# Non Adiabatic Processes in atom (ion)-atom collisions.

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# Ratko Janev

I wish to dedicate this presentation to the memory of my friend and colleague, Ratko Janev, who died in Belgrade on 31st December 2019.

It was on an extended visit to Belgrade in 1971 that I first had the opportunity of making acquaintance with Ratko. At the time, he was working at the Boris Kidrič Institute. In spite of the curious working hours (from 7.0 am to 3pm with no break for lunch) it was a memorable visit.  Ratko introduced me to a wide variety of people in Belgrade: not just his scientific colleagues but to those involved with other sectors of the country:  journalists, artists,  He was a highly cutivated person with aristocratic tastes. He opened up a new  vision of the Slav world. But coming myself from a country on the western fringe of Europe with a troubled complex history, almost as complex as Serbia, I felt quite at home.

In the following years, I had many occasions to meet Ratko, both in Belgrade and at SPIG meetings, which at the time were held in delightful locations on the Dalmatian coast.

Later, during the period from 1987 until near the end of the 20th century, Ratko worked at the International Atomic Energy Commisson at UNESCO in Vienna, where he directed the department for the formation of databases necessary for all of the world's nuclear fusion centres. He organized many meetings during this period and I admired his skill in conducting international negociations.

I last met Ratko at the ICPEAC conference in 2001 at Santa Fé in New Mexico, USA. He was relaxed and enjoying his retirement from the constraints of his work at IAEA.

But after his retirement he continued his activity ; at National Institute of Fusion Research in Tokyo 1999-2000, Julich Research Center 2000-2002 and then from 2005-2012 at the Institute of Applied Physics and Computational Mathematics in Beijing 2005-2012.

Ratko has left an amazing legacy. We will miss him.

Definition of an adiabatic state.   An electronic state of a molecular system with infinite nuclear mass.

Electronic states possessing a minimum are characterized by the existence of vibration rotation states . As a general rule, there are as many repulsive states as attractive states.

Non-adiabatic effects depend inversely on the nuclear mass.  So they are in general small provided the electronic states are well separated in energy.   Only electronic states of different symmetry can cross.  But sometimes, not always easy to predict, states of the same symmetry exhibit avoided crossings. Such avoided crossings are responsible for electronic transitions  and lead to electronic excitation and charge exchange.

The existence of such avoided crossings are not easy to predict, but they can be critical.

Adiabatic representation of a transition state complex (AB or AB$^+$) in a collision between two atomic systems ( A , B or B$^+$ )

- Valid for the description of inelastic and rearrangement processes covering a wide range of collision energies  E < a few keV/amu.

- Such processes occur via  non-adiabatic coupling between those adiabatic states correlated to the entry and exit channels.

- Non-adiabatic coupling is important not only via avoided crossings of states with the same symmetry but also in the asympotic region where states of different symmetry  become degenerate.

Typical example of a simple 2 state crossing
A model proposed in 1932 independently
by Landau (USSR)  by Zener (UK) can be
used to treat such a problem.  The LZ
model has been used ever since and does
give a reasonable approximation to the
collision cross section. But clearly a more
precise description of the non-adiabatic
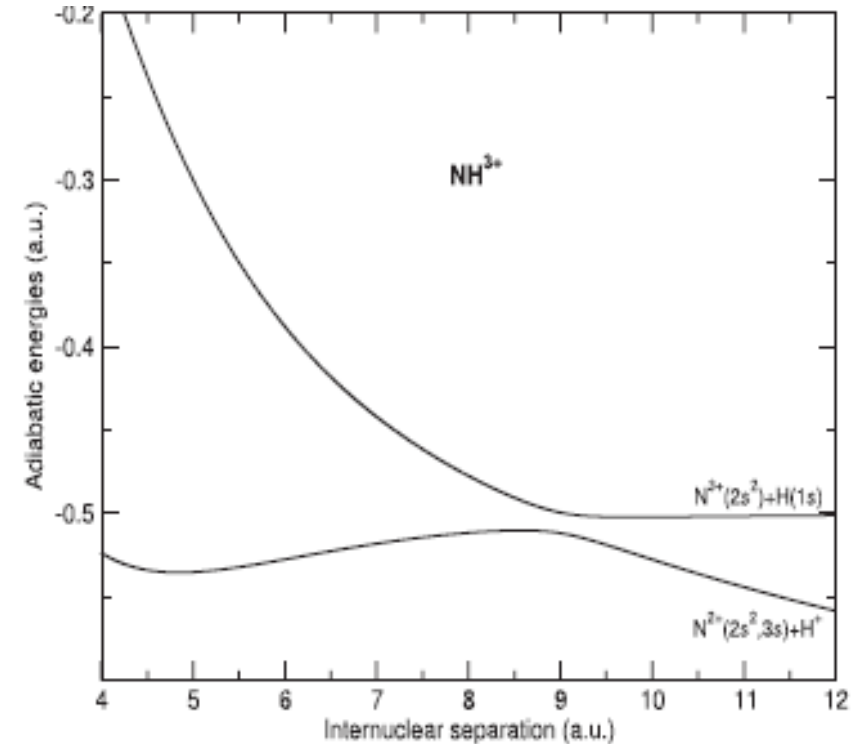mechanism is required.



**Figure 1.** Adiabatic energies as a function of internuclear distance.

# General Features

- Adiabatic representation of a transition state complex ( AB or AB$^+$ )

- in a collision between  two atomic systems ( A , B or B$^+$ )

- Collision processes occur via  non-adiabatic coupling between those adiabatic states correlated to the entry and exit channels.

- Non-adiabatic coupling is important not only via avoided crossings of states with the same symmetry but also in the asympotic region where states of different symmetry  become degenerate.

-  The validity of the adiabatic repesentation depends on the collision energy. As a general rule, it is valid for collision energies less than a few keV/amu

For many years, it seemed unrealistic to develop a consistent quantum mechanical formulation, mainly because of the difficulty of finding a suitable coordinate coordinate system capable of describing both the molecular adiabatic states and the asymptotic atomic state. See attempt by Bates & Massey 1947

A semi-classical approach assuming a rectilinear trajectory for the nuclear motion offered an attractive alternative.  But the introduction of a time variable, raises the difficulty of ensuring Galilean invariance. This led to the introduction notion of electron translation factors (ETF) , but such factors cannot be rigourously defined.

Besides,the use of rectilinear trajectories excludes applications to low energy collisions for collision energies less than 100 eV . But in such a formulation, it is not possible to exploit the simplification of angular momentum conservation as in the quantum mechanical approach.  This is not serious for total cross-sections.  But the calculations of differential cross sections is much more difficult. To understand the problem, let us look at the latest calculation of differential cross sections for a typical such as the system  $N^{3+}$ +H

Example of a quantum mechanical calculation of the differential scattering cross section for the charge exchange reaction $N^{3+} + H \rightarrow N^{2+} + H°$
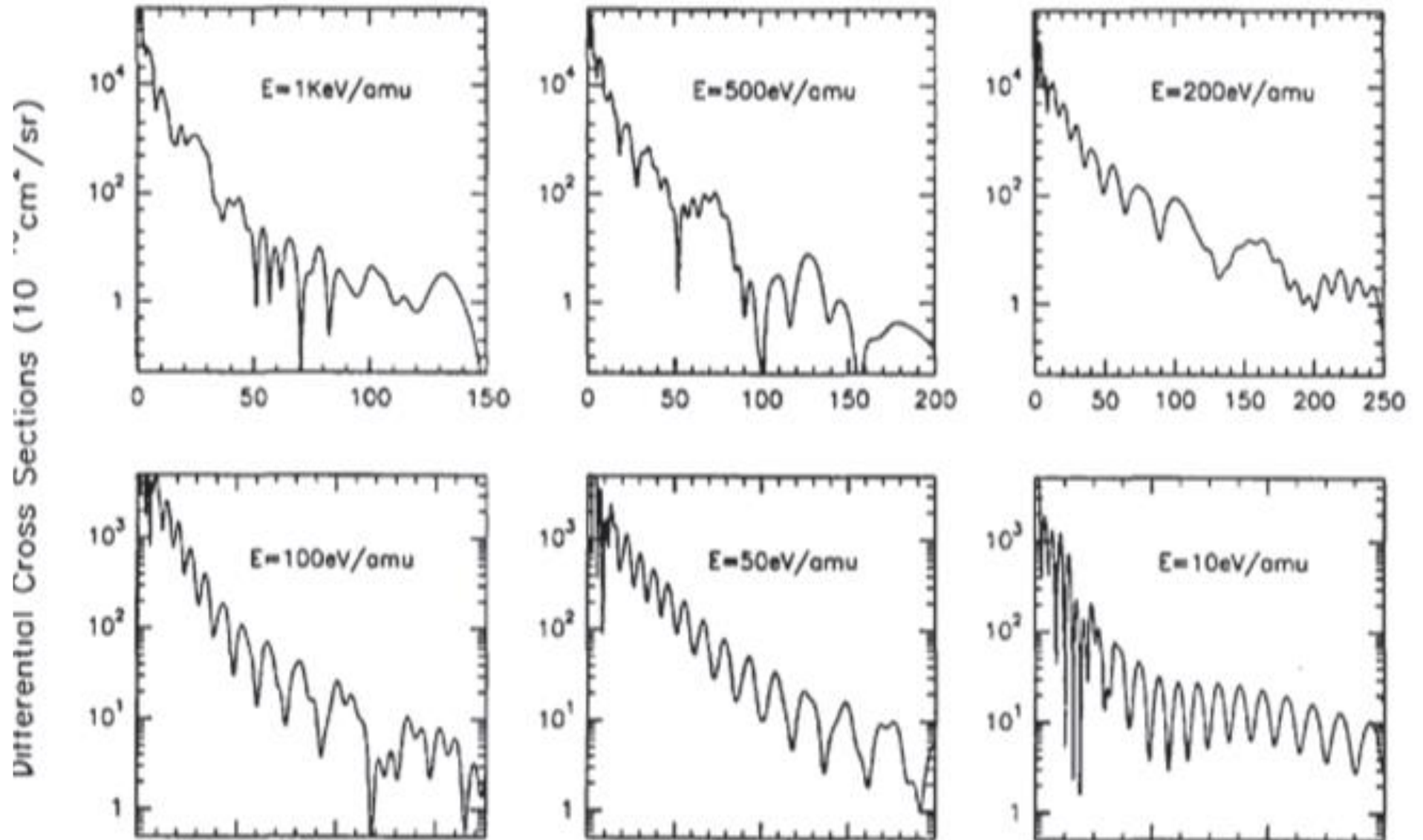
It is seen that for energies of 1 keV/amu, most of the scattering occurs for angles less than 50 mrad.(3°). In that case, the eikonal method can be used to calculate the differential cross section in an impact parameter approach(even though it is not a recommended approach.)  But for energies of energies of 100ev/amu  or less, large angle scattering differential cross sections cannot be extracted from impact parameter calculations.

Problem, is that an impact parameter does not correspond to a specific angular momentum. So angular momentum is not conserved for a given impact parameter and the extraction of the differential cross section by the eikonal method for angles angles greater than 100  mrad is not valid.  Whereas in a quantum calculation, the angular momentum is conserved and the differential cross section is a simple sum.

For many years, it seemed unrealistic to develop a consistent quantum mechanical formulation.

A semi-classical approach assuming a rectilinear trajectory for the nuclear motion offered an attractive alternative. But the introduction of a time variable, raises the difficulty of ensuring Galilean invariance. In particular, the Jacobi coordinates with origin on the nuclear centre of mass. This led to the notion of electron translation factors (ETF) by Bates & McCarroll even though such factors are to a large extent arbitrary and are only constrained by their asymptotic form. But their inclusion did not give satisfactory results. Subsequently, the notion of a so-called common translation factor (CTF) first introduced by Schneidermann & Russek (1967) and Errea et al (1982) has proved more successful.

But, impact parameter calculations have their limitations. The use of rectilinear trajectories excludes applications to low energy collisions in the range less than 100 eV range. Besides, it is not possible to exploit the simplification of angular momentum conservation as in the quantum mechanical approach. This is not serious for total cross-sections. But the calculations of differential cross sections is much more difficult.

The breakthrough in developing a quantum mechanical approach came in 1978 in a paper by Thorson & Delos. They realized that the Jacobi coordinates used hitherto for the determination of the vibration-rotation spectra of diatomic molecules (neutral or ionic) was not satisfactory for taking account of the non adiabatic terms responsible for excitation or charge exchange.

The derviation of their proposed reaction coordinates was rather confusing and their application to isotopic effects, although correct, did not seem to offer a simple way forward. Later a simpler approach via the use of Eckart-type coordinates by Gargaud & McCarroll (1987) provided a relatively simple solution. A more detailed resentation of the reactive coordinate procedure is given by Rahli & McCarroll (2005).

The reaction coordinate procedure is based on the introduction of Eckart-type coordinates, which are  (Rabli & McCarroll 2018)

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

$$\tan 2\phi = \frac{2\sqrt{M}\,\mathbf{r}.\mathbf{R}}{MR^2 - r^2}.$$

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

where

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

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

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

These coordinates allow for a correct description of the aymptotic states.

The introduction of the (r', R') coordinates involves a modification of the original Jacobi coordinates introduced in the diatomic molecular system. But there is no need to explicitly define the modfied basis functions since they only differ from the original adiabatic basis functions by variations of the order of 1/M. It is sufficient to treat  R' as the adiabatic coordinate and expand  the totlal wave function as

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

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

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

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

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

# IC-DIABATIC TRANSFORMATION

ix element of **U** is highly peaked at the avoided crossings and a direct solution

upled differential equations sometimes is not always practical. A simpler way is

a unitary transformation from the original adiabatic basis functions to a diabatic

a transformation matrix **C** which satisfies the equation

*abatic* basis the matrix U is transformed according to

$$\chi_j^d(\mathbf{r}, \mathbf{R}) = \sum_k \chi_k(\mathbf{r}, \mathbf{R}) C_{k,j}(\mathbf{R}).$$

er obvious constraint, namely that the matrix elements of U vanish in the

tic limit? This condition can be achieved if

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

$$\mathbf{U}\mathbf{C} + \frac{d\mathbf{C}}{dR} = 0,$$

Notion of a diabatic state (as opposed to the well defined adiabatic state) is mainly introduced for practical reasons involving the elimination of first order derivatives in a second order derivative equation. It happens to simplify the numerical equations and avoids some numerical problems in the solution of the equations.

So the adiabatic diabatic transformation  is simply a procedure to facilitate the numerical solution of the dynamical equations.  But there remains one question, which remains to be verified., namely  the completeness of the basis set.

But beware of the notion of a diabatic state in the literature if not specifically defined.

In most atom-atom or ion-atom systems where non-adiabatic transitions occur, the number of avoided crossings is fairly small. So it is to be expected that a minimal basis set which takes account of all posssible avoided crossings involving both radial and rotational coupling to be complete. This requirement can be easily verified . For if the basis set to be complete we require

$$\sum_n |\chi_n\rangle \langle \chi_n| = 1,$$

$$D_{ij} = \langle U\chi_i | U\chi_j \rangle = \sum_n \langle U\chi_i | \chi_n \rangle \langle \chi_n | U\chi_j \rangle$$

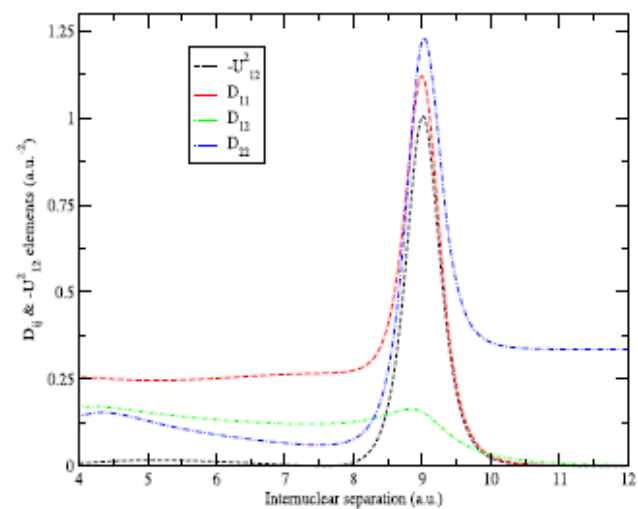$$= -\langle \chi_i | U^2 | \chi_j \rangle = -U_{ij}^2$$

This relation can be verified. Indeed it found that this is the case when the correct reaction coordinates are used. Even for a simple two state (Landau-Zener) avoided crossing, considerable error is induced unless the appropriate reaction coordinates are not used.
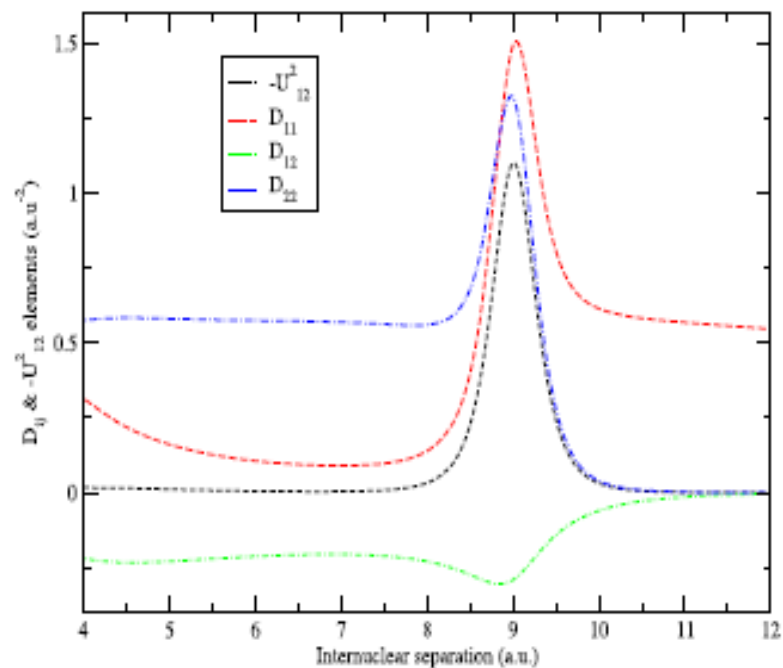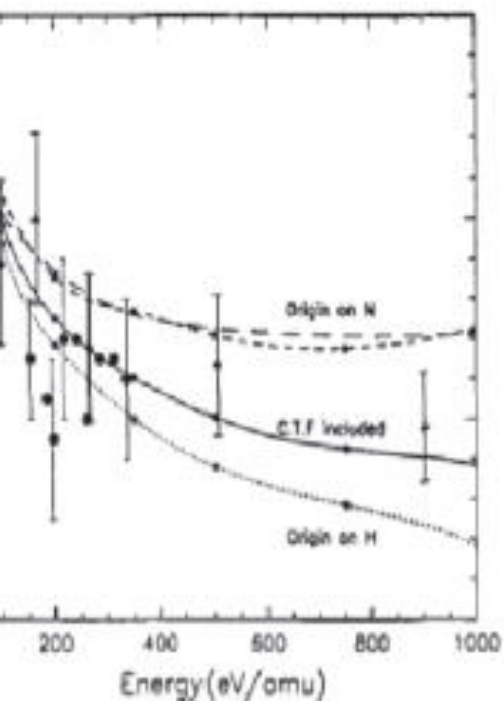
**Figure 4.** Non-adiabatic matrix elements, $U^2$ and $D_{ij}$ in the Jacobi system (origin on N nucleus). Index 1, 2 refer to entrance channel $N^{3+}(2s^2)^1S + H(1s)$ and exit channel $N^{2+}(2s^23s)^2S + H^+$, respectively.

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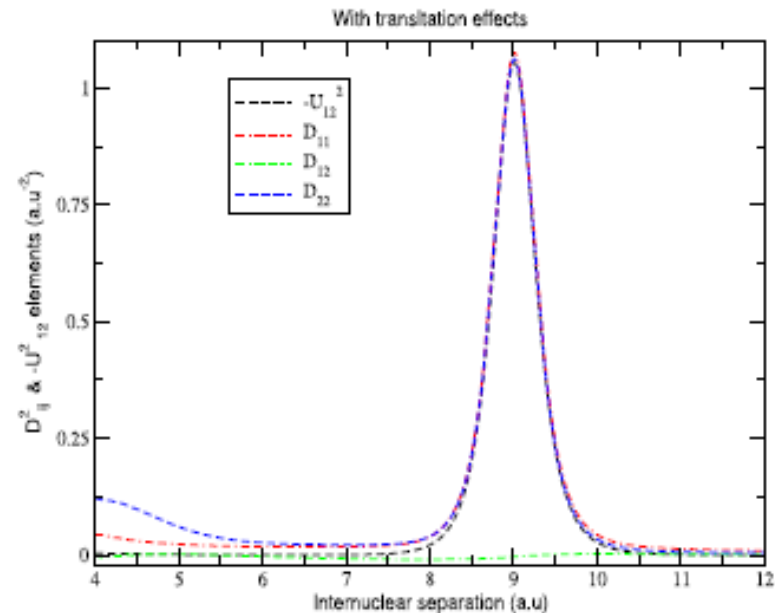
**Figure 6.** Equivalent matrix elements $U^2$ and $D_{ij}$ in the reaction coordinate system. Index 1, 2 refer to entrance channel $N^{3+}(2s^2)^1S + H(1s)$ and exit channel $N^{2+}(2s^23s)^2S + H^+$, respectively.

sections ($10^{-16}$ cm$^2$) for electron capture in
function of ion energy (laboratory system). The
the results with account taken of translation. The
ves refer to results (ours and those of Bienstock
slation and with the origin of electron coordinates
e lower short-dashed curve refers to our results
d with the origin of electron coordinates on the H
sults [27] are given with their error bars.



**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 $N^{2+}(2s^23s)^2S + H^+$, respectively.
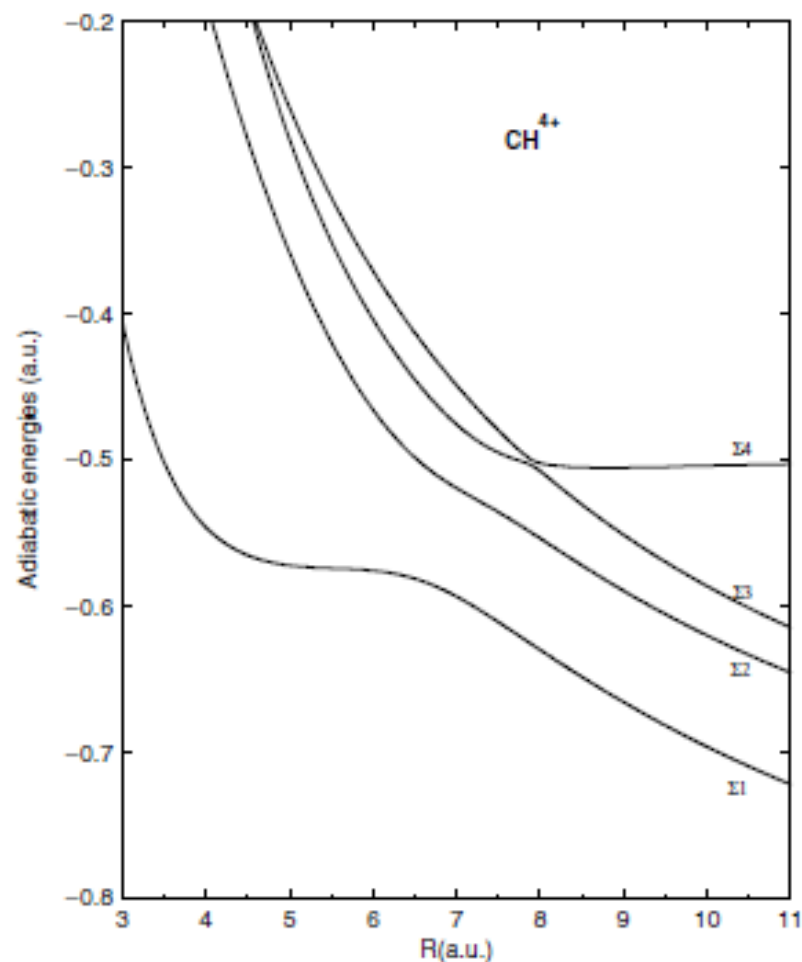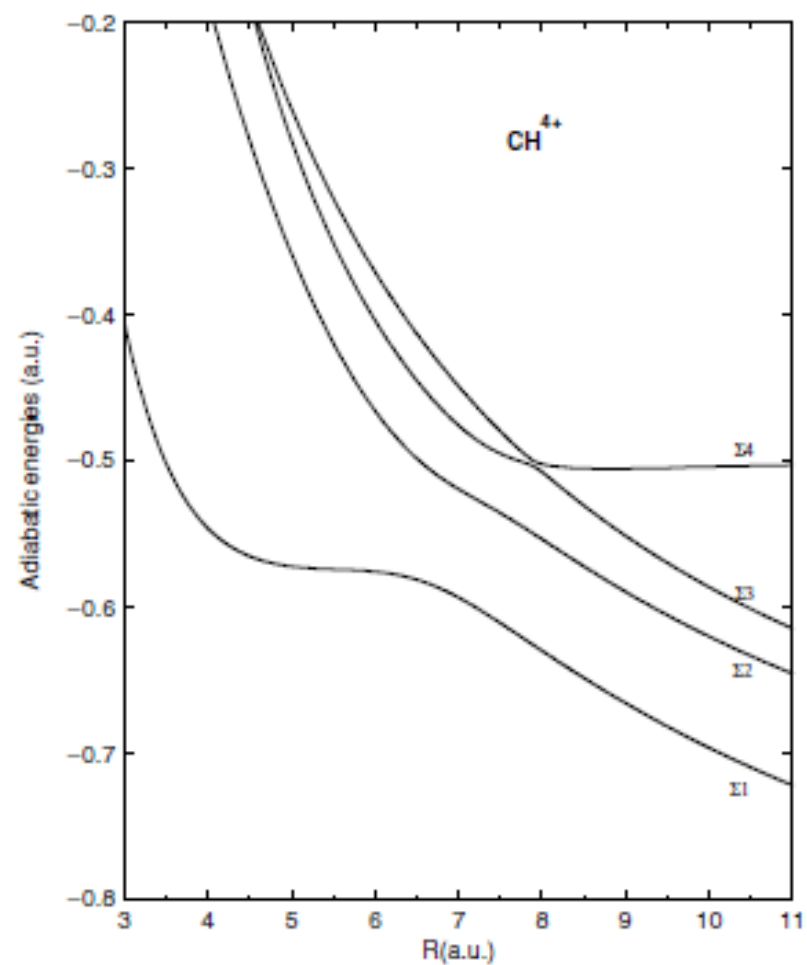
**Figure 1.** Adiabatic energies $\epsilon_i$ of the four sigma states of $C^{4+}/H$, correlat[ed] electron-capture channels: $\Sigma_1$, $C^{3+}(1s^23s)^2S + H^+$; $\Sigma_2$, $C^{3+}(1s^23p)^2P + H^+$; $\Sigma$[...] $H^+$; $\Sigma_4$, $C^{4+}(1s^2) + H(1s)$.
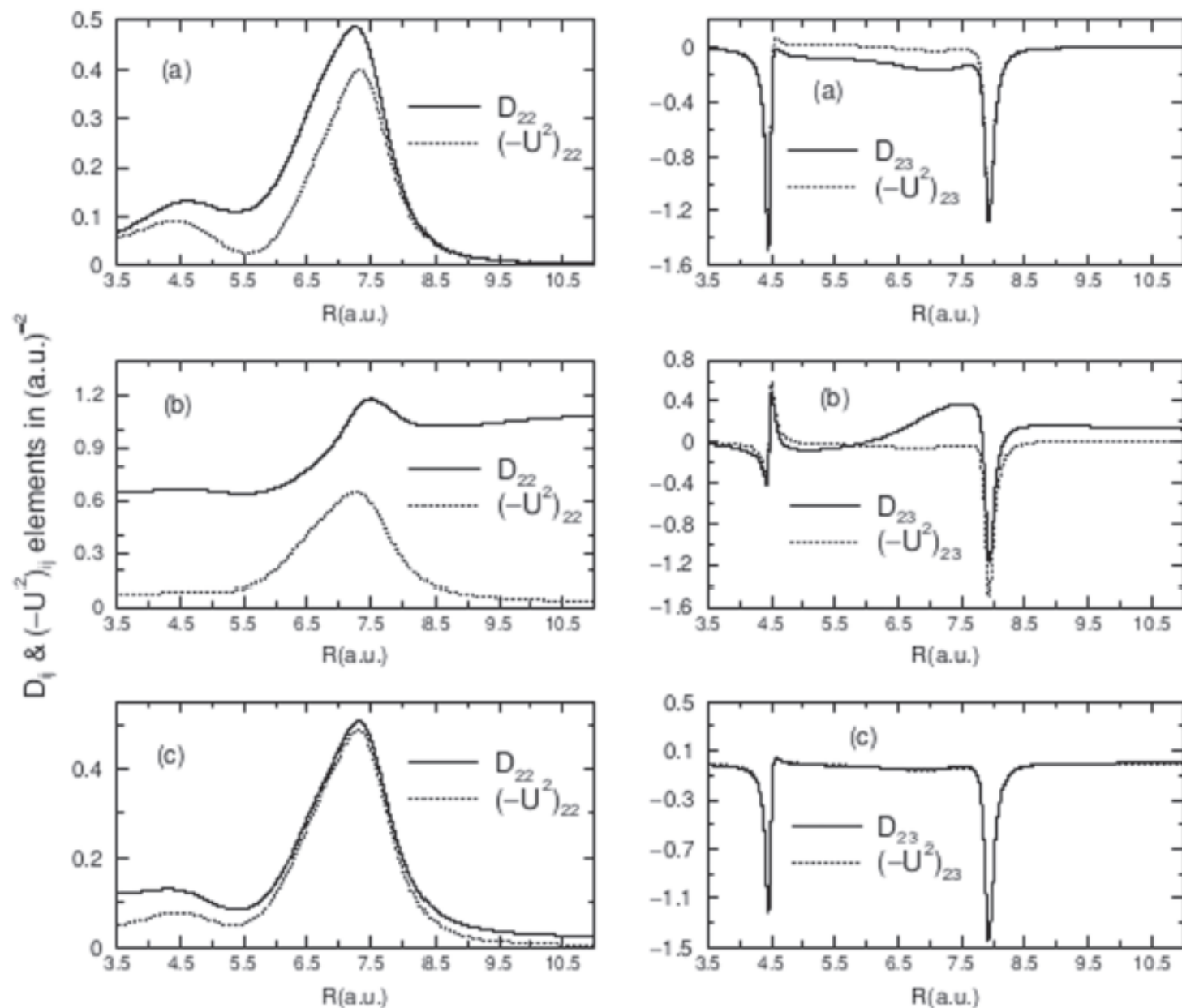


**Figure 9.** Matrix elements $D_{22}$, $(-U^2)_{22}$, $D_{23}$, $(-U^2)_{23}$, for the system $C^{4+}/H$. Case (a) corresponds to Jacobi coordinates with electron origin on the C nucleus, case (b) corresponds to Jacobi coordinates with electron origin on the H nucleus and case (c) corresponds to appropriate 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 1.** Adiabatic energies $\epsilon_i$ of the four sigma states of $C^{4+}/H$, correlated to the principal electron-capture channels: $\Sigma_1$, $C^{3+}(1s^23s)^2S + H^+$; $\Sigma_2$, $C^{3+}(1s^23p)^2P + H^+$; $\Sigma_3$, $C^{3+}(1s^23d)^2D + H^+$; $\Sigma_4$, $C^{4+}(1s^2) + H(1s)$.