{\partial z}\chi_j \rangle = B_{ij} + D_{ij},$$

where

$$D_{ij} = \langle U\chi_i \mid U\chi_j \rangle. \tag{37}$$

Equation (36) might be expressed in matrix form as :

$$\frac{d\mathbf{U}}{dR} = \mathbf{B} + \mathbf{D}. \tag{38}$$

If the basis set is complete, we have

$$\sum_n \mid \chi_n \rangle\langle \chi_n \mid = \mathbb{1}, \tag{39}$$

The expression (37) can then be expressed as:

$$D_{ij} = \langle U\chi_i \mid U\chi_j \rangle = \sum_n \langle U\chi_i \mid \chi_n \rangle\langle \chi_n \mid U\chi_j \rangle = -\langle \chi_i \mid U^2 \mid \chi_j \rangle = -U_{ij}^2 \tag{40}$$

and

$$\mathbf{B}^d = C^{-1}(\mathbf{B} - \mathbf{U}^2 - \frac{d\mathbf{U}}{dR})\mathbf{C} = 0. \tag{41}$$

It therefore follows that the matrix elements of $\mathbf{B}$ vanish in a diabatic representation if the basis set is complete. This result suggests a relatively simple way to test the adequacy of our basis set. The matrix element $\mathbf{D}_{ij}$ can be calculated directly by a simple extension of the method used to calculate the radial coupling elements $\langle U\chi_i \mid U\chi_j \rangle$. So the closure relation (39) can be directly used to test the adequacy of any finite basis set with using reaction coordinates.

4. Test of the adiabatic basis set

It is clear from section 3, the use of reaction coordinates ensures that all non-adiabatic matrix elements, arising either from the radial coupling between two states of the same symmetry with $\Delta\Lambda = 0$, or from the rotational (Coriolis) coupling between states of different symmetry with $\Delta\Lambda = 1$, vanish in the asymptotic limit. But the condition of vanishing asymptotic coupling is not a sufficient condition to ensure that the basis set is complete.

An illustration of the problem is given by Gargaud et al. [13] in their calculations of both differential and total electron capture cross sections in the reaction:

$$N^{3+}(2s^2)^1S + H(1s) \rightarrow N^{2+}(2s^23s)^2S + H^+, \tag{42}$$
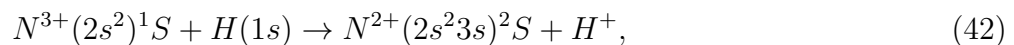
for which further details can be found in the work of Roudjane et al. [25].

From Figure 1 showing the adiabatic energies of the quasi-molecule NH^{3+} for different internuclear distances, it is clear that the reaction (42) is dominated by a
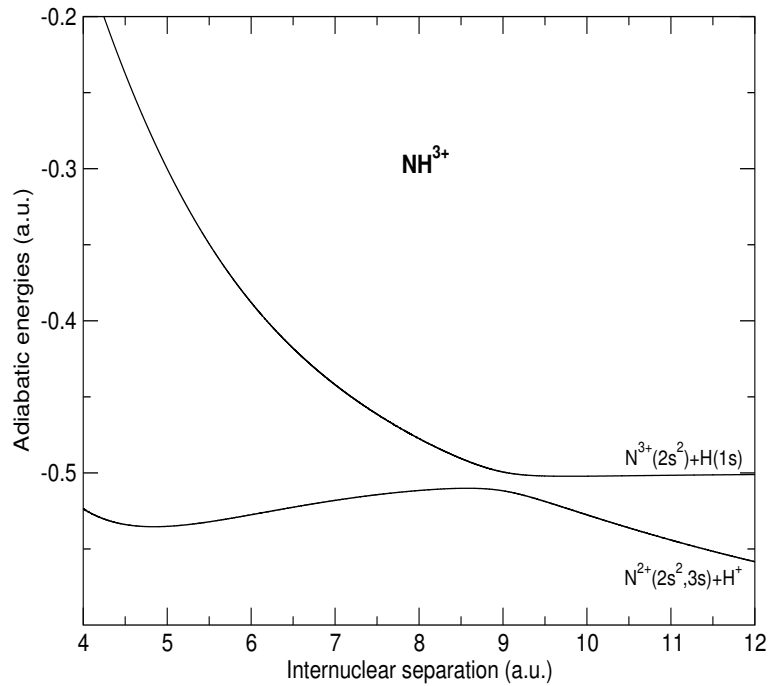
Figure 1. Adiabatic energies as a function of internuclear distance.

single avoided crossing occuring at an internuclear distance around 9 a.u., of two $^2\Sigma$ states leading to charge transfer from the N^{3+} +H entry channel to the N^{2+}+H^+ exit channel. In such a case, it is often assumed that even the standard Jacobi coordinates with the origin on the centre of nuclear mass can be used since the asymptotic radial coupling terms vanish asymptotically. However, a simple analysis of the radial coupling element shown in Figure 2, responsible for a charge transfer to the N^{2+}+H^+ exit channel, shows an important dependence of the non-adiabatic coupling element on the coordinate system, which should automatically lead to a dependence of the electron capture cross section.

As shown in Figure 3, when chosing the origin of coordinates on the centre of nuclear mass (close to coordinates centred on N), the cross section does not agree with experiment. This is a clear indication that using origin of coordinates on the centre of nuclear mass in a two-state basis does not allow for a correct representation of both the entry and rearrangement channels.

Indeed, a calculation of the matrix elements of D shown in Figure 4 indicates that the closure relation (39) is not satisfied when the origin is taken on the N nucleus. Equally, an inportant difference between the matrix elements of D and those of -U^2 is shown in Figure 5, when the origin is taken on the H nucleus. This confirms that even when the radial coupling terms vanish asymptotically, the two-state basis is far from being complete if standard Jacobi coordinates are used. On the other hand, from Figure (6), when using reaction coordinates, it can be concluded that the closure relation (39) is reasonably well satisfied, especially in the vicinity of the avided crossing, where charge transfer occurs. This clearly indicates that a two-state basis is sufficient to describe the
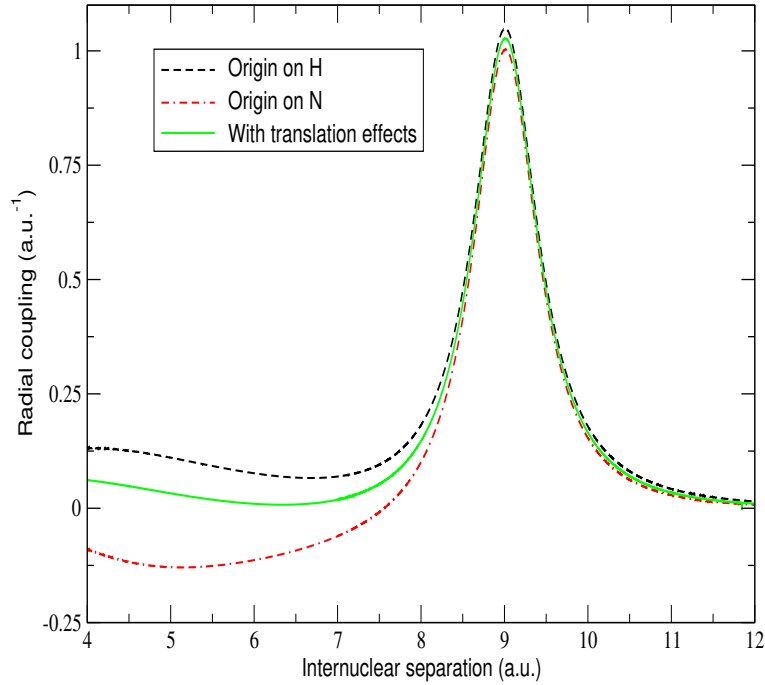
Figure 2. Three variants of the radial coupling matrix element

charge transfer process, when reaction coordinates are used.

A more spectacular demonstration of the necessity of reaction coordinates is furnished by the problem of the selective electron capture in collisions of multiply charged ions with neutral atoms, as described in the reaction:

$$H(1s) + C^{4+}(2s^2)^1S \rightarrow H^+ + C^{3+}(1s^2, nl)^2S(nl = 3s, 3p, 3d), \qquad (43)$$
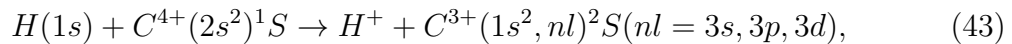
which has been extensively studied by detailed calculations [18, 19, 28] and by merged beams experiments [29, 30, 31] as well. Details of the calculations are given in the work by Rabli and McCarroll [19] and only a few of the more significant results will be shown here.

For this system electron capture can take place into the $(3s)^2S$, $(3p)^2P$, $(3d)^2D$ of C^{3+} ion. The electron capture takes place via avoided crossings involving the $4\,\Sigma$ states, and asymptotic rotational coupling involving Π and Δ states.

To test the convergence of the adiabatic basis, we can examine the closure relation (39). In Figures 7,8 and 9, we compare the matrix elements D_{ij} calculated directly with the results of the matrix elements derived from the matrix elements of U. It is clearly seen that only for the reaction coordinate system, there is excellent agreement, whereas for coordinates with origin on the heavy nucleus, (which is almost identical to the centre of mass), or origin on hydrogen, the closure relation (39) is not satisfied.

5. Miscellaneous Procedures

Over the years, several other variants have dealt with the problem of non-vanishing radial coupling matrix elements. One such is that proposed by Solovev and Vitinsky [32], who
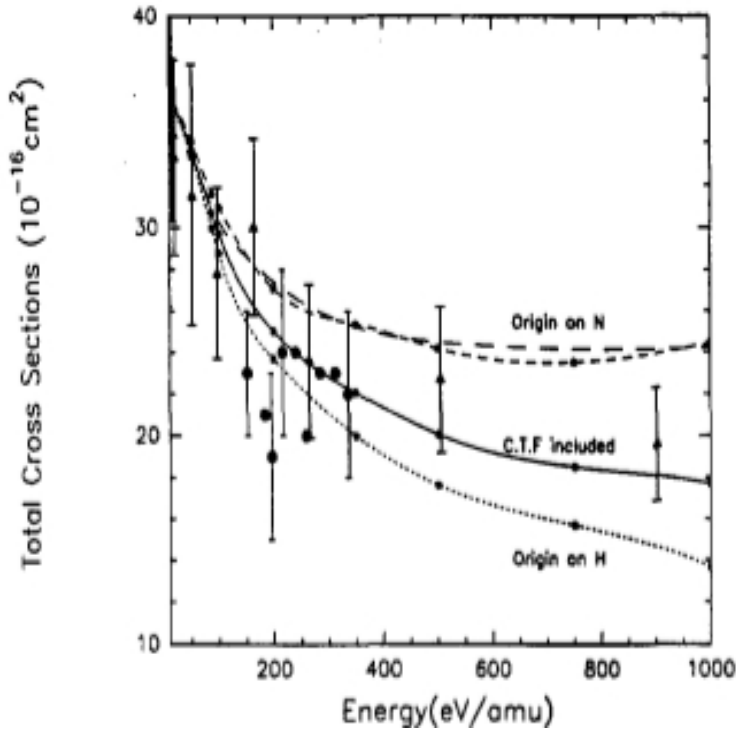
Figure 3. Total cross sections $(10^{-16}cm^2)$ for electron capture in N^{3+}/H collisions as a function of ion energy (laboratory system). The solid curve represents the results with account taken of translation. The two upper dashed curves refer to results (ours and those of Bienstock et al. [26]) with no translation and with the origin of electron coordinates on the N nucleus. The lower short-dashed curve refers to our results with no trans- lation and with the origin of electron coordinates on the H atom. Experimental results [27] are given with their error bars.

pointed out that by using as independent variable the scaled variable $r' = r/R$ rather than r, the radial couplings vanish in the asymptotic limit. Unpublished calculations by Gargaud and McCarroll using spheroidal coordinates, which indeed are scaled variables, produced results comparable with the reaction coordinate procedure. However, such scaled variables do not address the problem of the asymptotic rotational (Coriolis) coupling, and it can only be applied to relatively simple systems, where rotational coupling is negligible.

Another approach using the traditional Jacobi coordinates with electron coordinates centred on the cent re of mass of the nuclei (CMN), is the retro-projection method of Belyaev [33]. In the case of non-vanishing radial matrix elements, the scattering equations are integrated far into the asymptotic region and then re-projected on to the atomic centre. In the application of the retro-projection approach to inelastic collisions between Li and Na atoms, where there are no significant avoided crossings, it is expected that the computed cross sections should indeed be negligibly small (of the order of $10^{-23}cm^2$). Since the centre of nuclear mass is located neither on Li nor on Na there are quite large non-vanishing asymptotic radial matrix elements.
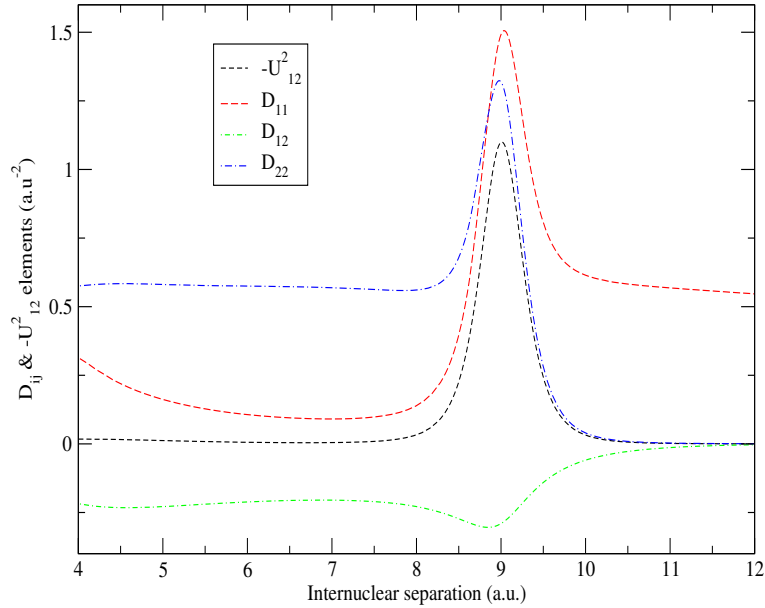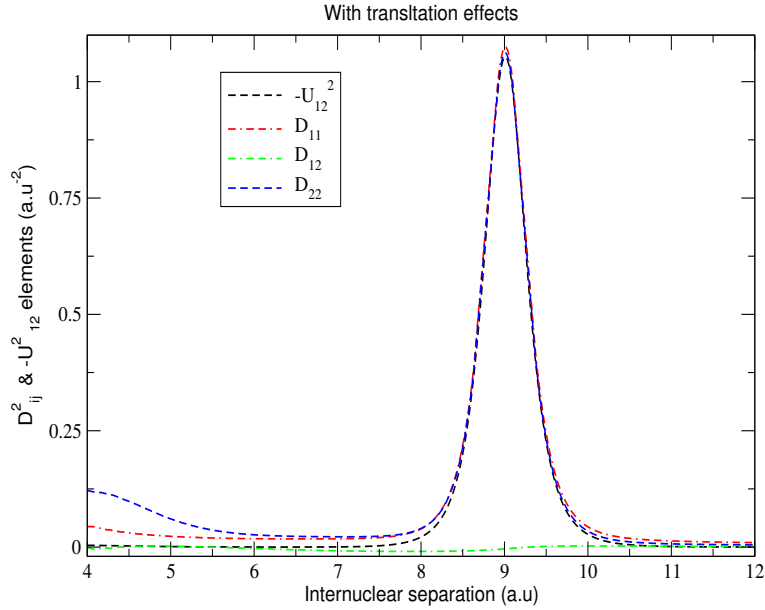
Figure 4. Non-adiabatic matrix elements, U^2 and D_{ij} in the Jacobi system (origin on N nucleus). Index 1,2 refer to entrance channel $N^{3+}(2s^2)^1S + H(1s)$ and exit channel $N^{2+}(2s^2 3s)^2S + H^+$, respectively.
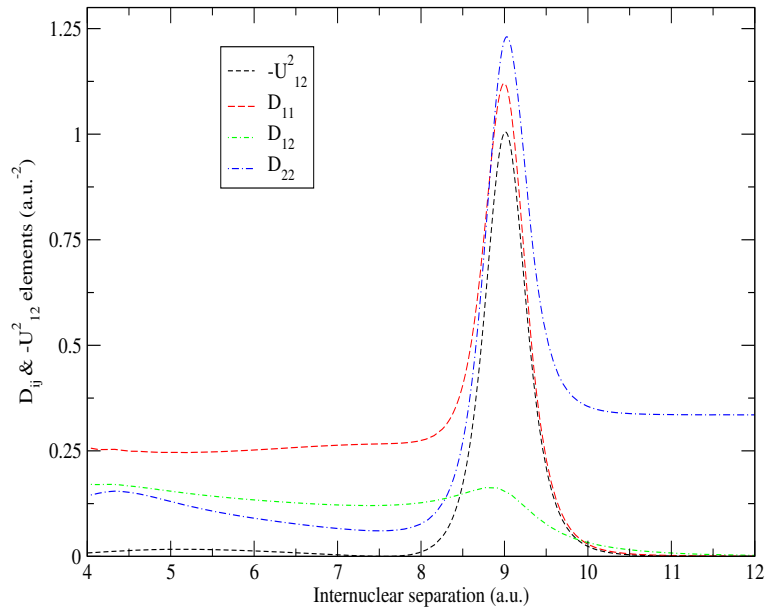

Figure 5. Non-adiabatic matrix elements, U^2 and D_{ij} in the Jacobi system (origin on H nucleus). Index 1,2 refer to entrance channel $N^{3+}(2s^2)^1S + H(1s)$ and exit channel $N^{2+}(2s^2 3s)^2S + H^+$, respectively.

The retro-projection procedure is in principle correct and a negligibly small cross section is found. On the other hand, had there been a significant non adiabatic coupling in the interaction region, the choice of the centre of nuclear mass as origin is not correct and the basis set would not converge.

Figure 6. Equivalent matrix elements U^2 and D_{ij} in the reaction coordinate system. Index 1,2 refer to entrance channel $N^{3+}(2s^2)^1S + H(1s)$ and exit channel $N^{2+}(2s^23s)^2S + H^+$, respectively.
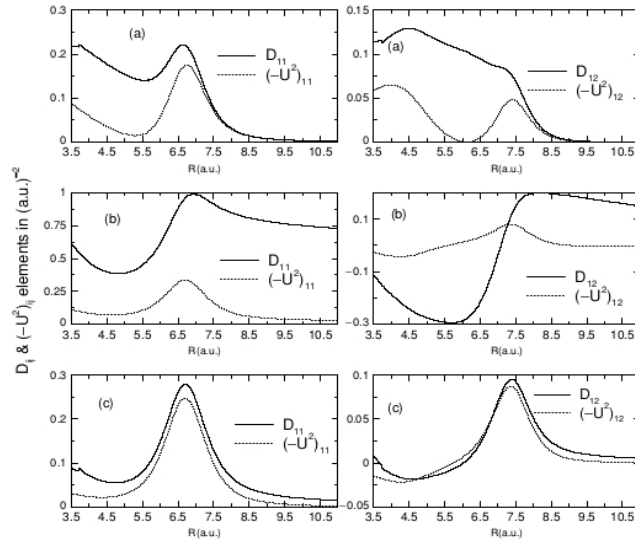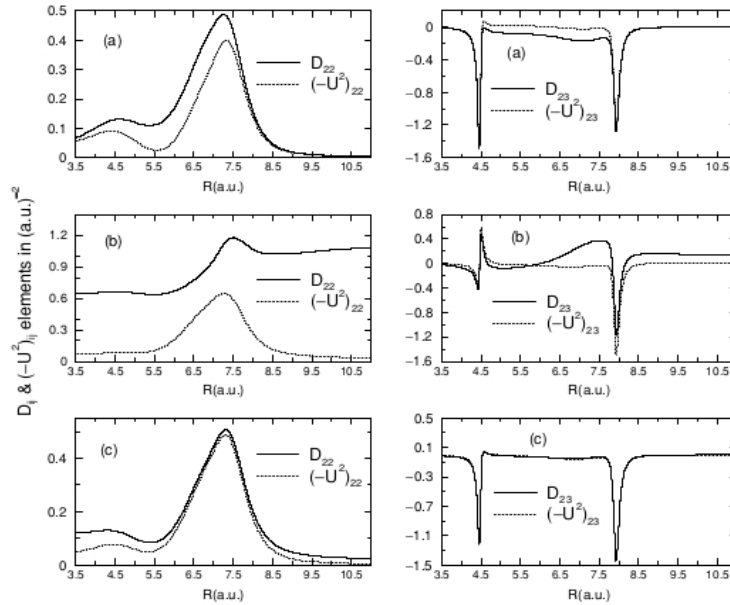

Figure 7. Matrix elements $D_{11}, (-U^2)_{11}, D_{12}, (-U^2)_{12}$, for the system C^{4+} /H. Case (a) corresponds to Jacobi coordinates with electron origin on the C nucleus, case (b) corresponds to Jacobi coordinates with electron origin on the H nucleus and case (c) corresponds to appropriate reaction coordinates. Index 1 and 2 refer to channels $\Sigma_1 : H^+ + C^{3+}(1s^2, 3s)^2S$ and $\Sigma_2 : H^+ + C^{3+}(1s^2, 3p)^2P$, respectively

6. Concluding remarks

Finally, some general remarks on why it took such a long time to develop consistent and reliable theoretical methods using an adiabatic basis set to study excitation and
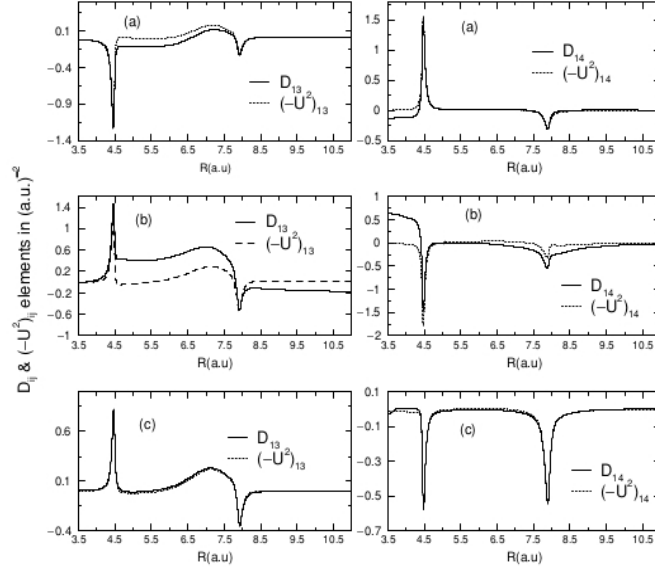
Figure 8. Matrix elements $D_{13}, (-U^2)_{13}, D_{14}, (-U^2)_{14}$, for the system C^{4+} /H. Case (a) corresponds to Jacobi coordinates with electron origin on the C nucleus, case (b) corresponds to Jacobi coordinates with electron origin on the H nucleus and case (c) corresponds to appropriate reaction coordinates. Index 1,3 and 4 refer to channels $\Sigma_1 : H^+ + C^{3+}(1s^2, 3s)^2S$, $\Sigma_3 : H^+ + C^{3+}(1s^2, 3d)^2D$ and $\Sigma_4 : H(1s) + C^{4+}(1s^2)$, respectively.

Figure 9. Matrix elements $D_{22}, (-U^2)_{22}, D_{23}, (-U^2)_{23}$, for the system C^{4+} /H. Case (a) corresponds to Jacobi coordinates with electron origin on the C nucleus, case (b) corresponds to Jacobi coordinates with electron origin on the H nucleus and case (c) corresponds to appropriate reaction coordinates. Index 2 and 3 refer to channels $\Sigma_2 : H^+ + C^{3+}(1s^2, 3p)^2P$ and $\Sigma_3 : H^+ + C^{3+}(1s^2, 3d)^2D$, respectively
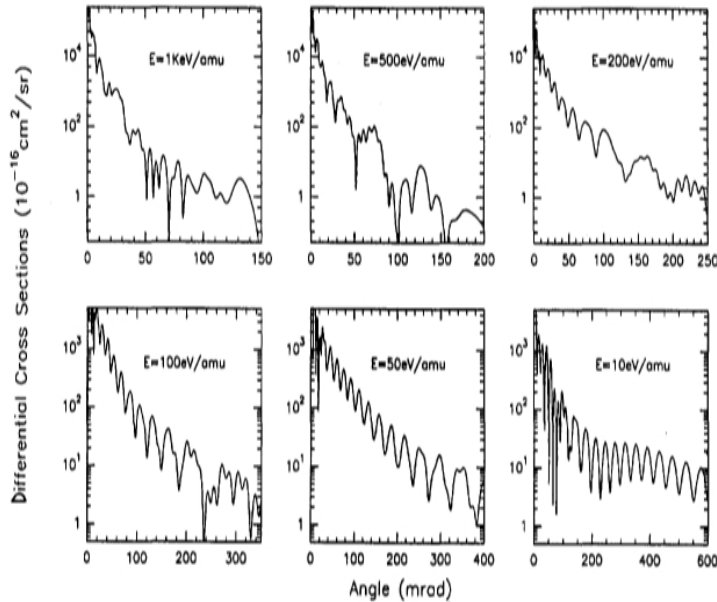
Figure 10. Differential cross sections $(10^{-16}cm^2/sr)$ in CM system for electron capture in N^{3+}/H collisions as a function of scattering angle $\theta_{cm}(mrad)$ for a selection of incident ion energies (in lab system).

rearrangement processes in ion-atom and atom-atom collisions. In particular, it is now clear that the impact parameter method, which transforms the time-independent Schrödinger equation to a time-dependent equation, in which the nuclear motion is described by classical rectilinear trajectories, is more restrictive than originally thought. In reality, the time-dependent impact parameter equation may be considered as an asymptote of the stationary Schrödinger equation in the limit $\hbar^2/M \rightarrow 0$ and E $\rightarrow \infty$. But, recently, Solovev [12] pointed out that for the typical collision energies of interest, the nuclear momentum of the different channels can be significantly different, in which case a unique time for all channels does not exist. And it was for this reason that it proved necessary to modify the impact parameter equation by the introduction of ETF. But it is also clear from the reasons invoked by Solovev that it would have been preferable to avoid altogether the notion of translation factors. In retrospect, it now seems regrettable that a consistent quantum mechanical formulation of the problem was not exploited sooner. It is clear that had the problems of the impact parameter approach been understood correctly, there would have been no need to introduce the notion of translation factors. Contrary to what is often believed, the quantum mechanical formulation offers some simplifying features. The quantum calculations reduce to the solution of differential equations and angular momentum being a constant of motion, the calculation of the differential cross sections is simple and valid for all energies. Of course the since the adiabatic basis set is limited to energies of the order of 1 keV, the number of partial waves required to represent the collision remains reasonable.

There seems to be a belief that the impact parameter equations are simpler than those resulting from a quantum mechanical approach. But it should be borne

in mind that the impact parameter equations involve complex functions whereas the time-independent Schrödinger equation only involves real functions. Furthermore,since angular momentum is conserved, the contribution of a given angular momentum L to the collision cross section can be calculated independently in a quantum method. It then suffices to sum over all L to determine the cross section. So in practice quantum methods are more efficient when both the differential and total cross sections are required. For calculation of the total cross sections which depend only on the modulus of the transition amplitude, impact parameter methods are satisfactory at energies in the keV range. On the other hand, the calculation of differential cross sections shown in Figure (10) are simpler in a quantum mechanical method.

In conclusion, this work shows that the quantum mechanical approach, which retains terms in the Hamiltonian correct to first order in the electron/nuclear mass ratio, leads naturally to the notion of reaction coordinates and makes it possible in test the completeness of the adiabatic basis set used in any specific calculation on inelastic and rearrangement collision processes in ion-atom collisions.

7. References

[1] L. D. Landau, Phys. Z. Soviet Union **2** 46 (1932)

[2] E. C. G Stueckelberg, Helv. Phys. Acta. **361** 361 (1932)

[3] C. Zener, Proc. Soc. A **137** 696 (1932)

[4] D. R. Bates, H. S .W. Massey and A. L. Stewart, Proc. Roy. Soc. A **216** 437 (1953)

[5] N. S. F. Mott, Proc. Camb. Phil. Soc. **27** 553 (1931)

[6] E. A. Solovev, Sov. Phys. Usp. **32** 228 (1989)

[7] D. R. Bates and R. McCarroll R, Proc. Roy. Soc. A **245** 175 (1958)

[8] Schneiderman S B and Russek A, Phys. Rev. **181** 311 (1969)

[9] L.F. Errea, L. Méndez and A. Riera, J. Phys. B: At. Mol. Phys. **15** 101 (1982)

[10] B. H. Bransden and M. R. C. McDowell,Charge Exchange and the Theory of Ion-Atom Collisions, Clarendon Press Oxford (1992)

[11] L.F. Errea, L. Méndez and A. Riera, , in *The Physics of Multiply and Highly Charged Ions*, ed. F. J . Currell,**2**, 237, Kluwer Academic Publishers (Dordrecht) (2003)

[12] E. A. Solovev, Physics Essays, **25** 27 (2012)

[13] M. Gargaud, S.F.C. O'Rourke, R. McCarroll and L.R. Andersson, Physica Scripta **48** 436 (1993)

[14] W.R. Thorson and J.B. Delos, Phys. Rev. A **18** 135 (1978)

[15] J.B. Delos, Rev. Mod. Phys. **53** 287 (1981)

[16] M.H. Mittleman, Phys. Rev. **188** 221 (1969)

[17] C. Eckart, Phys. Rev. **46** 383 (1934)

[18] M. Gargaud, R. McCarroll and P. Valiron, J. Phys. B:: At. Mol. Phys. **20** 1555 (1987)

[19] Rabli D and McCarroll R, J. Phys. B **38** 3331 (2005)

[20] F T Smith, Phys. Rev. **120**, 1058 (1960)

[21] R. McCarroll, in *The Physics of Multiply and Highly Charged Ions*, ed. F. J . Currell,**2** 275 Kluwer Academic Publishers (Dordrecht) (2003)

[22] R. McCarroll and D.S.F. Crothers, Advances in Atomic and Molecular Physics **32**, Academic Press (New York)(1993)

[23] M. Gargaud and R. McCarroll,Ion-Atom Charge Transfer Reactions at Low Energies, Section 51, Springer Handbook of Atomic, Molecular and Optical Physics, Editor Gordon F. Drake (2006) (Springer Science+Business Media, Inc. New York)

[24] P. Barragn, L. F. Errea, L. Méndez, A. Macias, I. Rabadn and A. Riera, Phys. Rev. A **70** 22707 (2004)

[25] M. Roudjane, R. McCarroll and D. Rabli, J. Phys. B **40** 2471 (2007)

[26] Bienstock, S., Dalgamo, A. and Heil, T. G., Phys. Rev. A **29** 2239 (1984)

[27] M. S. Huq, C. C. Havener and R. A. Phaneuf, Phys. Rev. A **40** 1811 (1989)

[28] M. Gargaud, J. Hanssen, R. McCarroll and P. Valiron, J. Phys B **14** 2259 (1981)

[29] F.W. Bliek, R. Hoekstra, M.E. Bannister, and C.C. Havener,Phys. Rev. A **56** 426 (1997)

[30] R.A. Phaneuf, I. Alvarez, F.W. Meyer, and D.H. Crandall, Phys. Rev. A **26** 1892 (1982)

[31] M. Pieksma, M.Gargaud, R. McCarroll and C. Havener, Phys Rev. A **54** R13 (1998)

[32] E. A. Solovev and S. I. Vinitsky, J. Phys. B: At. Mol. Phys. **18** L557 (1985)

[33] A. K. Belyaev, Phys. Rev. A **82** 060701(R) (2010)