CROATICA CHEMICA ACTA CCACAA **64** (2) 89–109 (1991)

ISSN 0011–1643
UDC 541
CCA-1983

Feature Article

Long Lived States in Atom-Molecule Collisions

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Received October 31, 1990

Understanding of the processes in molecular collisions is of great importance for many areas of research. In chemistry and molecular astrophysics, there is great interest in calculating reaction rates. For elementary particle and nuclear physics, it is of interest to find fundamentally new concepts underlying the mechanism of collisions. And for some, the molecular collision problems are interesting on their own. The most elementary process that is usually studied is a binary collision. If this encounter is brief, we talk about direct collisions. However, if during an encounter, the species are stuck to each other for a long time, we talk about collisions mediated by a long lived state. The theory of collisions mediated by long lived states is very complex and only few basic principles were given in quantum theory; a central place being given to resonances. However, as it will be shown, the theory of such collisions is far from being completed and, in fact, is in its infancy. It is the purpose of this paper to review what is known about the subject and locate the problems.

1. INTRODUCTION

One of the most important and interesting theoretical problems in chemistry and molecular astrophysics is the prediction of molecular reaction rates. Of common interest to both these fields are reactions in gases which, in many cases, can be understood in terms of binary encounters of molecules. However, originally this was not how reactions in gases were analyzed. Since the chemical reactions are controlled in bulk, it was natural to analyze them in terms of the two parameters that were readily available: concentrations and temperature. On the microscopic level, however, these parameters have no meaning and the reactions are described in terms of much more specific parameters. The aim of the theory is, therefore, to understand binary collisions and their relevance to bulk processes. This relationship can only be achieved if, in a particular environment, we are certain that binary collisions are the dominant processes. Although one expects this to be the case of the gas phase, this is not always so. In order to get a better understanding of the nature of gases, we will review a few facts about them.

We can assume that the molecules of a gas move freely between collisions. The collision frequency of a single molecule in a gas at room temperature and one atmosphere pressure is typically between 10^9 and 10^{10} encounters per second[1], which suggests that the molecule moves freely for 10^{-10} seconds. On the other hand, for an averaged relative velocity of the molecules[1] of the order of 1000 ms^{-1} and a typical interaction distance of 1A, the collision time is of the order of 10^{-13} seconds or shorter. This is a conservative estimate because when molecules are close to each other, their relative velocity is increased by their potential, which can be considerable. This collision time is much shorter than the time between encounters and when reaction occurs in short times, we can safely assume that the bulk properties are dominated by the binary collisions. Such reactions are normally called impulsive reactions and as a bulk process, they are very well described by the rate equation[2]

$$d[A]/dt = -k\,[A]\,[B] \tag{1}$$

where [A] and [B] are the concentrations of the reactant molecules in reaction A + B → anything. k is the rate coefficient. Arrhenius described empirically that the reaction rate increases with temperature according to the relation $k \approx \exp(-E_{**}/kT)$, where E_{**} is a parameter with a dimension of energy. This relation is the basis of statistical theories of chemical reactions, of which the transition state theory is the best known[3,4]. It also provides a link between the descriptions in terms of binary encounters and bulk behaviour, although within statistical arguments.

A much more accurate relationship between rate constant k and the parameters that describe binary encounters is for the reaction A+B → C+D given by[5,6]

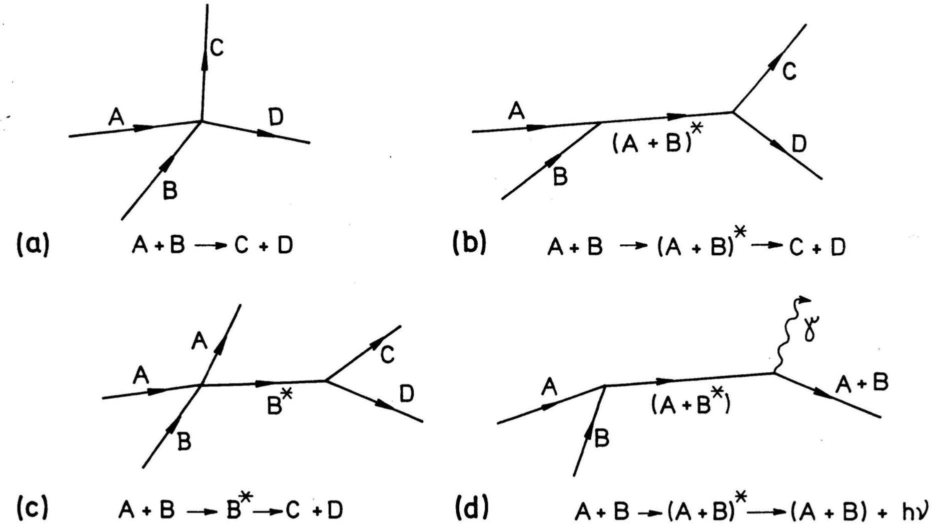
$$k(T) = \int dE\ \sigma_{A+B->C+D}\ P(E) \tag{2}$$

where $P(E)$ denotes the velocity distribution in gas and $\sigma_{A+B\to C+D}$ is the reactive scattering cross section. The relationship (2) is valid when the binary collisions are the predominant mode of reaction in bulk media.

The are, however, reactions in which the time for the completion of a binary collision is much longer and in these cases we say that the collision is mediated by a long lived state. There are several reasons why this happens[7] but usually it is because the relative kinetic energy of molecules A and B becomes distributed among the internal degrees of freedom of the merged species (A+B) and is not necessarily immediately available as relative translational energy of the separating species, whether A and B or C and D. Such a state will live as long as this relative translational energy is unavailable and one of the objectives of collision theory is to determine the lifetime of such long lived states. If the lifetime is comparable with the time that molecules move freely between collisions in the gas phase (ca. 10^{-10} s),then there is a great chance that the long lived state will experience a collision with another molecule. In such a case, we talk about three-body collisions, or in general, multiple collisions. Such collisions definitely alter the outcome of binary collisions and, therefore, the simple relationship between k and the cross section, given by (2), will no longer be applicable. Also, the relationship (1) becomes questionable because the rate of chemical reaction becomes pressure dependent[8], when sufficiently long lived states are formed. The reason is that increasing the pressure effectively shortens the time between collisions and, therefore, enhances the chance of multiple encounters.

In molecular clouds, the densities are much larger than in typical chemistry experiments with gases, apart from molecular beam experiments where special care is taken not to have other than binary collisions. In that space environment, the frequency of collisions, for a typical density of 10^{11} molecules/m^3 in dark molecular clouds, is so low that two molecules encounter each other in approximately 11 hours. To talk about three body collisions, even for long lived intermediaries, is academic. Therefore, the rate coefficient of chemical reactions in that environment is given with a good confidence level by (2).

Figure 1 shows schematic diagrams of several important cases of binary collisions. The pictorial representation has been borrowed from elementary particle physics where, by convention, the star designates the long lived state.



(a) $A + B \rightarrow C + D$ (b) $A + B \rightarrow (A + B)^* \rightarrow C + D$

(c) $A + B \rightarrow B^* \rightarrow C + D$ (d) $A + B \rightarrow (A + B)^* \rightarrow (A + B) + h\nu$

Figure 1. Typical examples of binary collisions. a) collision without intermediate long lived state, b) collision mediated by a long lived state, c) dissociation process mediated by a long lived state and c) photon recombination process.

The list includes a fast reaction (Figure 1a) and a reaction mediated by a long lived state E^* (Figure 1b). The collision induced dissociation reaction in Figure 1c is also referred to as a unimolecular process. The process in Figure 1d, in which a photon is emitted, is called radiative recombination. The list in Figure 1 is not complete; for instance, photodissociation processes are not included.

Two important types of three body collisions are shown in Figure 2. As we have already mentioned, they are important for understanding the bulk properties of reactions when the binary collisions are mediated by long lived states, as in the case shown in Figure 1b.

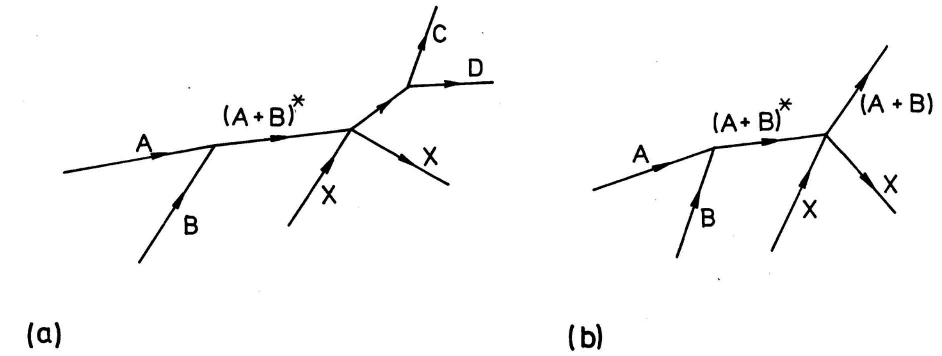


Figure 2. Examples of three body collisions that occur in gases when reaction is mediated by a long lived state.

Great interest in a detailed understanding of long lived states was initiated by development of large and fast computers[9-11]. Before that, very little was known about their properties and most of that knowledge was derived from statistical models, such as Slater's[12] or Lindemann's models[13]. By using computers, it is possible to test these models and also to learn the properties of long lived states that were not envisaged. Classical mechanics is normally used for this purpose, which is a help in understanding the processes that lead to the formation of long lived states. A more practical reason for using classical mechanics in the analysis of long lived states is that the few bodies collision problem is very difficult to solve in quantum theory. Even nowadays, solving a simple reaction collision problem in quantum description requires resources of a large computer. Strictly speaking, the molecular collision problem requires quantum description. As we will show, the use of classical mechanics for a description of long lived states may produce meaningless results because, in such cases the uncertainty principle may be violated. However, there is the problem of how to define a long lived state in quantum theory. A resonance has such an attribute[14] but we will show that it does not have properties consistent also with the properties of a long lived state in the classical description.

We have so far described only one aspect of long lived states and this is their appearance as intermediaries in collisions. Very often by a long lived state one means a decaying state, of which there are many examples. An α decaying U^{238} nucleus, with the half-lifetime of $\tau \approx 4.5\ 10^9$ years, would not be considered as an intermediary in collision. A He atom in its 2^3 S state has such a long lifetime that it can be measured in terms of hours rather than fractions of seconds. Muon is called a »stable« particle, although it has a lifetime of $\tau \approx 10^{-6}$ sec., because it is measured against the lifetime of other elementary particles that decay via strong interactions. In the fragmentation processes of molecules (*e.g.* photodissociation) or clusters, examples of decaying states can be found, although their lifetime is considerably shorter than in the examples mentioned earlier. A common feature of all of them is that the decay probability of unstable species shows exponential form. Such behaviour is traced to the existence of what is called the resonance or a complex energy eigenvalue of the Hamiltonian of the system. Since resonances are also found in collision events, it was natural to associate them with the long lived states, which was further supported by the calculation of time delay in these processes. Straightforward calculation showed that the decay time of an unstable species is half the appropriate time delay in collisions, which confirmed our intuition that decay is half an appropriate collision event. In this review we shall not discuss decays but only the long lived states in collisions.

The purpose of this article is to give a review of the work that has been done in this field together with the problems arising in a description of the long lived states.

2. GENERAL REMARKS ON LONG LIVED STATES

There are two conceptually different approaches to the analysis of the collisions of molecules. One is the approach of classical mechanics (based on Newton's equations of motion) and the other is the quantum theory approach (which is based on Schrödinger's equation). Strictly speaking, all molecular collisions should be described by quantum theory, but under some circumstances classical mechanics provides equally good results. When and why both of these approaches give nearly the same results has been discussed in the literature[18,16] and we shall not do it here. Later, we shall discuss this in the context of long lived states.

In the case of long lived states, we have a good idea of what they are. We say that a long lived state is formed when two colliding molecules are stuck to each other for a period of time before the composite system fragments. This picture is entirely classical since it implicitly incorporates the notion of the trajectory. It is relatively easy to observe when such a state is formed in a classical description. It is sufficient to follow the relative coordinates of atoms in time[10,17,18]. If their values are smaller than some typical distance (say five times the diameter of molecules) for a period of time which is much longer than the time for free molecules to travel the same distance, we say that a long lived state is formed[11]. Figure 3. shows a schematic description of a typical collision in which a long lived state is formed.

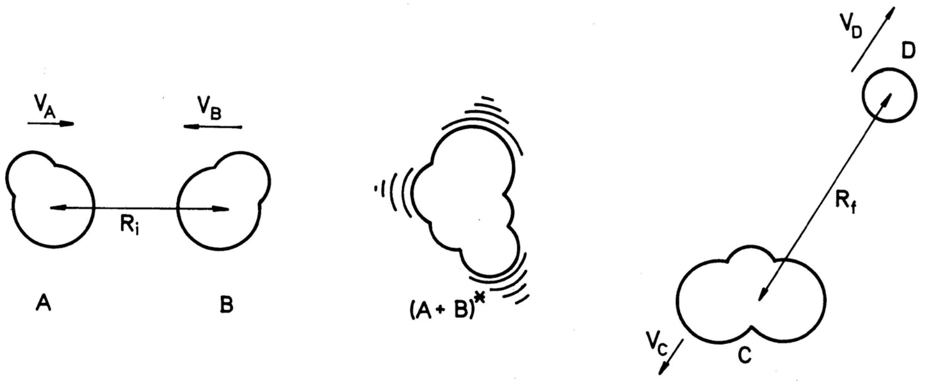


Figure 3. Pictorial representation of the formation of long lived state in collision of molecules A and B.

In a strict sense, we define a long lived state using the notion of time delay. The time required for two molecules to come together (when they travel a distance R_l) to interact and for the products to fly apart when they travel R_r, is the absolute travel time. If from this time we subtract the time which the particles would travel R_i and R_r, with the assumption that the potential between the molecules is zero, we obtain a quantity that measures how long the two molecules interact. This quantity is called the time delay τ[18,19]. From its definition it can have positive and negative values. If the time delay is positive, then a long lived state is formed. In the case when the potential between molecules is nearly all repulsive, one can show that the time delay is usually small and negative[20]. There are other criteria for long lived state but this classical criterion is easily generalized in quantum theory, while the others rely more or less on a knowledge of the classical trajectory[10,11,17,18,21,22].

Long lived states in the quantum treatment are more difficult to define since there is no trajectory. In order to see the problems involved in such a definition, we shall review certain basic principles of quantum theory. At the root of the quantum description lies the concept of probability. What this means is that, at any instant, the position of a particle has a certain probability, which is a result of the inherent inability to measure its position and momentum accurately. The uncertainty in the position and the momentum of a molecule depends on the circumstances. For instance, the uncertainty in position of a molecule in the gas phase could be its mean free path. The uncertainty in position of a molecule in a molecular beam experiment is given by the area of the nozzle aperture and the length of the pulse defined by the product of the time the beam chopper stays open and the velocity. The probability distribution of finding a molecule near a certain averaged position may have various forms but, in general, its mean extent is much larger than the size of the molecule, *e.g.* in the case of a molecular beam experiment. At different instants, the probability distribution moves, at a speed that is related to the averaged velocity of the molecule. The time evolution of this distribution is obtained as a solution of the quantum dynamic equation, *i.e.* the Schrödinger equation. The equation applies to the probability amplitude (the wave function) from which the probability distribution is obtained by squaring the modulus of the wave function. The form of the wave function that reproduces the probability distribution is also called a wave packet. Instead of the trajectory in the classical theory, we work with wave packets in quantum theory. Likewise, the time delay which is defined for a trajectory in the classical description must be appropriately defined for a wave packet in a quantum description. From the value of such a time delay we should be able to determine the lifetime of a long lived state in the quantum treatment.

The time delay, in the quantum treatment, is obtained by initially fixing a specific point on the wave packet and seeing when this point comes out of the interaction region. However, we have a problem here because the wave packet before collision is in principle localized along the line of impact between the two particles (its delocalization in the molecular beam experiment is related to the opening time of shutter and, therefore, can be controlled), but it is entirely delocalized perpendicular to this line. Thus, it can be assumed that along the line of impact the wave packet has an certain shape but orthogonal to it, it is uniform, and hence when we choose a point along the line of impact we are in fact choosing the whole plane that is perpendicular to it. This plane can coincide with the maximum of the wave packet, for example, when its shape is a Gaussian function[23], or it can be the plane at the front of the wave packet[18], which is called a wave front. Gaussian type wave packets are rather artificial but they are used primarily because they are mathematically convenient so one should be wary of them. For example, since the beginning and the end of the pulse are not distinguished, there is no way one can study the onset of the scattering process from the zero value of the probability amplitude to the full plane wave situation.

A more appropriate form of a wave packet is the one which is produced in a molecular beam experiment and it is shown in Figure 4a. Point P defines the wave front, *i.e.* the plane which is perpendicular to the line of impact. As the time progresses, the whole wave packet moves together with the wave front. It should be noted that when the wave packet moves freely, it does not retain its shape and its extent. Figure 4b shows what the wave packet in Figure 4a. looks like after certain length of time. This point will be discussed later.

In order to measure the time delay involving a wave packet, we fix initially its distance from the target. The wave front is followed and after collision, its arrival time at some fixed point relative to the target is measured. The time delay is now obtained

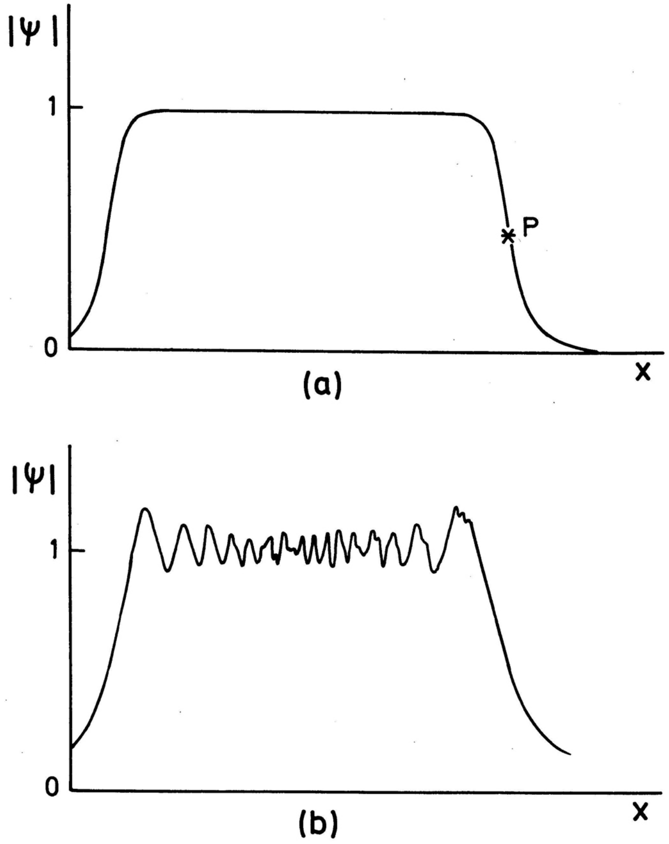


Figure 4. Typical wave packet produced in molecular beams (a) and its shape at a later time (b).

in the same way as for a trajectory in the classical description; from this time we subtract the travel time of the wave packet to the target and from the target to detector. It might appear that this time delay is the same as in the classical description. However, this is not quite so because the wave front (the plane defined by *P* in Figure 4.). though initially straight, may have various shapes after a collision. Figure 5a. shows an example of the scattered wave front in the case of elastic atom-atom collisions. The wave front is shown in two dimensions since the system has cylindrical symmetry. Before collision, the wave front P_I is shown by the broken line and after collision, it is shown by the full and broken-dotted line *P*. The scattered wave front progresses radially from the target *T*.

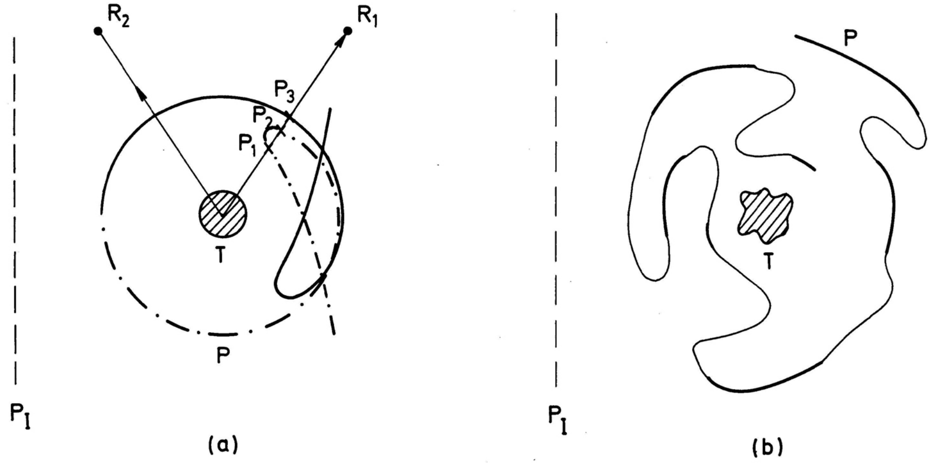


Figure 5. Scattering wave front in elastic collisions (a) and in more complete collisions (b). Initial wave front is indicated by OP_I and scattered by *P*. The target is indicated by *T*. The broken-dotted line is also *P* but is a mirror image of the full line.

We notice that a point R_z the arrival of a single point of the wave front is expected and, therefore, the time delay at this angle is the same both in the classical and quantum theories. However, at point R_1, we expect the arrival of three points, P_1, P_2 and P_3, of the wave front, which correspond to the atom scattering at three different impact parameters[24,15,20]. The definition of time delay at R_1 is, therefore, different in quantum theory from that in the classical theory because the former does not have a unique value.

For more complex collisions, the scattered wave front may have a very complicated shape, as shown schematically in Figure 5b. The thick sections of the scattered wave front in this figure will be discussed later.

The meaning of the quantum time delay is, therefore, different from that in the classical description. In quantum theory, it is associated with the arrival time of the wave front and, thus, it is a multivalued function, while in the classical theory it has a single value because it is associated with a given trajectory.

3. CLASSICAL DESCRIPTION OF LONG LIVED STATES

Fundamental in any classical description of collisions are Newton's equations of motion, which for a given set of N particles are

$$m_i \frac{d^2}{dt^2} \mathbf{r}_i = F_i \qquad ; \quad i = 1, 2, \ldots N \tag{3}$$

where m_i is the mass of the i^{tn} particle, E_i is the force that acts on the i^{tn} particle and r_i is its coordinate. The coordinate function $\mathbf{r}_i(t)$ will be called the trajectory of the i^{tn} particle. The set (3) represents the initial value problem meaning that given a set of values for the coordinates and velocities of particles at some given time t_o, the solution of (3) gives their values at any later (or earlier) time t. However, the initial conditions for (3) cannot be directly measured for the system on the atomic scale since the coordinates and velocities of particles are not observables. Information about these initial conditions can be obtained form the quantities which can be directly measured experimentally (observables), and these are for example the vibrational energy or the rotational angular momentum of molecules. These observables give only one half of the initial conditions for the integration of (3).[15]

The other half are arbitrary due to the uncertainty principle, and are referred to as the set of phases P_i. Therefore, if we are interested in state-to-state transitions between the initial observables O_i^{I} and the final ones O_i^{F}, then the set of phases which connect them is specified, but not necessarily uniquely[28]. Finding all these sets of phases is the most difficult task in the classical description of collisions. It is particularly difficult to find these sets when long lived states are formed because they usually appear in a large number[26]. However, when all of them are found, then the cross section for the transition $O_i^{I} \rightarrow O_i^{F}$ is proportional to the inverse of the Jacobian[18]

$$\sigma_{O^I \to O^F} \sim \sum_{P_i} \left(\mathrm{Det} \left| \frac{\partial O^F}{\partial P_i} \right| \right)^{-1} \tag{4}$$

where the sum includes all the sets of phases which connect the initial and the final states. We can, therefore, define the partial cross sections so that (4) can be written as

$$\sigma_{O^I \to O^F} = \sum_{P} \sigma^{P}_{O^I \to O^F} \tag{5}$$

For each set of phases P_i and observables O^I the relevant trajectory, obtained by the integration of (3). has a time delay. This time delay, as discussed in Section 2., is the most relevant for the study of the long lived states in collisions, and can have any value between a small negative or some large positive time delay. It is, thus, relevant to ask what happens if the sum in (5) is replaced by a sum that includes only the trajectories of a certain time delay. We obtain the time dependent cross section, which in principle can also be measured since the time delay is a well defined quantity (such a cross section appears under different names *e.g.* the complex decay curve[27]. The value of this cross section is given by

$$\sigma_{O^{\mathrm{I}}\rightarrow O^{\mathrm{F}}}(\tau_o) = \sum_{P(\tau_o)} \sigma^{\mathrm{P}}_{O^{\mathrm{I}}-.\,O^{\mathrm{F}}} \tag{6}$$

where now the sum extends over all sets of phases for which the relevant trajectories have a time delay τ_o. Obviously, such a cross section carries more information about collision than (4).

General features of cross section (6) can be obtained by analyzing the time dependence of the difference between two trajectories. This difference is designated ε_i and is assumed to be small. By definition

$$\varepsilon_i = r_i(t) - r_i(t) \tag{7}$$

and if only the first order terms in ε_i are retained, then the equations for (7) are

$$m_i \frac{d^2}{dt^2} = - \sum_{j=1} \left(\varepsilon_j \nabla_j\right) \nabla_i V \tag{8}$$

where V is the potential. This set of equations, though appearing to be linear, is coupled to the set (3) via the potential V and, therefore, it does not have an analytic solution. However, in the neighborhood of the reference trajectory we can assume that V is given by an expansion up to quadratic terms in r. In such a case, the matrix of the second derivatives (the Hessian matrix) in r is constant so that (8) can be written in a general form

$$\frac{d^2}{dt^2} \varepsilon_i = - \sum_{j=1}^{3N} U_{i,j}\, \varepsilon_j \tag{9}$$

where ε_i is now a scalar and designates one of the components of (8). In matrix form, this set has a general solution

$$\varepsilon = \sin(\mathbf{U}^{1/2}\, t)\, \mathbf{A} + \cos(\mathbf{U}^{1/2}\, t)\, \mathbf{B} \tag{10}$$

where the matrices A and B are determined from the initial conditions.

The properties of solution (10) are determined by $U^{1/2}$. Two cases in particular are distinguished. In one U is positive definite, *i.e.* all its eigenvalues are positive, and in the other at least one eigenvalue is negative. In the first case, solution (10) oscillates within certain bounds and we call it the stable solution. In the second case the solution is unbounded and is called an unstable solution. This means that in the first case two close trajectories remain permanently so but in the second case they separate exponentially. On this basis, we distinguish two kinds of systems, which we shall call stable and unstable. In the stable systems, solution of (10) oscillates within certain bounds, but in the unstable systems it diverges exponentially. A typical example of a stable system is the set of coupled harmonic oscillators, for which (9) is the exact solution. However, if at least one harmonic force is replaced by a repulsive linear force (the inverted harmonic oscillator), U is not necessarily positive definite and the systems goes into the unstable regime. Slater's model[12] of molecules (developed for describing unimolecular reactions) is an example of a stable system, while most other real systems are unstable[28-30].For unstable systems, there is the estimate

$$\varepsilon \approx \exp(t\ |\lambda|^{1/2}) \tag{11}$$

which is valid only locally because globally the trajectory passes through the regions of stability and instability. Therefore, λ in (11) can be considered as an »effective« eigenvalue. It should be pointed out that the term »stable system« does not mean that the system is stable, *i.e.* that it has infinite lifetime, and vice- versa for the unstable system. In our context, these two terms describe systems that behave differently when the system of equations (8) is solved.

From (11) an estimate of the cross section is obtained. A small change in the value of the initial phases causes a change in O^F of the same order as in (11). The Jacobian is, therefore, of the same order of magnitude and the partial cross sections are calculated by the expression

$$\sigma_{O^I \to O^F}(\tau) \approx \exp(-\tau\,|\lambda|^{1/2}) \tag{12}$$

which indicates that they are small for the long lived states. It appears, therefore, that sum (3) is rapidly convergent, and that the long lived states have little influence on state-to-state cross sections.

For Slater's model, the estimate of the partial cross sections is different from (12). The trajectories do not have the exponential separation rates and the partial cross sections are approximately of the same order of magnitude for all time delays. However, neither Salter's model nor entirely unstable systems are truly representative of real systems. The estimate of the partial cross sections for real systems lies between these two limiting cases and, generally speaking, the more the system behaves like a stable one, the greater will be the contribution of the long lived state.

One question of great interest from the point of view of the statistical theory of chemical reaction rates is how the total collision energy is distributed among the degrees of freedom of the long lived state. In particular, it is of interest for unimolecular reaction rates to know whether this distribution is random of not[7,8]. Classical theory should be able to answer this question, but one is immediately confronted with a puzzle; how is one going to answer this question? For one thing, given an initial and a final state, there is no intermediate state in the unimolecular rate theory (in Figure 1c. it corresponds to B^*, and the lifetimes for these intermediate states range from almost zero to a very large value. Furthermore, when long lived states are formed, then at certain gas pressure multiple collisions of the form shown in Figure 2. start to play a role, as explained in the Introduction. Multiple collisions alter the distribution in the long lived states and make the task of its determination impossible by simple analysis. Even when an isolated long lived state is studied, it is not clear how to determine whether the distribution of its internal states is random or not. Randomness is not a uniquely defined entity and various criteria of randomization have been suggested[31-33]; among which the most attractive is that the unstable systems are also ergodic[34]. This possibility comes from the analysis of bound (infinite lifetime) systems, but the long lived states, by their very nature, do not have infinite lifetimes and, therefore, this criterion is only of limited applicability[18].

TABLE I

Systems for which the classical long lived states have been investigated

$O + CO$[26,68]	$C(1D) + HI$[66]	$H + H_2$[67]
$NaBr + KCl$[10]	$K + NaCl$[29]	$F + H_2$[48]
$O(^1D) + H_2$[66]	$H + ICl$[29]	$H^+ + H_2$[27,68]
$C(^1D) + H_2$[66]	$Ar + Ar_n$[11]	rare gas + CO_2[69]
		$Ar + ArNNAr$[70]

There has been a number of classical studies of long lived states in collisions. A partial list is given in Table I. and a few of them should be briefly mentioned.

Collision $O+CO$ is one of the earliest attempts to analyze vibrational predissociation (decay) of $(OCO)^*$ as a »half collision« problem. This and the analysis of reaction $NaBr+KCl$ pointed to two specific characteristics of long lived states. One is that there is a severe loss of numerical accuracy of the trajectories with long time delay and the other that the final values of observables of these trajectories change very rapidly with the initial phases. The explanation was found in the exponential separation of two close trajectories[15,29]. This was a direct implementation of the ideas already developed in the study of chaos in the bound systems and one of them is that the exponential separation of trajectories is direct evidence of the ergodic behaviour of the system[34]. The same idea was tested on the example of long lived states in the reactions $K+NaCl$ and $H+ICl$. However, there is as yet no conclusive evidence which would indicate this relationship.

On the example of $Ar+Ar_n$ collisions it was shown that time dependence of cross section has an exponential decrease with the increasing value of time delay for trajectories. No conclusions were drawn which would indicate that this time dependence of cross sections is a result of the exponential separation of trajectories. However, it was indicated that there was no evidence of energy randomization.

Of particular interest is the reaction $H+H_2$ (and similarly $F+H_2$), with various combinations involving D. It is usually believed that a necessary condition for the formation of long lived states is that the atom-molecule potential should have a well. In such a case, an incoming atom is trapped in this well provided it has been able to transfer most of its kinetic energy into the internal energies of molecule. However, a long lived state can be formed without this condition being fulfilled. The $H+H_2$ potential is nearly all repulsive and yet it was found that a long lived state can be formed. The mechanism of its formation is an interplay of two factors; large energy transfer of the incoming atom into the molecule (H atom is equal in mass to the atoms in H_2 molecule) and the fact that the H_3 breakup is not possible. Therefore, it can happen that for a particular phase of H_2 the kinetic energy of the incoming atom is transferred into vibrations of H_2 in such a way that the system H–H_2 is in a stretching mode of vibrations leading to breakup. Since this is not possible, the system will vibrate until its internal energy is redistributed to allow a normal dissociation to the products $H+H_2$. It is obvious that such states can only be relatively short lived and in fact they are rather rare events.

Another example of a long lived state, where it is not necessary for the potential to have a well, is random walk. Take a cluster of n fixed and separated hard spheres and shoot a projectile[38]. Most of the time the projectile recoils from the spheres but for certain initial conditions it penetrates the cluster and is trapped until it finds its way out. A long lived state is formed, but such a state is not typical of atom-molecule collisions but more of a diffusion process.

Most of the research of long lived states involved reactions. There have been relatively fewer studies of much simpler systems although they allow a more thorough study of long lived states, without loss of generality. In the elastic collisions of atoms[36] (where the long lived state is also called orbiting), they did not attract too much attention because it is assumed that they have not been studied in great detail, but it is believed that they are short lived[15]. Figure 6. shows a long lived state in the rotational excitation of Li_2 by atom[37]. Between the two bounces of the He atom, the molecule made 41 rotations. On the other hand, long lived states in vibrationally inelastic collisions may have a much longer lifetime[38].

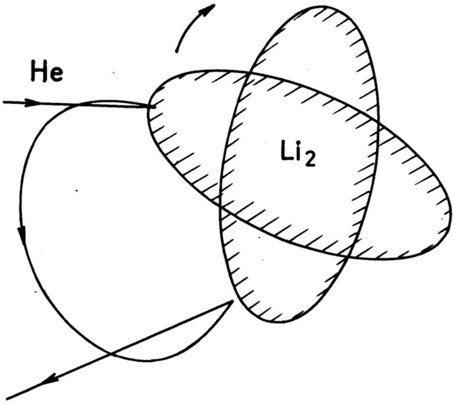


Figure 6. Long lived state in the rotational excitation of $Li_2(A^1\Sigma$ molecule by He atom, at the collision energy of $E = 1$ meV. Between the two collisions the molecule made 21 rotations.

A classical description of atom and molecule collisions is valid only if certain conditions are met, and one of them is related to the uncertainty principle. Thus principle says that the phase space of a system with N degrees of freedom cannot be fragmented into the volume elements smaller than the N-th power of Planck's constant, *i.e.* h^N. This means that any two trajectories with initial conditions from the same smallest volume element cannot be distinguished experimentally, even in principle.

Let us consider a one dimensional case and the corresponding area $\delta x \delta p$ in the phase space. This area can be larger than Planck's constant and corresponds to the uncertainty in preparing the initial conditions for the particle. As the time progresses, the area slowly changes its shape and for a free particle it will spread uniformly in the x coordinate. In reality though (*i.e.* when calculated from the quantum theory), the shape of the area along the x axis is as shown in Figure 4b. When the particle encounters another particle, the shape of the area changes far more dramatically. Different parts of the phase space are now affected differently and for complex collisions the area can even split into fragments or increase its size. What happens if a small element of the original area, smaller than h, increases its size much beyond h? In principle, we would be able to distinguish various trajectories within the enlarged area whose initial conditions are in an area much smaller than h. In other words, we would have a »microscope« that would enable us to »look« into the elements of the phase space which is smaller than h, thus contradicting the uncertainty principle. However, this is exactly what happens in the case of the exponentially separating trajectories in the unstable systems. Their separation is so rapid that very fine selection of the initial conditions is necessary in order to distinguish various final states. As a result, the classical cross sections become meaningless. Nevertheless, classical theory is very often adequate for many systems in which long lived states are formed simply because the short lived states dominate the cross section by virtue of estimate (12).

4. QUANTUM DESCRIPTION OF LONG LIVED STATES

The basis of the quantum description of collisions is the time dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \tag{13}$$

where H is the Hamiltonian of the system and ψ is the wave function. The square of the modulus of the wave function gives the probability density of finding system in a certain state at a certain time. The time evolution of the wave function is specified by the value of ψ at an initial time, say $t=0$, which we designate ψ_0. The value of ψ_0 is determined (except for a phase factor) by the initial probability distribution of the system which, in turn, depends on the experimental circumstances. For the collision of two molecules, say A and B, we assume that their internal states are given by φ_A and φ_B, while the translational wave function for their relative motion, in the centre of mass coordinate system, is φ. If the initial probability distribution is ρ, then φ_0 is given by

$$\varphi_0 = \sqrt{\rho}\exp(ip_0R/\hbar) \tag{14}$$

where p_0 is the relative momentum of the two molecules and R is their relative separation. The phase factor gives the non-zero probability current in the direction of p_0. The initial wave function is, therefore,

$$\psi_o = \varphi_A \varphi_B \varphi_0 \tag{15}$$

If $k_0 = p_0/\hbar$ is parallel to the z axis and if it is assumed that the extension of the wave packet in the x and y direction is infinite (for molecular beams this reflects the ~~fact~~ that the nozzle is much wider than the size of molecules), then φ_0 is a function of only the z coordinate. An example of the modulus of φ_0 is shown in Figure 4a.

Solution of (13) is given in the form of the integral

$$\psi = \int d^3 k\, \varphi_k A(K)\, e^{-1Et/\hbar} \tag{16}$$

where $A(k)$ is the amplitude determined from the initial condition (15) and ϕ_k is the solution of the time independent Schrödinger equation

$$H\,\varphi_k = E\,\varphi_K \tag{17}$$

The boundary condition on φ_k determines the solution ψ. For scattering problems, this condition is given when the molecules are infinitely separated. If, for simplicity, we assume that there is rearrangement of the atoms during collision and only energy is transferred between the two molecules, then this boundary condition, for $R \rightarrow \infty$, is given by

$$\varphi_k \sim e^{ik_n z} \varphi_{a_n} \varphi_{B_n} + \frac{1}{R} \sum_m e^{ik_m R} \varphi_{A_m} \varphi_{B_m} f_{m,n}(\Theta,\Phi) \tag{18}$$

where the initially molecules A and B are in states A_n and B_n respectively. The wave number for the relative momentum of molecules is k_n. The second term in (18) describes the spherical waves emerging from the collision region. Function $f_{m,n}$ is also called the scattering amplitude and depends on the scattering angles Θ and Φ.

As we are, usually interested in the intensity of the wave packet (or probability distribution) far away from the collision region, we can replace φ in (16) by (18). We obtain two terms for ψ; one corresponds to the non- scattered wave packet [it is described by the first term in (18)] and the other is the scattered wave packet, which is given by

$$\Psi_{SC} = \frac{1}{R} \sum_m \varphi_{A_m} \varphi_{B_m} \int d^3 k\, e^{ik_m R - iEt/\hbar} f_{m,n} A(K) \tag{19}$$

from which it is easy to obtain the cross section in a particular state.

Integral (19) can be calculated by the method of the stationary phase, which applies to the integrals of a general form

$$I = \int dz\, F(z)\, e^{ig(z)} \tag{20}$$

We shall briefly review the main points of the method since they are essential for later discussion. According to the method, most of the contribution to integral (20) comes from around the vicinity of points z, for which $dg/dz = 0$. They are called stationary points of $g(z)$. We can write

$$\begin{aligned} g(z) &\approx g(z_j) + \frac{1}{2}(z - z_j)^2 g''(z_j) \\ F(z) &\approx F(z_j) \end{aligned} \tag{21}$$

in which case integral I is approximately

$$I = \sum_j e^{ig(z_j)} F(z_j) \int dz \; e^{\frac{i}{2} g''(z_j)(z - z_j)^2} \qquad (22)$$

Depending on the sign of $g''(z_j)$, the integration path is now rotated around each z, by $\pm\pi/4$ into the complex z plane. In this form, the integral can easily be evaluated and we obtain that most of the contribution comes from the interval $|\Delta z|_j < |g|^{-1/2}$.

The stationary phase method rests on several assumptions that limit its applicability. These assumptions are: a) the radius of convergence for the expansion of $g(z)$ around each stationary point should be much larger than $|\Delta z|_j$, b) no two stationary points should be close to each other, otherwise the next term in the expansion of $g(z)$ in (21) should be considered and c) within radius $|\Delta z|_j$ the function $F(z)$ should be analytic and nearly constant, and definitely not as rapidly varying as e^{ig}. If one of these three conditions are not fulfilled, the method cannot be applied, not even as an approximation.

We shall now evaluate integral (19) by formally applying the stationary phase method. If we assume that $A(k)$ is a slowly varying function of k (which is usually, though not necessarily always, the case) and if we write

$$f_{m,n} = \left| f_{m,n} \right| e^{i\delta_{m,n}} \qquad (23)$$

where $\delta_{m,n}$ is the phase of the scattering amplitude, then integral (19) is formally in the form (20). By applying the stationary phase method to (19), we obtain an equation that gives the time when a characteristic portion of the wave packet arrives at a point from the scattering region. If from this time we subtract the time the free wave packet travels the same distance, we obtain the time delay, given by[18,19]

$$\tau = \hbar \frac{d}{dE} \delta_{m,n} \qquad (24)$$

However, it should be recalled that this formula was derived formally, without taking into account the conditions under which the stationary phase method is applicable. One of the conditions says that the modulus of the scattering amplitude should not be a rapidly varying function of energy. Though in some cases (such as some elastic atom-atom collisions[20] this condition may be satisfied, this is not generally so[39], as it will be demonstrated in the case of resonances.

Mathematically, a resonance is associated with a complex energy eigenvalue of the Schrödinger equation, or equivalently with a complex energy pole of the scattering amplitude. Therefore, near a resonance, the scattering amplitude parametrizes as

$$f_{m,n} = \frac{b_{m,n}}{E - E_r} \qquad (25)$$

where E_r is a complex eigenenergy, $E_r = E_R - i\Gamma$. The imaginary part Γ is small and almost always positive (an exception to this rule was found in atom-surface scattering[40], and is a measure of the resonance width. Quantity $b_{m,n}$ is a complex function of energy and, for brevity, we shall call it the residue, though by definition a residue is constant.

If for the moment we assume that $b_{m,n}$ is constant, then the phase $\delta_{m,n}$ in (23) is

$$\delta_{m,n} = -\tan^{-1}\left(\frac{\Gamma}{E - E_R}\right) \tag{26}$$

and if (24) is formally applied, then the time delay for $E=E_R$ is $\tau=\hbar\Gamma^{-1}$. This result is a formal proof that at a resonance energy, the wave packet is delayed by τ, meaning that a long lived state is formed. However, the modulus of the scattering amplitude is

$$\left|f_{m,n}\right| \approx [\,(E - E_R)^2 + \Gamma^2\,]^{-1/2} \tag{27}$$

which is a rapidly varying function near $E=E_R$ and, therefore, the basic condition (c) in derivation of (24) is not satisfied. In fact the module (27) has a pole and a branch point in the vicinity of the stationary point.

In this example we have shown that a rapid change of the phase of the scattering amplitude is a necessary but not sufficient condition to ensure formation of a long lived state. Indeed, it has been confirmed numerically that the time delay in the presence of a resonance is not affected by Γ[41]. The time delay is only affected by the change of phase of the residue, which has been disregarded here. The true value of time delay is given by (24) but $\delta_{m,n}$ is now the phase of the residue.

We have demonstrated that it is a common feature of the scattering amplitude that its modulus is a rapidly changing function of energy. Therefore, the first step in a study of long lived states is to find a convenient parametrization of the scattering amplitude that would allow the use of the stationary phase method. The simplest parametrization is to represent $f_{m,n}$ as a sum

$$f = \sum_j f^{(j)} \tag{28}$$

where the indices m and n have been omitted for convenience. It is important to note that, though the sum extends over an unspecified number of indices j, relation (28) does not correspond to the partial wave decomposition of the scattering amplitude (in which j plays the role of angular momentum).

Resonances are always present in the system and, thus they are a source of rapid change of the modulus of the scattering amplitude. Each resonance affects all $f^{(j)}$ in (28) and, therefore, we must further parametrize the partial amplitudes $f^{(j)}$ in the form of (25). For a single resonance we write

$$f^{(j)} = \frac{b^{(j)}(E)}{E - E_R} \tag{29}$$

where now the modulus of $b^{(j)}$ is a non–rapidly varying function of E. As we have seen, the time delay is now entirely determined by the phase of b^j. For a large number of resonances, the parametrization is more complicated, but it will always be the phase of residue that determines the time delay and the properties of long lived states.

The aim of quantum theory is to find all $b^{(j)}$ in (28), if they exist, or to find another form of parametrization for f. This problem is still unsolved, but there have been various attempts to solve it. One is based on the concept of complex angular momentum[18,42] (called the Regge method), which parametrizes f in the forms of (28) and (29). The method has been quite successful in explaining the orbiting phenomenon in elastic collisions[43,44]. It can be extended to inelastic processes[15,45], but it still needs further testing. However, there is no reason to believe that this is the only method or, for that matter, the best suited one for parametrization.

A time delay τ, can be associated with each $f^{(j)}$ in (28) and they do not necessarily have the same value. In this respect, these amplitudes are analogous to classical trajectories. However, each partial amplitude represents a separate wave packet emerging from the interaction region and not a single trajectory. These wave packets arrive at different times and if we fix the wave front of the initial wave packet, then the same wave front after collision will appear as in Figure 5b. The thick regions in this figure correspond to the relative stability of the wave front and thin regions to its instability, *i.e.* two close points on the initial wave front are also close on the scattered wave front for the thick sections while for thin sections they are not.

There have been no quantum studies of long lived states, except in the case of elastic collisions of atoms. Resonances have been investigated, but, as we have seen, they cannot represent long lived states of the sort that are found in the classical studies. A partial list of systems for which resonances have been analyzed is given in Table II.

TABLE II

Systems for which resonances have been investigated

F + H_2[71]	H + FH73	F + HBr78
He + H_2^+ [72]	H + CO[78]	Ar + CH_4[79]
Cs + H_2[73]	H + H_2[76,77]	He + $Li_2(A^1\Sigma)$[37]

Again, a special case is the H + H_2. system. A rapid change of the phase of S-matrix was observed and was associated with a resonance. This, however, does not necessarily mean that a classical long lived state should be found. This can only happen if the phase of the »residue« changes rapidly, a fact that needs investigating.

5. CONCLUSION

Much theoretical research has been done into the properties of long lived states in molecular collisions, but very little using quantum theory, if we exclude the study of resonances[46-51].

As we have seen, resonances and long lived states are different phenomena[15]. Resonances are of interest for analyzing decaying states, like in predissociation and in those cases where they are observed in scattering experiments. The latter is quite a difficult task and resonances have been observed only in a few instances[52-55].

Other theoretical studies of long lived states have involved the classical theory. The amount of research in this field is considerable but the question that has not been addressed is what is the relevance of these results to the real (essential quantum) systems? We have shown that for long lived states in predominantly unstable systems the classical approach loses its meaning. One reason why this question has not been answered lies in the fact that very complex systems are usually investigated and quantum calculations are almost impossible for them. An exception is the famous $H+H_2$ »resonance«, investigated both classically and quantally[56].

Experiments on long lived states are difficult for several reasons. In order to see this, one should compare them to somewhat similar experiments in elementary particle physics. Long lived states in elementary particle physics are produced in collisions of stable particles (*e.g.* proton or electrons) and they are relatively easy to observe since they leave a visible trace in, say, a bubble chamber. Neutral particles, such as the neutron, are difficult to see but they can be observed indirectly, through their interactions. In molecular collisions, such experiments are not possible. Firstly, molecules are much larger than elementary particles, so that a gas, let alone liquid, cannot be used to observe the path of molecular long lived states. Secondly, the velocities of molecules are much smaller than those of elementary particles, so that during their lifetimes the latter travel much longer distances than as molecules. An elementary particle with a lifetime ca. 10^{-8} sec., which travels near the speed of light, leaves a trace 3 m. long. On the other hand, a long lived molecular state of the same lifetime would leave a trace only 10^{-5} m. long if it traveled at 1000 m sec^{-1}. These states are usually observed in an indirect way[57-61], or directly but only as decaying states (unimolecular processes)[62-64].

Research into the properties of long lived states is only in its infancy and many questions are as yet unanswered. Some of these questions are of a fundamental nature and concern the general theory of collisions. Some questions are more practical, such as calculations of chemical reaction rates, or at least understanding their orders of magnitude. In this respect, this contribution has aimed at highlighting some of the problems involving long lived states in collisions.

Acknowledgement. – The author wishes to thank Professor H. Kroto for many discussions concerning this article and general aspects of this subject.

REFERENCES

1. R. C. Weast, *Handbook of Chemistry and Physics* (Boca Raton: CRC Press) 1967. pg. F–142
2. P. W. Atkins, *Physical Chemistry* (Oxford: Oxford University Press) 1986.
3. K. J. Laidler, *Theories of Chemical Reaction Rates* (London: McGraw Hill) 1969. Ch. 3
4. P.Pechukas, *Dynamics of Molecular Collisions*, Ed. W. H. Miller (New York: Plenum) 1976.
5. M. S. Child, *Molecular Collision Theory* (New York: Academic) 1974.
6. R. N. Porter and L. M. Raff, *Dynamics of Molecular Collisions*, Ed. W. H. Miller (New York: Plenum) 1976.
7. W. L. Hase, *Potential Energy Surfaces and Dynamics Calculations*, Ed. D. G. Thrular (New York: Plenum) 1981.
8. P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (London: Wiley) 1972.
9. L. M. Raff and M. Karplus, *J. Chem. Phys.* **44** (1966) p.1212.
10. P. Brumer and M. Karplus, *Farad. Disc. Chem. Soc.* **55** (1973) 80.
11. J. W. Brady, J. D. Doll and D. L. Thompson, 1981. in Thrular, 1981. pg. 213,.
12. N. B. Slater, *Theory of Unimolecular Reactions* (Ithaca: Cornell University Press) 1959.
13. F. A. Lindemann, *Trans. Farad. Soc.* **17** (1922) 598.
14. J. R. Taylor, *Scattering Theory* (New York: Wiley) 1972.
15. S. D. Bosanac, *Long Lived States in Collisions* (Boca Raton: CRC Press) 1988.
16. D. Bohm, *Quantum Theory* (New York: Prentice Hall) 1952.
17. R. L. Jaffe, M. D. Pattengill, F. G. Mascarello and R. N. Zare, *J. Chem. Phys.* **86** (1987) 6150.

18. M. K. Osborn and I. W. M. Smith, *Chem. Phys.* **91** (1984) 13.
19. F. T. Smith, *Phys,. Rev.* **118** (1960) 349.
20. S. Bosanac, *Phys. Rev.* **A24** (1981) 777.
21. D. L. Bunker, *J. Chem. Phys.* **32** (1960) 1001.
22. C. Neyland, L. L. Poulsen and G. D. Billing, *J. Phys. Chem.* **88** (1984) 5858.
23. E. J. Heller, *J. Chem. Phys.* **62** (1975) 1544.
24. U. Buck, *Adv. Chem. Phys.* **30** (1975) 313.
25. W. H. Miller, *J. Chem. Phys.* **53** 1970) 3578.
26. J. N. Murrell and S. Bosanac, *Farad. Disc. Chem. Soc.* **55** 1973) 73.
27. C. Schlier and U. Vix, *Chem. Phys.* **95** (1985) 401.
28. J. Ford, *Fundamental Problems in Statistical Mechanics,* Ed. E. D. G. Cohen (Amsterdam: North-Holland) 1975.
29. J. W. Duff and P. Brumer, *J. Chem. Phys.* **67** (1977) 4898.
30. P. Brumer, *Adv. Chem. Phys.* **XLVII** (1981) 201.
31. J. M. G. Llorente and E. Pollack, *Chem. Phys. Lett.* **138** (1987) 125.
32. M. L. Koszykowski, D. W. Noid, M. Tabor and R. A. Marcus, *J. Chem. Phys.* **72** (1980) 6169.
33. J. M. Green, *J. Math. Phys.* **9** (1968) 760.
34. M. Tabor, *Adv. Chem. Phys.* **XLVI** (1981) 73.
35. P. Gaspard and S. A. Rice, *J. Chem. Phys.* **90** (1989) 2225.
36. H. J. Horsch and K. E. Thylwe, *J. Phys.* **B16** (1983) 793.
37. L. Cooper, *PhD thesis* University of Sussex, 1989.
38. S. D. Bosanac, *Phys. Rev.* **A32** (1985) 871.
39. S. D. Bosanac, *Phys. Rev.* **A30** (1984a) 153.
40. S. D. Bosanac, *Phys. Rev.* **A30** (1984b) 142.
41. S. D. Bosanac, – unpublished work.
42. S. Bosanac, *Mol. Phys.* **35** (1978) 1057.
43. S. Bosanac, *Phys. Rev.* **A19** (1979) 125.
44. S. Bosanac, *Phys. Rev.* **A28** (1983) 1344.
45. S. Bosanac, *J. Math. Phys.* **21** (1980) 1881.
46. D. A. Micha, *Acc. Chem. Res.* **6** (1973) 138.
47. J. R. Stine and R. A. Marcus, *Chem. Phys. Lett.* **29** (1974) 575.
48. E. Pollak and R. E. Wyatt, *J. Chem. Phys.* **81** (1984) 1801.
49. H. Ramanowski, K.-T. Lee, J. M. Bowman and Harding, *J. Chem. Phys.* **84** (1986) 4888.
50. S. K. Gray and S. A. Rice, *J. Chem. Phys.* **83** (1985) 2818.
51. M. Baer, *Adv. Chem. Phys.* **49** (1982) 191.
52. J. P. Toennies, W. Welz and G. Wolf, *J. Chem. Phys.* **71** (1979) 614.
53. A. Schutte, D. Bassi, F. Tommasini and G. Scoles, *J. Chem. Phys.* **62** (1975) 600.
54. K. A. Kohler, R. Feltgen and H. Pauly, *Phys. Rev.* **A125** (1975) 1407.
55. M. Konrad and F. Linder, *J. Phys.* **B15** (1982) L405.
56. E. Pollak and M. S. Child, *Chem. Phys.* **60** (1981) 23.
57. J. M. Parson and Y. T. Lee, *J. Chem. Phys.* **56** (1972) 4659.
58. J. M. Parson, K. Shobatake, Y. T. Lee and S. A. Rice, *J. Chem. Phys.* **59** (1973) 1402.
59. M. M. Oprysko, F. J. Aoiz, M. A. McMahan and R. B. Bernstein, *J. Chem. Phys.* **78** (1983) 3816.
60. M. S. Mehde, F. J. M. Al-Imarah and A. J. McCaffery, *Chem. Phys. Lett.* **96** (1983) 595.
61. F. J. Al-Imarah, A. J. Bain, M. S. Mehde and A. J. McCaffery, *J. Chem. Phys.* **82** (1985) 1298.
62. W. Begemann, K. H. Meiwes-Broer and H. D. Lutz, *Phys. Rev. Lett.* **21** (1986) 2248.
63. C. Schlier and U. Vix, *Chem. Phys.* **95** (1986) 401.
64. C. G. Schlier and U. Vix, *Chem. Phys.* **113** (1987) 211.
65. S. Bosanac, *Studies of Three-Atom Systems, PhD thesis,* University of Sussex, 1972.
66. P. A. Whitlock, J. T. Muckerman and P. M. Kroger, in Thrular 1981. pg. 5451.
67. Extensive discussion see in: G. D. Thrular *Potential Energy Surfaces and Dynamics Calculations* (New York: Plenum) 1981.
68. M. Berblinger, E. Pollak and C. Schlier, *J. Chem. Phys.* **88** (1988) 5643.
69. B. G. Sumpter, D. Thompson and D. W. Noid, *J. Chem. Phys.* **87** (1987) 1012.

70. H. K. Shin, *Chem. Phys. Lett. 156 (1989) 536.*
71. V. K. Babamov and A. Kuppermann, *J.Chem. Phys.* **77** (1982) 1891.
72. N. Sathyamurthy, M. Baer and T. Jospeh, *Chem. Phys.* **114** (1987) 73.
73. B. Lepetit, J. M. Launay, M. L. Dourneuf and F. X. Gadea, *Chem. Phys.* **117** (1987) 17.
74. J. M. Launay and B. Lepetit, *Chem. Phys. Lett.* **144** (1988) 346.
75. K.-T. Lee and J. M. Bowman, *J. Chem. Phys.* **85** (1986) 6225.
76. F. Webster and J. C. Light, *J. Chem. Phys.* **85** (1986) 4744.
77. M. Zhao, D. G. Thrular, D. J. Kouri, Y. Sun and D. W. Schwenke, *Chem. Phys. Lett.* **156** (1989) 281.
78. R. H. Bisseling, P. L. Gertitschke, R. Kosloff and J. Manz, *J. Chem. Phys.* **88** (1988) 6191.
79. L. N. Smith, D. J. Malik and D. Secrest, *J. Chem. Phys.* **71** (1979) 4502.

SAŽETAK

Dugo-živuća stanja u sudarima atom-molekula

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Razumijevanje procesa u molekulskim sudarima je od velike važnosti u mnogim područjima istraživanja. U kemiji i molekulskoj astrofizici veliko se zanimanje pokazuje za računanje brzine reakcije. Za elementarne čestice i nuklearnu fiziku od interesa je pronaći nova načela kojima se objašnjava mehanizme sudara. Za nekoga su molekulski sudari zanimljivi sami po sebi.

Najjednostavniji proces koji se najčešće istražuje jest dvojni sudar. Ako je taj susret kratak, govori se o direktnom sudaru, međutim, ako se tijekom susreta čestice zalijepe jedna za drugu, govorimo o sudaru koji je posredovan dugo-živućim stanjem.

Teorija sudara posredovana dugo-živućim stanjem vrlo je složena pa su dana samo neka temeljna načela u vrijeme najvećeg razvoja kvantne teorije. Među tim načelima središnje mjesto dano je rezonancijama. Međutim, kako je pokazano, teorija takovih sudara još je daleko od toga da bude završena, u stvari još je u začetku. Namjera je ovog članka dati pregled što je znano o tom području i gdje su problemi.