

## Simulation Chemical Reactions in Faddeev Approach

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### ABSTRACT

The main features of resonance in scattering are described and resonances are determined on the basis of the theory of collisions in a two-body system, as well as resonances emerging as a result of collisions in a few-body system. Regularities in the emergence of such resonances and their characteristics are analyzed. The results of calculations of these resonant processes occurring during collisions of electrons with diatomic molecules, made on the basis of the quantum theory of scattering in a few body system, based on Faddeev-Yakubovsky equations are discussed. The results of calculations of the resonant cross sections of electron and atom collisions with molecules are presented. Obtained results are compared with the available experimental data and with the results of calculations based on other approximations. In addition some biological applications (e.g. properties biopolymer molecules) are presented.

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### Introduction

Resonances offering a variety and peculiarities of physical patterns of phenomena exist in any branch of physics from molecular physics to elementary particle physics. The concept of resonance is one of fundamental concepts in quantum physics. We can attach a broad physical meaning to the term resonance, including stable levels and implying their effect on scattering processes [1, 2].

Resonances play a special role in the physics of irreversible processes. In this case, in accordance with the Poincare theorem, resonances are responsible for nonintegrability of most dynamic systems [3]. A theoretical explanation of resonances and their parameters can be constructed on the basis of forces of interaction between particles that are treated as elementary particles in such processes. For example, resonant processes in atomic physics are determined by the forces of interaction between electrons and nuclei, while resonances in nuclear physics are determined by forces acting between nucleons. A resonance in scattering is any peak on the experimental curve describing the scattering cross section. The resonance is characterized by the moment, parity, spin, lifetime, etc.

Collisions of electrons with molecules often result in the formation of metastable negative molecular ions, which are also traditionally referred to as molecular resonances [4-11]. In this case, since atoms move slowly as compared to electrons, the electron + molecule system can be regarded as a quasi-molecule whose electron shell at each instant corresponds to a quasistationary state of such a quasimolecule. This is in accordance with the well-known adiabatic approximation in quantum mechanics. In this approximation, various electron transitions (excitation, ionization, charge transfer) are hampered for collisions of electrons, atoms, or ions with

molecules under ordinary conditions. The necessary condition for such a charge transfer is  $\Delta E \Delta \tau \sim \hbar$ , where  $\Delta E$  is the change in the quasimolecule energy and  $\Delta \tau$  is the collision time. Thus, for slow collisions, when the value of  $\Delta \tau$  is large, transitions can occur only if  $\Delta E$  is small; i.e., two states of the quasimolecule before and after the collision must be close and such a process can also be treated as a resonant process. Such a treatment of a resonance reveals the relation between equilibrium and dynamics on the one hand and the physics of dissipative processes on the other hand [5,6,12].

The importance of resonant processes is determined by the fact that all practical applications of experimental studies are based on resonances since it is resonant processes that are characterized by large cross sections or long lifetimes as compared to nonresonant processes and play an important role in low-temperature plasmas (resonant processes determine the emergence and disappearance of excited and charged particles, i.e., determine optical and electrical properties of a plasma), in controlled thermonuclear synthesis, mu-catalysis, and so on [4-12].

Proceeding from the theory of collisions in a two-body system in which the target molecule is regarded as a force center, the following type of resonances can be distinguished [4-11].

1. A form resonance appears in the case when the impinging electron is trapped to a quasi-stationary level separated from the level in the continuum by a centrifugal barrier formed by a combination of attractive and repulsive fields of the target molecule. This type of resonance appears only when the electron possesses an angular momentum relative to the target molecule. In the case of low-energy *s* scattering ( $l = 0$ ), electron cannot be trapped and form resonance is absent.

2. A vibrationally excited resonance appears when the impinging electron excites vibrations of the target molecule and is temporally bound. In this case, the kinetic energy of the electron is directly transformed into the vibrational energy of motion of the nuclei of the negative molecular ion; thus, this type of resonance is associated with violation of the Born-Oppenheimer principle. The lifetimes of such resonant states are extremely long (especially for polyatomic molecules) and attain tens of microseconds.

3. An electron-excited resonance is formed when the projectile electron excites the electron system of the target molecule and also becomes temporally bound. In this case, the detachment of an electron is impossible as long as the molecule remains in the excited state. Nevertheless, an electron still may be detached if closed and open channels are coupled.

Theoretical description of such resonances appearing as a result of formation of negative metastable ions is presented in on the basis of the theory of scattering in a two-body system [5-11]. In these works, resonances are defined as complex poles of the scattering matrix  $1$  continued to the non-physical energy sheet or as poles of an analytic continuation of the Green function. Collisions between electrons and molecules occurring without the formation of intermediate complexes as well as collision processes at thermal energies of impinging electrons, in which a nonmonotonic energy dependence of scattering cross section is also observed, remain unstudied. In the latter case, the application of standard techniques for calculating cross sections is unjustified in view of violation of the Born-Oppenheimer approximation [4-9]. The application of the theory of collisions in a two-body system for calculating such processes encounters considerable difficulties since the system considered here is essentially a many-particle system [13, 14].

For this reason, we will describe resonant processes occurring during collisions of an electron and atoms with molecules by using a more consistent approach based on the quantum theory of scattering in a few-particle system [13, 14]. The main approximation in this case is that the interaction of the projectile electron or atom with the electrons and nuclei of the target molecule is replaced by the interaction of the electrons or atoms with the atoms of the molecule, the atoms being treated as force centers. Thus, a complex many-particle system consisting of the electron and the nuclei is replaced by a system of few interacting bodies, which can be described with the help of Faddeev equations [13]. Naturally, this approximation imposes certain constraints on the energy of the projectile electron: this energy should not be higher than that the ionization energy of the atoms constituting the molecule. However, it is precisely this energy range that is interesting in connection with the presence of resonance peaks in the effective cross sections of collisions of electrons with various molecules [4-11].

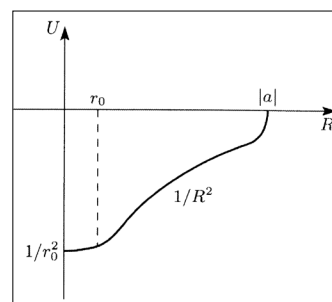
In such a formalism, a resonance in a three-particle system is determined by two particle resonances under certain conditions [1, 13, 14]. Thus, the reason for the emergence of three-particle resonances is the existence of resonant states in paired subsystems. This not very popular point of view is due to the fact that such a coupling does not exist always and cannot be determined explicitly even when it is present. This was demonstrated for the first time in nuclear physics and in elementary particle physics where the interaction between particles leading to the existence of resonances is determined by the exchange between the particles of the same resonances; thus, resonances produce themselves [1, 2].

In atomic physics, coupling between resonances is observed for a large number of phenomena (such as scattering of electrons by molecules, coupling between clusters in biopolymer molecules, and in Bose condensate) [4-7, 14, 15]. In this type of coupling, two-particle resonances lead to a series of three-particle resonance. A peculiar feature of this phenomenon is that the stronger the two-particle resonance, the larger the number of three-particle resonances produced by it. Experiments show [1, 14, 15] that such resonant states in many-particle systems lead to anomalously high rates of chemical reactions, dynamic coupling of noninteracting particles, etc. [14-16]. The importance of studying such states is directly associated with determining the binding energy of a system of  $N$  bodies using information on subsystems of this many-particle system, i.e., the construction of dependences  $E_N = f(E_{N-1}, E_{N-2}, \dots)$  and the determination of the conditions for the formation of a coupled many-particle system provided that some subsystems are not coupled [16].

The physical foundation of the effect considered here is presented in, where the following aspects are revealed [1].

1. The effect of two-particle resonances on the spectrum of a three-particle system is clearly manifested; i.e., a two-particle resonance can radically reconstruct the discrete spectrum of three particles. However, not every two-particle resonant state can reconstruct the spectrum of three particles, but only the state whose size  $r_{res} \sim (2m_{ij}|e_0|)^{1/2}$  is much larger than the range  $r_0$  of its action ( $e_0$  is the binding energy and  $m_{ij}$  is the reduced mass of a pair of particles). Such a resonance can only be an  $s$  resonance ( $l = 0$ ) since such resonant states strongly differ in size from other types of resonant states. For  $e_0 \rightarrow 0$ , size  $r_{res} \rightarrow \infty$ . The size of a resonant state is manifested in the scattering of particles in the form of a large scattering length  $a$ , which is equal to the size of this resonant state for small  $e_0$ . Analyzing resonant states from the standpoint of their size, we can observe that all these states sharply differ from the resonance considered above. For example, the state occupied by the system in a partial wave with  $l \neq 0$  has a size on the order of the range of forces due to the centrifugal barrier; a compound resonance is not large either. Thus, a two-particle  $s$  level with a small binding energy occupies an exceptional position among resonant states as regards its size.

2. Three-particle levels are stable and their number is proportional to  $\ln(a/r)$ . It can be proved that the interaction responsible for the emergence of these levels has the form  $U \sim A/R^2$  where  $R^2 = 2/3(r_1^2 + r_2^2 + r_3^2)$ ,  $r_i$  is the distance between a pair of particle, and is operative in the interval  $(r_0, a)$  (Figure 1) [1, 13-15].



**Figure 1:** Effective potential responsible for resonances in a three-body system

In the general case, the constant  $A$  of this interaction is a function of quantum numbers of the three-particle state, angular momentum,

parity, and symmetry relative to the transposition of the particles. The value of  $A$  is estimated in [1,14, 15]. The strongest attraction should be observed for the orbital angular momentum  $L = 0$  for three particles since centrifugal forces are absent in this case. The symmetry of this state must be maximal; otherwise, the wave function has nodes and the coupling becomes weaker.

3. Centrifugal forces suppress the effect.
4. Such states possess the maximal symmetry.
5. Triple and many particles forces do not influence on the effect.
6. The addition of a particle to the three-particle system suppresses the effect.
7. The particle charge has no influence on the effect which is manifested less clearly in this case.

8. For particles with spins, the effect is also pronounced less clearly. It should be noted that such peculiar states of three particles are independent of the specific form of the potential (i.e., independent of the forces of interaction between particles) and are universal in the sense that these states reflect only the fact of existence of a resonance. Thus, irrespective of the form of pair forces between the particles, if it leads to a low-energy two-particle resonance, this automatically leads to the formation of a family of three-particle resonances. Consequently, the reason for the emergence of three-particle level lies in the production of long-range interaction between three particles by a two-particle resonance with a large spatial size. Thus, the number of resonant states in a three-particle system is determined only by specific properties of paired subsystems. The masses of the particles have the strongest influence on the effect. The following three characteristic regimes can be singled out: the mode of identical particles, the mode of a heavy center, and the molecular mode [1, 13-15]. The heavy-center mode takes place when the masses of two particles are of the same order  $m_l$ , while the mass  $m_h$  of the third particle is much larger. The pair of light particle has no energy level and these particles do not interact with each other, but interact with the heavy particle through the attracting potential. In this case, if the mass of the third particle is infinitely large, we are dealing with the case of a pair of particles in a force center; naturally, three-particle levels do not emerge in such a system. In this case, the heavy particle does not respond to the motion of the noninteracting particles moving independently from each other in the field of the stationary heavy particle. Consequently, in this limit, the binding energy of the three particles is the additive sum of the binding energies of two-particle systems. However, for a finite mass of the heavy particle, the motion of all the three particles is correlated, so that the center of mass of the system remains at rest. In this case, the heavy particle responds to a change in the position of other particles whose motion becomes correlated in spite of the absence of a direct interaction between them. Thus, dynamic correlation in the motion of coupled particles can be treated as a sort of attraction. It should be noted that such a dynamic attraction also appears in the case when repulsive force act between the particles coupled in this way. In this case, dynamic attraction compensates mutual repulsion and leads to stabilization of the system. This can be clearly seen, for example, for the ion of positronium  $e^+e^-$  [14-16]. In this case, for any finite mass of a heavy center, the number of levels is

$$N \sim \frac{m_l}{m_h} \ln \frac{1}{e_0 m_l r_0^2}$$

A special feature of this mode is that extremely shallow levels in paired subsystem are required for the existence of three-particle levels in contrast to the molecular mode, where the requirements imposed on paired levels are much less stringent and more realistic. In the molecular mode, when a light particle has shallow levels in the interaction

with the heavy particles, the number of levels is

$$N \sim \sqrt{\left(\frac{m_l}{m_h}\right)} \ln \frac{1}{|e_0| m_l r_0^2}$$

and the potential of the interaction produced by the light particle has the form

$$V \sim \frac{-0.32}{m_l r_{hh}^2},$$

which is precisely the energy of the molecular energy level. The simple example of this mode is a system consisting of an electron and two neutral atoms. The molecule formed in this way differs from a conventional molecule in that its nuclei vibrate in region  $R$  whose size is determined by the energy  $e_0$  of the shallow paired level; in addition to vibrational levels, this system also has a rotational spectrum. Thus, two-particle levels in this mode lead to the formation of a series of not only vibrational, but also rotational levels [1, 13-15]. It should be noted that such peculiar resonance states are manifested in a wide range of conditions and form a stable phenomenon which can be reliably identified and confirmed experimentally.

### Basic Equations and Main Approximation

We will analyze these peculiar resonant states quantitatively in the case of the molecular mode using the Faddeev integral equations [13]. In the given approximation (three particles, viz., two atoms and an electron), these equations are formulated for three parts into which the total wave function of the three-body system splits,

$$\Psi = \sum_{i=1}^3 \Psi_i,$$

Each part corresponds to possible divisions of the system of three particles into noninteracting subgroups. In the momentum space, in the case of scattering of particle 1 from the coupled pair (2,3) the equations have the form [13,14]

$$\Psi_i = \Phi_i \delta_{i1} - G_0(Z) T_i (\Psi_j + \Psi_k), \quad i, j, k = 1, 2, 3; 3, 1, 2; 2, 1, 3; \quad (1)$$

Here,  $\Phi_1$  describes the initial state of the three body systems: free motion particle 1 and the bound state of pair (2,3);  $G_0(Z) = (H_0 - Z)^{-1}$ ,  $Z = E + i0$ , where  $H_0$  is the operator of free motion of three particles;  $E$  is the total energy of three-body system, which is equal to the sum of kinetic energy of projectile 1 and the binding energy of pair (2,3);  $T_i$  is a paired T-matrix that can be unambiguously defined in terms of the paired interaction potential  $V_i$  with the help of the Lippmann-Schwinger equations

$$T_i = V_i + V_i G_i T_i, \quad G_i = (h_i - Z_i)^{-1}, \quad h_i = \Delta_i + V_i \quad (2)$$



To describe the motion of three particles in center-of-mass system we use the generally accepted Jacobi coordinates. It should be borne in mind that we must use as integration variables in Eq. (1) a certain system of variables which is found to be most convenient. For example, in the integral corresponding to the expression  $G_0 T_1 \Psi_2$ , it is more convenient to take  $\vec{k}_2$  and  $\vec{p}_2$  as integration variables. In this case, variables  $\vec{k}_1$  and  $\vec{k}_2$  determining the kernel of operator  $T_1$  should be expressed in terms of variables  $\vec{p}_1$  and  $\vec{p}_2$ . Sometimes, it is more convenient to use variables  $\vec{p}_1$  and  $\vec{p}_2$  in the same situation.

Paired  $T$  matrices  $t_i(\vec{k}_i, k'_i; Z)$  appearing in the kernels of the equations have singularities in variable  $Z$ : the poles corresponding to the discrete spectrum of paired subsystems and a cut along the positive part of the real axis generated by the spectrum of the two-body problem. The explicit form of these singularities gives the spectral representation of matrix  $T$ . The poles of the  $T$  matrix corresponding to the discrete spectrum generate singularities in the wave function components  $\Psi_i$ ; separating these components, we obtain the representation

$$\Psi_i(\vec{k}_i, \vec{p}_i; \vec{p}'_i) = \varphi(\vec{k}_i) \delta(\vec{p}_i - \vec{p}'_i) - B_i(\vec{k}_i, \vec{p}_i; \vec{p}'_i; Z) / (p_i^2/2n_i + k_i^2/2m_{jk} - Z), \tag{3}$$

where

$$B_i(\vec{k}_i, \vec{p}_i; \vec{p}'_i; Z) = - \sum_{j=1}^3 [Q_j(\vec{k}_i, \vec{p}_i; \vec{p}'_i; Z) - \varphi_j(\vec{p}_j) R_{ji}(\vec{k}_j; \vec{p}'_j; Z) / (p_j^2/2n_j - \kappa_j - Z)],$$

and  $Q_j, R_{ji}$  are smooth function of their variables. Such a division of singularities appears automatically in the numerical solution of integral equations. To define functions  $Q_j$  and  $R_{ji}$  unambiguously, we can proceed as follows. We substitute  $\Psi_i$  in form (3) into initial equations (1) and equate the coefficients of identical singularities. This gives the equations for these functions which can be used for expressing explicitly all main characteristics of the three-body problem: wave function, elements of the  $S$  matrix, as well as the amplitudes and cross sections of all processes occurring in the three-body system.

$$1 + (2, 3) \rightarrow \begin{cases} 1 + (2, 3) \text{ -elastic scattering processes} \\ 1 + (2, 3)^* \text{ -excitation processes} \\ 3 + (1, 2)^* \text{ -rearrangement processes} \\ 2 + (1, 3)^* \text{ with excitation} \\ 1 + 2 + 3 \text{ -ionization processes} \end{cases}$$

Thus, the cross section of the elastic scattering process has the form

$$d\sigma_{11}/d\Theta = (2\pi)^4 n_1 |R_{11}|^2,$$

the cross section of rearrangement processes is given by

$$d\sigma_{1i}/d\Theta = (2\pi)^4 n_i p_f |R_{1i}|^2 / p_1^0$$

$$d\sigma_{1 \rightarrow 3}/d\Theta dp = (2\pi)^4 n_i p_f |B_{0i}|^2 / p_1^0,$$

where

$$p_f^2 = 2n_i(p_i^{02}/2n_i - \kappa_1^2 - \kappa_i^2)$$

The main advantage of the Faddeev equations (1) is that

(i) the solution of this equation gives simultaneously the amplitudes and crosssections of all processes occurring in the three-particle system;

(ii) the accuracy in determining the bound state from the solution of the Faddeev equations is much higher than the accuracy obtained by solving the Schrodinger equations (this peculiarity is associated with the fact that Eqs. (1) were formulated for the wave function components and, hence, take into account possible asymptotic

forms of the three-particle system);

(iii) these equations make it possible to carry out a correct (from the standpoint of mathematics) analysis of scattering processes, in which all three free particles are in the initial state this is impossible in all approaches proposed earlier [5-13]:

$$1 + 2 + 3 \rightarrow \begin{cases} 1 + (2, 3) \text{ -elastic scattering processes} \\ 1 + (2, 3)^* \text{ -excitation processes} \\ 3 + (1, 2)^* \text{ -rearrangement processes} \\ 2 + (1, 3)^* \text{ with excitation} \\ 1 + 2 + 3 \text{ -ionization processes} \end{cases}$$

In this case, we have the following representation for the wave function [13-15]:

$$\Psi_0(\vec{k}, \vec{p}; \vec{k}^0, \vec{p}^0) = \delta(\vec{k} - \vec{k}^0) \delta(\vec{p} - \vec{p}^0) - \frac{\sum_{i,j} M_{ij}(\vec{k}, \vec{p}; \vec{k}^0, \vec{p}^0, \frac{k^{02}}{2m} + \frac{p^{02}}{2n} + i0)}{\frac{p^2}{2n} + \frac{k^2}{2m} - \frac{k^{02}}{2m} + \frac{p^{02}}{2n} + i0},$$

where functions  $M_{ij}$  satisfy the following system of equations:

$$M_{ij}(Z) = \delta_{ij} T_i(Z) + T_i(Z) G_0(Z) \sum_{k \neq i} M_{kj}(Z)$$

For cross sections of these processes, we obtain the following expression [13,15]

$$S_{00}(\vec{k}, \vec{p}; \vec{k}', \vec{p}') = \delta(\vec{k} - \vec{k}') \delta(\vec{p} - \vec{p}') - 2\pi i \delta(\frac{p^2}{2n} + \frac{k^2}{2m} - \frac{p'^2}{2n} - \frac{k'^2}{2m} - i0) - \sum_{i,j} M_{ij}(\vec{k}, \vec{p}; \vec{k}', \vec{p}'; \frac{k'^2}{2m} + \frac{p'^2}{2n} + i0);$$

corresponds to processes in which three free particles are in the initial and final states,

$$S_{0s}(\vec{k}, \vec{p}; \vec{p}'_i) = 2\pi i \delta(\frac{p^2}{2n} + \frac{k^2}{2m} + \kappa_{s_i}^2 - \frac{p_i'^2}{2n_i}) \sum_k Q_{ki}^s(\vec{k}, \vec{p}; \vec{p}'_i; -\kappa_{s_i}^2 + \frac{p_i'^2}{2n_i} - i0) + \sum_{s_k} \psi_{s_k}(\vec{k}_k) R_{ki}^{s_k s_i}(\vec{p}; \vec{p}'_i; -\kappa_{s_i}^2 + \frac{p_i'^2}{2n_i} + i0),$$

$$S_{s_i 0}(\vec{p}_i; \vec{k}', \vec{p}') = 2\pi i \delta(-\kappa_{s_i}^2 + \frac{p_i'^2}{2n_i} - \frac{p'^2}{2n} - \frac{k'^2}{2m}) \sum_j \tilde{Q}_{ji}^{s_i}(\vec{p}_i; \vec{k}', \vec{p}'; \frac{k'^2}{2m} + \frac{p'^2}{2n} + i0) + \sum_{s_j} \psi_{s_j}(\vec{k}_j) R_{ij}^{s_i s_j}(\vec{p}_i; \vec{p}'_i; \frac{k'^2}{2m} + \frac{p'^2}{2n} + i0),$$

correspond to processes in which a coupled pair of particles  $s_j$  is present in the initial or the final state. The equations for functions  $Q_j, Q_j^s$  and  $R_{ij}$  are analogous to the equations for  $M_{ij}$  and are given in [13-15]. It should be noted that potentials do not appear explicitly in integral equations (1); these equations contain a more general characteristic, viz.,  $T$  matrices, which are connected with the potentials of the Lippmann-Schwinger equations (2). Consequently, although potentials are formally used in the given method, we essentially model  $T$  matrices, which are constructed on the basis of the Bateman method suitable for any local potential. This method considerably simplifies numerical solution of the system of integral equations (1) and sometimes even leads an analytic solution [13-17].

Integral equations (1) possess good properties (from the mathematical point of view) such as the Fredholm property and unambiguous solvability only under certain conditions imposed on two-particle data [13]:

(i) paired potentials  $V_i(\sim \vec{k}, \sim \vec{k}')$ , which are nonlocal in the general case, are smooth functions of  $\vec{k}, \vec{k}'$  and satisfy the condition

$$|V_i(\vec{k}, \vec{k}')| \leq (1 - |\vec{k} - \vec{k}'|)^{1-\epsilon}, \quad \epsilon > 0;$$

(ii) point  $Z = 0$  is not a singular point for Eqs. (2); i.e., all three scattering lengths in pair channels are finite;

(iii) the positive two-particle spectrum is continuous. This condition is essential for nonlocal potentials since positive eigenvalues may appear only in this case, and this condition is satisfied virtually for all physical processes.

Coulomb potentials and hard-core potentials do not satisfy the first condition:

Coulomb potentials lead to a singularity of the type  $|\vec{k} - \vec{k}'|^{-2}$  in  $T$  matrices, while hard-core potentials result in a slow decrease in the  $T$  matrix for large momenta. When the second condition is violated, the Fredholm property of Eqs. (1) is lost for  $Z = 0$ , which leads to the above-mentioned effect of emergence of an infinitely large discrete spectrum in a three-body system under certain conditions. A similar situation emerges in the case of scattering of electrons from diatomic molecules, for which the Efimov levels were experimentally observed for the first time. The approximation considered here reproduces these experimental results in a quite natural way.

It should be emphasized once again that the given approximation appears quite reasonable for values of the impinging electron energy lower than the electron excitation energy of the molecule. As the initial data in such a formulation of the problem, we use pair interaction potentials, masses, and energies of colliding particles.

Numerical solution of integral equations (1) involves considerable difficulties because the kernels of integral equations (1) contain the same singularities but here, we propose a quite universal method for solving system of equations (1) for calculating bound states as well as scattering states in systems with arbitrary masses, which interact via arbitrary pair short-lived potentials that can also be defined numerically [13-15]. In the method proposed here, the domain of an unknown function is divided into a number of intervals on each of which the function is approximated with the help of corresponding interpolation polynomials. The method for solving system of equations (1) is a modification of the standard method for solving integral equations, in which the integral on the right-hand side is replaced with the help of a quadratures formula for solving Eq. (1). As a result, we arrive at a system of algebraic equations for values of the sought function at the nodes of the quadratures formula. In the proposed method, the domain of the sought function is divided into a number of segments, on each of which the function is determined with the help of interpolation polynomials reproducing the correct behavior of the function in the vicinity of the above singularities, after which integration is carried out using quadratures formulas. A package of applied programs was used for realization of the proposed numerical method for solving system of integral equations (1)[13,15].

Computational difficulties encountered in calculation of cross sections in the given approximation are mainly associated with the long-range Coulomb interaction potentials. It was mentioned above that in this case the integral Faddeev equations cannot be applied directly; either these equations should be modified, or the differential formulation of the Faddeev equations in the coordinate state should be used [13-15]. In case for three charged particles Faddeev equation in the coordinate space, which have the form [13-15].

$$(-\Delta_{x_i} - \Delta_{y_i} + V_i(x_i) - E)\Psi_i = -V_i \sum_{j \neq i} \Psi_j, \quad (6)$$

where

$$V_i = n_i/x_i + V_{st}(x_i), \quad n_i = \frac{q_k q_j}{\sqrt{2m_{kj}}},$$

$$\vec{x}_i = \sqrt{\frac{2m_j m_k}{m_j + m_k}}(\vec{r}_j - \vec{r}_k), \quad \vec{y}_i = \sqrt{\frac{2m_i(m_j + m_k)}{m_i + m_j + m_k}}\vec{r}_i - \frac{m_j \vec{r}_j + m_k \vec{r}_k}{m_j + m_k},$$

and the coordinates are connected via the relations

$$\vec{x}_i = c_{ij}\vec{x}_j + s_{ij}\vec{y}_j, \quad \vec{y}_i = -s_{ij}\vec{x}_j + c_{ij}\vec{y}_j,$$

$$s_{ij}^2 = \frac{m_k \sum_k m_k}{(m_i + m_j)(m_j + m_k)}, \quad s_{ij}^2 + c_{ij}^2 = 1$$

$V_{st}$  being pair short-range interaction potentials. The relation between the momentum and coordinate representations is defined by the Fourier transformation,

$$\Psi(\vec{k}_i, \vec{p}_i) = (2\pi)^{-3} \int \exp -i(\vec{k}_i \vec{x}_i + \vec{p}_i \vec{y}_i) \Psi(\vec{x}_i, \vec{y}_i) d\vec{x}_i d\vec{y}_i$$

To obtain a unique solution of integrodifferential equations in the coordinate space, we must add the boundary conditions, which have the form [13-15]

$$\Psi_i(\vec{x}_i, \vec{y}_i)_{x_i, y_i \rightarrow 0} \rightarrow 0,$$

$$\Psi_i(\vec{x}_i, \vec{y}_i)_{\rho = \sqrt{x^2 + y^2} \rightarrow \infty} \rightarrow \phi_i(x_i) \exp(i\vec{k}_i \vec{y}_i - iw_i^0) + \sum_j A_{ij}(\vec{y}_j, \hat{k}_i) \phi_i(x_j) \frac{\exp(i_j |\vec{y}_j| + iw_{ij})}{|y_j|} + A_{0i}(\hat{X}, \hat{k}_i) \frac{\exp(i\sqrt{E}|X| + iw_0)}{|X|^{5/2}}, \quad (8)$$

where

$$w_i^0 = \frac{n_i}{2|k_i|} \ln[|\hat{k}_i| |\hat{x}_i| - (k_i, x_i)], \quad w_{ij} = \sum_{k \neq j} \frac{n_k}{2|s_{jk} \sqrt{E_k}} \ln 2\sqrt{E_k} |\vec{y}_k|,$$

$$w_0 = -\frac{|X|}{2\sqrt{E}} \sum_i \frac{n_i}{|\vec{x}_i|} \ln 2\sqrt{E} |\vec{X}|, \quad n_i = \frac{k_i q_i q_j}{\sqrt{2m_{ij}}}, \quad E_k = E - \kappa_j,$$

A large number of various numerical methods have been developed on the basis of approximation of components  $\Psi$  by bicubic Hermite splines, quintet basis splines, etc. However, an effective, reliable, and universal algorithm of numerical solution of Eqs. (6) with boundary conditions (7) and (8) in the coordinate space has not been developed for the following reasons.

First, an algorithm of numerical solution for processes with three free particles in the initial and final states does not exist in view of rather complex boundary conditions.

Second, point-by-point convergence of the obtained result to the exact solution upon a decrease in the mesh size cannot be proved analytically in any of the known numerical methods based on finite different approximation.

Consequently, the application of the mesh method in the polar coordinate system for solving numerically the system of coupled integrodifferential equations (6) in partial derivatives with boundary conditions (7) and (8) appears as most justified since analytic solutions also exist in this case for some potentials determining the resonant states under investigation [13,14,18]. This makes it possible to monitor the accuracy of the solutions obtained by the numerical method.

Let us consider the geometrical (topological, spatial) characteristics of the above-mentioned peculiar resonant states. Since it is quite difficult to study these characteristics experimentally in the case of electron collisions with molecules, we will consider the systems that are accessible for experimental studies, viz., clusters of molecules of inert gases [19].

It should be noted that these molecular clusters consisting of atoms of helium, lithium, and a number of inert gases attract attention of both theoreticians and experimentalists primarily due to applied studies such as superfluidity, superconductivity, Bose condensation, chemistry and physics of clusters, laser physics (i.e., the possibility of developing molecular laser), as well as the possibility of observing such a peculiar quantum effect in real systems [19, 20].

However, a direct theoretical analysis of even the simplest of the above systems, viz.,  $He_3$  consisting of three helium nuclei and six electrons, is an extremely complicated problem. To analyze the  $He_3$  system, we consider the cluster approximation in which this system is replaced by a simpler system consisting of three force centers (helium atoms). The validity of this approximation for calculations of bound states is obvious since the difference between the binding energy of the system and the ionization energy of the atom is several orders of magnitude. It is well known that helium atoms are bosons; consequently, the problem boils down to analysis of three pairwise identical neutral spinless particles. To solve this problem, we propose mathematically correct model-free methods in the theory of scattering in the three-body system [13-15].

It should be emphasized that virtual levels in paired subsystems in the case of complex many-particle systems do not lead to the emergence of resonant states in a many-particle system [1]. This, however, does not mean that this effect is absent in these systems since it can be due to many-particle and not two-particle virtual states.

For this reason, we will consider the interpretation of a number of peculiar properties of systems  $He_3$ ,  $Ar_3$ ,  $Kr_3$ ,  $Ne_3$ ,  $Xe_3$ ,  $Li_3$ , and  $Rn_3$  precisely on the basis of the three-particle approximation. It should be noted that a large number of theoretical and experimental methods exist for studying clusters consisting of atoms of helium and a number of inert gases. Most methods are intended for studying bound states; however, scattering states, which are most informative for confirming the existence of peculiar resonant states, were practically ignored [19-22].

It was stated by a number of authors that the main difficulties in studying the  $He_3$  system are associated with its low binding energy (1 mK), an unusually large size of the excited state ( $\sim 150A^0$ ), and a strong repulsion at small distances. However, the results obtained in, where an analogous three-particle approximation was used for calculating the  $He_3$  system, differ from the statements made in [15,21,22].

For this reason, it would be also interesting to verify the conclusions drawn in on the basis of the three-particle approximation with the short-range pair potentials used in [23]. The main purposes of this investigation are

- (i) determining the number of possible resonant states;
- (ii) clarifying the role of pair interaction potentials in the characteristics of these states;
- (iii) estimating the effect of repulsion at short distances, which can be approximated by a hard core in the model for the boundary conditions imposed on the characteristics of these peculiar states [13-15].

Thus, the theoretical analysis of the  $He_3$  system is reduced to solving equations in the quantum theory of scattering in a three-body system, which makes it possible to use the well-known methods [13-15]. In contrast to, where resonances in a three-particle system were studied using the Faddeev equations on the basis of analytic continuation of the scattering matrix to the range of complex energy values, we are using here direct numerical solution without an analytic continuation [21].

In this case, after the separation of angular variables, the Faddeev equations (6) in the coordinate space for the  $He_3$  system in the three-particle approximation with pair short-range potentials have the form [13-15, 23]

$$[H_{\lambda,l} - z]\Psi_{aL}(x, y) = -V(x)(\Psi_{aL}(x, y) + \sum_{a'} \int_{-1}^{+1} \Psi_{a'L}(x', y') h_{aa'}^L(x', y', \eta) d\eta), \quad (9)$$

Where

$$H_{\lambda,l} = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + \frac{l(l+1)}{x^2} + \frac{\lambda(\lambda+1)}{y^2}$$

$$z = E + i0, \quad L = l + \lambda, \quad a = (l, \lambda),$$

For calculations with a hard core in the model of boundary conditions, the righthand side is equal to zero for  $x < c$ , where  $c$  is the core size. To obtain an unambiguous solution to the equations, we must preset boundary conditions (7), (8),

$$\Psi_{aL}(x, y) |_{x=0} = 0, \quad \Psi_{aL}(x, y) |_{x=0} = 0, \quad (10)$$

which assume the following form in the boundary-condition model:

$$\Psi_{aL}(c, y) + \sum_{a'} \int_{-1}^{+1} \Psi_{a'L}(x', y') h_{aa'}^L(x', y', \eta) d\eta = 0$$

$$x' = \sqrt{x^2/4 + 3y^2/4 - \sqrt{3}xy\eta/2}, \quad y' = \sqrt{3x^2/4 + y^2/4 + \sqrt{3}xy\eta/2},$$

For  $\rho \rightarrow \infty$  the boundary conditions in the case of short-range pair potentials can be written in the form [13]

$$\Psi_{aL} \sim_{\rho \rightarrow \infty} a_{aL,v} \sum_v \psi_{l,v}(x) H_v(\sqrt{E - E_{2,l,v}}) + A_{aL}(\theta) \frac{e^{x\rho i \sqrt{E}\rho + i\pi L/2}}{\sqrt{\rho}} \quad (11)$$

where  $\psi_{l,v}(x)$  are the partial components of the wave functions of paired subsystems with binding energy

$\epsilon_{l,v}$ ;  $\rho = \sqrt{x^2 + y^2}$ ;  $\theta = \arctan y/x$ ;  $a_{aL,v}$  and  $A_{aL}(\theta)$  are the scattering amplitudes of processes with two or three particles, respectively, in the final state; and  $H_v(x)$  are the Hankel spherical functions.



In calculations of bound states, the wave functions decrease quite rapidly at infinity; consequently, at a large distance  $x = Rx$ ,  $y = Ry$ , the asymptotic boundary conditions can be replaced by the conditions

$$\frac{\partial_x \Psi_{aL} |_{x=R_x}}{\Psi_{aL} |_{x=R_x}} = i\sqrt{\epsilon_v}$$

$$\frac{\partial_y \Psi_{aL} |_{y=R_y}}{\Psi_{aL} |_{y=R_y}} = i\sqrt{\epsilon_v - E}$$

For the  $He_3$  system in the three-particle approximation with angular momentum  $L = 0$ , we have

$$H_{\lambda,l} = H_{0,l} = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + l(l+1)(1/x^2 + 1/y^2),$$

where partial components  $l$  assume even values.  $l = 0, 2, 4, \dots$ ; and

the expression for functions  $h_{aa'}^L(x, y, \eta)$  is given in [13-15].

The asymptotic behavior of the components of Eqs. (9) for scattering processes with short-range potentials can be described by the function [13-15].

$$\Psi_l(x, y, z) = \delta_{l0} \psi_d(x) [\sin(\sqrt{z - \epsilon_d} y) + \exp(i\sqrt{z - \epsilon_d} y) [a_0(z) + o(y^{-1/2})]]$$

$$+ \frac{\exp(i\sqrt{z}\rho)}{\sqrt{\rho}} [A_l(z, \theta) + o(\rho^{-1/2})], \quad (12)$$

where  $a_0(z)$ ,  $z = E + i0$  is the elastic scattering amplitude for  $E > \epsilon_d$ , and  $A_l(E, \theta)$  is the decay amplitude for  $E > 0$ .

We also assume that the helium molecule  $He_2$  has only one bound state with binding energy  $\epsilon^d < 0$  and with the corresponding wave function  $\psi_d(x)$ .

For processes of scattering, the scattering matrix for  $z = E + i0$ ,  $E > \epsilon^d$ , the scattering phases and lengths in the  $s$  state can be expressed with help of the following formulas

$$S_0(z) = 1 + 2ia_0(z),$$

$$\delta_0(p) = \frac{1}{2} \text{Im} \ln S_0(\epsilon_d + p^2 + i0), \quad p > 0,$$

$$L_{sl} = -\sqrt{3}/2 \lim_{p \rightarrow 0} a_0(p)/p$$

To solve the system of equations (9) with boundary conditions (10), (12) numerically, we used the standard method described in detail in [13-15, 17].

### Results of Calculations

We will analyze these peculiar resonant states quantitatively using the Faddeev equations (1-12) in different systems.

For pair interaction potentials, we used potentials HFDHE2, HFD-B, HFDID, LM2M1, LM2M2, and TTYPT with appropriate parameters, which reproduce in detail the main parameters of the corresponding molecules [23,24].

The results of calculation of the energy of bound states in systems  $He_3$ ,  $He_3^*$ ,  $He_3$  and  $He_3^*$  with and without taking into account the hard core are given in [14-17].

The results of calculation of the ground and the first excited states systems  $Ne_3$ ,  $Ar_3$ ,  $Kr_3$ ,  $Xe_3$  and  $Rn_3$  in the given approximation with the HFD-B potential and the parameters borrowed from are presented in Tables 1,2 [32].

**Table 1: Binding energies of inert gas molecules calculated by using HFD-B potential, a.u.  $10^{-6}$**

Energy	$Ne_2$	$Ar_2$	$Kr_2$	$Xe_2$	$Rn_2$
$E_{thr}$	178	394	619	854	9268
$E_{exp}$	135	446	629	874	-

**Table 2: Binding energies of the ground state and the first excited state of the inert gas molecules calculated by using HFD-B potential**

$Ne_3$	$Ne_3^*$	$Ar_3$	$Ar_3^*$	$Kr_3$	$Kr_3^*$	$Xe_3$	$Xe_3^*$	$Rn_3$	$Rn_3^*$
398	330	1278	1215	1885	1811	2509	2438	30875	30801

In calculations based on the boundary-condition model, the value of core  $c$  was chosen so that even a slight change in this quantity did not affect the binding energy of paired subsystems. In our calculations,  $c = 1.5A^0$ , the value of binding energy for the helium molecule was 1.69 mK, and the value of  $r_0$  was  $100A^0$ . A detailed description of the numerical method for solving system of equations (9) with asymptotic boundary conditions (11), and (12) is given in [13-15].

We will consider the results of calculation of these resonant processes using as an example the calculation of cross sections for the simplest chemical reaction of dissociative attachment of electrons to hydrogen molecules. In this calculations for potentials of pair interaction of electrons with atoms of the molecule, we used potentials of the form

$$V(r) = \lambda \exp(-\beta r)/r, \quad (4)$$

whose parameters were determined on the basis of the electron binding energy at a negative ion, scattering lengths, and effective radius. Allowance for spin (in the case of homonuclear molecules) was made as follows. For the scattering length, we used the quantity [5, 6, 14-17]

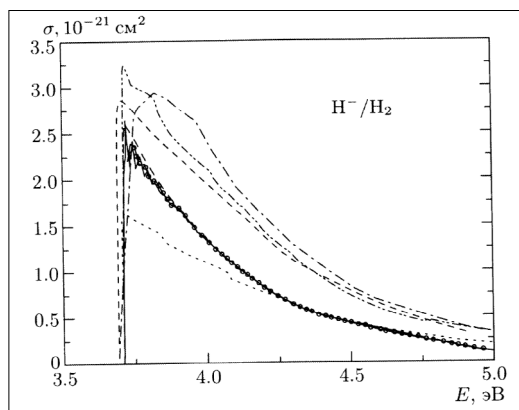
$$\frac{1}{a} = \frac{1}{a_1} = \frac{1}{a_2} = \frac{1}{4} \left( \frac{3}{a_t} + \frac{1}{a_s} \right),$$

where  $a_t$  and  $a_s$  are the triplet and singlet scattering lengths, respectively. Pair potentials of interaction between atoms in molecules was simulated by the Morse potentials

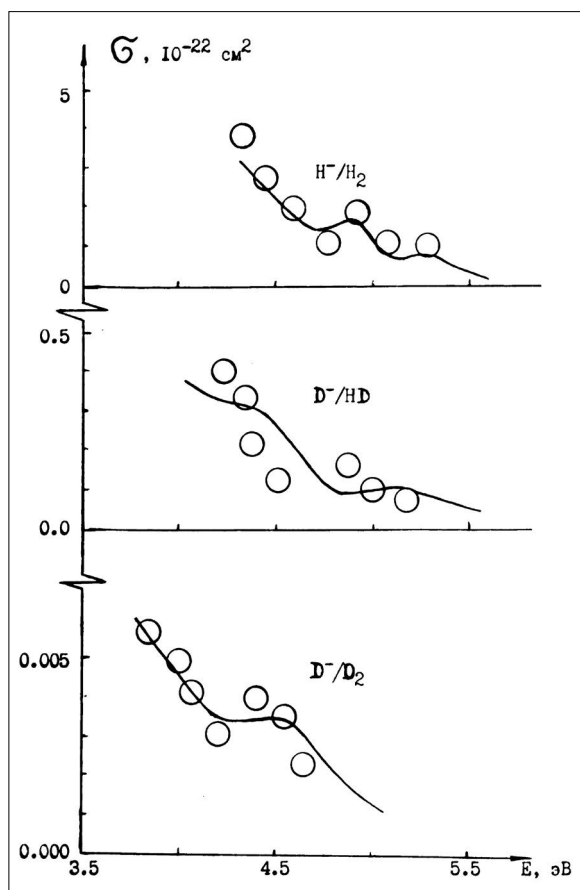
$$V(r) = D(1 - \exp(-\alpha(r - r_0)))^2, \quad (5)$$

whose parameters were determined on the basis of spectroscopic data [24]. These results are shown in Fig.2 together with the latest experimental data and the results of calculations based on other approximations [4,5,11,25-27]. These results confirm the existence in this system of the resonant states considered above. It should be noted here that experimental results of observation of three-particle resonant states were presented for the first time in for the dissociative attachment of an electron to hydrogen molecules. However, in view of the energy distribution for the electron beam of width 0.1 eV, only nonmonotonicity of the energy dependence

of the dissociative attachment cross section was noted in these experiments; this nonmonotonicity was confirmed in theoretical calculations published more than 20 years ago [3,14, 17]. The oscillatory structure of the dissociative attachment cross sections was confirmed only recently in the experiments, in which special technique was used for energy stabilization of the electron beam (meV) [25]. The detailed structure of cross section in  $\sim 3.75\text{eV}$  region are presented on Fig.3.



**Figure 2:** Dependences of the cross section of electron dissociative attachment to hydrogen molecules on the energy of projectile electrons: the solid curve corresponds to experimental data [19]; the results of calculations performed in [11], [7, 10], [10, 26], [21], and [20] are represented by the fine-dash, large-dash, dot-and-dash, dotted, and double dot-and-dash curves, respectively; our results of calculation are presented by circles.



**Figure 3:** Dissociative attachment of electrons to  $H_2$  molecules. Region 3.75 eV. The solid lines correspond results of our calculation, experimental data presented by circles [4].

To estimate the influence of particle charges on the effect, we consider the scattering of electrons from hydrogen halide molecules. Since the electron affinity to the hydrogen atom is much smaller than to a halogen atom, a hydrogen halide molecule can be visualized as a system consisting of a proton and a negative halogen ion [24]. Thus, in the approach proposed here, the main approximation is that the interaction of the projectile electron with the nuclei of the target molecule is replaced by the interaction of the impinging electron with the proton and the negative halogen ion. The complex many-particle problem of calculation of electron scattering cross section at diatomic molecules is reduced to the problem of collision in a three-body system, which can be solved using the method of quantum scattering problem in a few-particle system. Naturally, this approximation is valid for energies of the impinging electron lower than the electron excitation energy of the molecule.

Computational difficulties encountered in calculation of cross sections in the given approximation are mainly associated with the long-range Coulomb interaction potentials between a projectile electron, a proton, and a negative halogen ion. It was mentioned above that in this case the integral Faddeev equations cannot be applied directly; either these equations should be modified, or the differential formulation of the Faddeev equations in the coordinate representation should be used [13-15]. It should be noted that in the general case of scattering of an electron from halogen molecules in the given approximation,

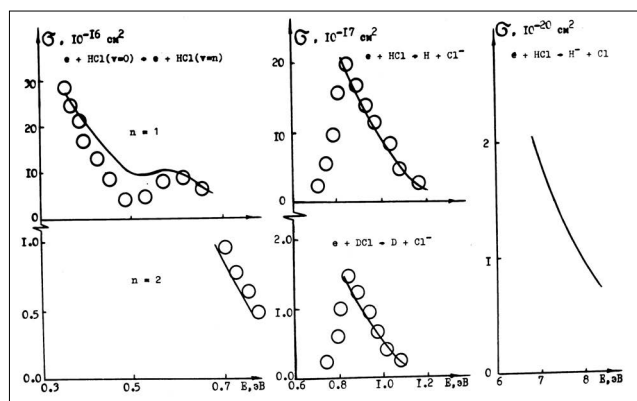
$$e + (H^+G^-) \rightarrow \begin{cases} e + (H^+G^-) & \text{elastic scattering processes} \\ e + (H^+G^-)^* & \text{excitation processes} \\ H^+ + (e, G^-)^* & \text{rearrangement processes} \\ G^- + (e, H^+)^* & \text{with excitation} \\ e + H^+ + G^- & \text{ionization processes} \\ e + e + H^+ + G & \text{ionization processes} \\ e + H + G & \text{processes} \end{cases}$$

the Faddeev equations for four mutually interacting bodies (two electrons, a halogen atom, and a proton) should be used. However, for some processes such as dissociative attachment reactions, we can confine our analysis to equations for three pairwise interacting bodies.

In our case, to calculate dissociative attachment of an electron to hydrogen halide molecules, we apply the Faddeev equation for three charged particles in the coordinate space [13-15].

Figures 4 show the results of calculation of the cross sections of electron dissociative attachment to hydrogen halide molecules and their isotope-substituted modifications in the ground state and in excited vibration-rotation states as well as experimental results and the results of calculations based on other approximations [4-11], which demonstrate suppression of oscillations in the scattering cross sections [4-11, 25, 27].

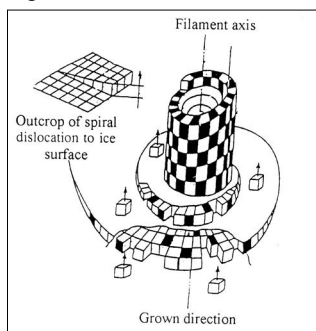




**Figure 4:** Scattering of electrons by hydrogen halide molecules: (dots) experimental results of [11, 12] and (solid lines) calculated results of this work.

Let us consider the effect of these peculiar resonances on the rates of chemical reactions, which appears interesting for explaining electron transport in proteins (physically, this transport is one of the main functionally important processes in a cell [15, 28]). Knowing this transport mechanism, it would be possible to explain how a transition is made from structurally disorganized chemical transformations (e.g., in solutions) to coordinated subsequent stages typical of biological systems [15]. It should be noted that no new interactions are used in nature and the process is organized due to an appropriate choice of molecular structures and the corresponding wellknown interactions. Thus, identification and analysis of these interactions will make it possible to understand physical mechanisms of processes occurring in proteins and other molecular structures such as DNA and RNA.

The application of the method presented above for calculation of real biopolymer molecules now encounters many difficulties, namely, absent of reliable spectroscopic data on clusters as distinct from diatomic and poliatomic molecules [4,7, 28] and some others. Yowever, in some particular cases certain estimates can de made. One can prove that under certain condition biopolymers consisting of similar elements from spiral strutures. This is experementally confirmed by sublimation of frozen water solutions of organic compounds, including amino acids (protein monomers), nucleotides (DNA and RNA vomomers) and their mixtures. In this experiments [23], for solution concentrations exceeding  $10^{-2}$  gmol/l porous remnants (matrices of crystals of dissolved substances) are formed, while for lower consrtrations the struture of matrices changes drastically and they have the form ofundirectional tubular lines [28]. The formation of this lines is due to solution freezing which is accompanied by replacement of impurity components be front of the newly formed ice and the component density fluctation lead to shifts in the ice cristal lattice, i.e. dislocations that form steps. In the course of crystallization the step winds, which is shown schematically in Fig.5.



**Figure 5:** Schemanic drawing of spiral type structure growth

Experiments demonstrated that monomers may joint in lines in course of their assembly because freezing of water solutions of amino acids of certain concentration was revealed to initiate, under UV irradiation ( $\lambda = 250-300nm$ ), an intaraction between comonents and to lead to reaction of biopolymer synthesis. The calculation dased on the proposed model show that the mutual orientation of monomers in chains under self-assembly is due to precisely the above-described specific multiparticle interaction? where molecules attach to each other tending to occupy a position with minimum potential energy. As a results of assembly of L-amino acid chains the role of matrix is played by nucleotides and vice of versa. This is how one-to-one correspondence between molecules, i.e., a genetic code appears owing to multiparticle dynamic interactions. The estimates obtained of the bases of proposed model shows that

- amino acids and nucleotides form their individual chains and pratically no restrictions exist for asstmbly of large ( $10^6 - 10^9$  atoms) molecules of nucleic acid,
- alternation of regions with periodic and aperiodic character of succession of different monomers in the chains depends on the velocities of molecular motion at different dislocation steps upon freezing,
- not only nucleotides and amino acids but also their isomers, if they were present in the initial solution, are distributed in independent chains. This proves that L-amino acids that rotate the polarizftion plane of light to the left form the chain in space with a shape of the right helix and are located near the right helix of nucleotides, while Damino acids that form the left helix are located across the nuclejtide spiral. This fact proves the natural separation of stereoisomers in the course of evolution [28]. These results, i.e., the formation of ordered helical structures of impurity molecules, or a one-dimentional assembly, are directly related to the problem of appeance of life. The practical importtance of this phenomenon refers to the creation of biopolymers with prescribed properties and to the possibility of constraction on their basis of various technical elements of bioelectronics.

To study the processes described above, we first consider a simple system of two identical coupled particles tunnelling through a potential barrier by using a mathematically correct quantum theory of scattering in a few-body system [13-15].

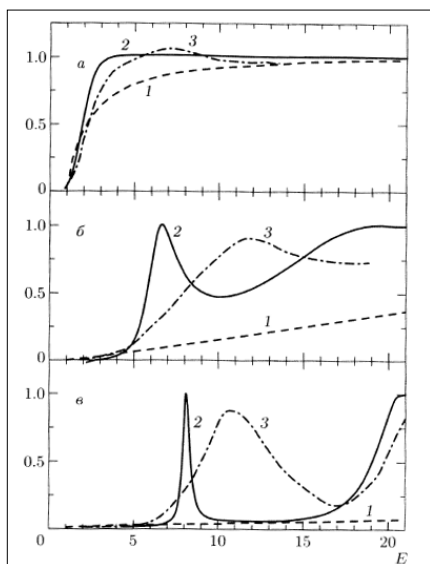
It should be noted that tunnelling of particles (including structured ones) is usually considered on the basis of well-known theories and results are automatically extended to many-particle systems (especially in applied studied, e.g., in biology [28, 29]). Most results in these applications are associated precisely with analysis of tunnelling through various potential barriers of multicomponent structured complexes. Quite often, such results do not correspond to the initial problem and do not reproduce experimental data. It should be noted that if the barrier size is much larger than the characteristic size of a complex, the difference from the structureless case is insignificant. If the size of the complex is commensurate with the barrier width, mechanisms appear leading to anomalous transparency of the barrier (analogously to the Ramsauer effect [4, 5, 7, 15, 30]).

The physical reason for the barrier transparency is associated with the possibility of formation of a barrier resonance since the potential energy of the system may have a local minimum ensuring the metastable state of the complex; to this end, the interaction of all particles of the complex with the barrier is required.

To demonstrate this effect, we use the quantum scattering theory to consider the tunnelling of a pair of identical particles  $m_1 = m_2 = m$  coupled through various types of interaction (harmonic oscillator, Morse and Gauss potentials) through a potential barrier which was simulated by a potential of the form [30].

$$V(x_{\pm}^{\pm}y) = a \exp((x_{\pm}^{\pm}y)^2/2b)/\sqrt{(2\pi b)},$$

where  $a$  and  $b$  are the barrier height and width. The results of calculations are shown in Fig.6. It can be seen from the figure that, for a barrier height much larger than the characteristic size of the incident complex, its transmission probability differs insignificantly from the transmission probability in the case of structureless particles. If the size of the complex is commensurate with the spatial size of the barrier, mechanisms appear which lead to a substantial transparency of the barrier and even to its total transparency in some cases.



**Figure 6:** Tunneling probabilities for a structureless (1) and structured (2, 3) particles as functions of the energy of the projectile particle for the harmonic potential (2) and the Morse potential (3) for various characteristics of the barrier  $a = 1$  (a),  $6$  (b), and  $11$  (c). Energy  $E$  is given in units of the corresponding potential.

In the simplest case of a complex consisting of two particles, the physical pattern of the barrier transparency is determined by the formation of a resonant state upon the passage of only one of the particles through the barrier. Thus, two particles are on different sides of the barrier (i.e., this resonant state is preserved until the other particle passes through the barrier). The barrier width is determined by the lifetime of this resonance.

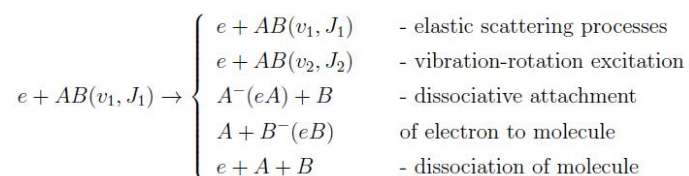
It should be noted here the penetrability symmetry breaking for structured particles may serve as a possible mechanism explaining different penetrabilities of biomembranes in opposite directions (osmosis). Another explanation of penetrability of a biomembrane is given in on the basis of the assumption that an isothermal phase transition of the melting/crystallization type occurs in a monolayer of the membrane, but in 2D and not in 3D system [28]. This makes it possible to interpret some peculiarities of blood circulatory system, which could not be explained earlier.

Analogous results are considered in however, the results concerning the penetrability of potential barriers for structured particles are completely different.

Figure 12 shows that the tunnelling probability in some cases may attain unity, which can be explained by interference suppression of the reflected wave (this phenomenon is widely used for blooming of optical systems). As the number of interacting particles increases, the effect of enhancement of the barrier penetrability may substantially increase. Thus, under certain conditions, coupled clusters not only surmount obstacles more easily, but can also be themselves transparent to other particles (this is often encountered in biological systems).

The most astonishing fact is that this mechanism of potential barrier transparency for structural particles was confirmed in experiments [25-30].

These features are commonly observed in real systems, e.g., in the simplest chemical reactions induced by electrons:

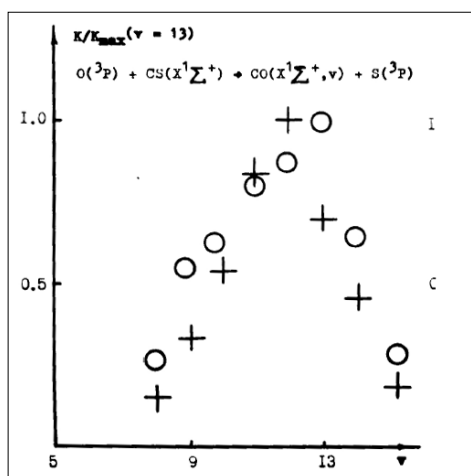


In the approximation of the quantum theory of scattering in a few-body system, it is possible to reproduce the experimental data on the simplest chemical reactions occurring during the interaction of electrons with diatomic molecules in the ground state as well as in excited vibration-rotation states [9-11, 25-31]. These results are presented in all calculations in this case are performed in the above-mentioned approximation, in which the interaction of an electron with nuclei and electrons of the target molecule was replaced by the interaction of the electron with each atom as a whole (the atom was treated as a force center) [13-17]. The same figures also show the results of calculations performed in the resonance model approximation with nonlocal potentials based on the quantum theory of scattering in a two-body system [31].

It should be noted once again that this approximation appears as reasonable for energies of the projectile electron lower than the electron excitation energy of the molecule. Otherwise, it is necessary to use the many-particle approximation instead of the three-particle approximation since the contributions from the dissociation channels become significant (this is demonstrated in Figures. 2-4). Consequently, we can speak of the agreement with the experimental results only on the average in view of the initial model of the process as well as the simplest pair potentials simulating the interaction of an electron with atoms [14, 15, 17]. A comparison of the results of our calculations with the available experimental data [4-11, 19-23] shows that simulation of the electron interaction with each atom of the molecule based on Eqs. (1,6), which correspond to the multiple scattering pattern [6, 14, 17], makes it possible to attain satisfactory agreement with experiment (coincidence of the orders of magnitude of cross sections, including isotopic effects and threshold singularities [14-17]).

The well-known theoretical methods for studying resonant processes occurring during electron collisions with molecules (the boomerang method, the R matrix method, the method of time evolution of the wave function, the Feshbach operator method, etc.) are based on interpreting this process as a multistage process [4-11]. The first stage involves the electron capture by a molecule and the formation of a negative molecular ion. The

second stage is the decay (evolution) of this state to various states of the decay products: a negative ion and a neutral or excited atom, two neutral or excited atoms and an electron (dissociation of the molecule), and an excited molecule and an electron (excitation of the molecule by electron impact). The basis of this formalism i.e., the formation of an intermediate state of a negative molecular ion) appears as not always substantiated from the physics point of view. For example, in the case of dissociative attachment of an electron to a hydrogen molecule, the lifetime of this complex is comparable with the electron mean free time, during which it covers a distance equal to the diameter of the hydrogen molecule. An analogous situation also emerges for the reaction  $O(^3P) + CS(X^1\Sigma^+) \rightarrow CO(X^1\Sigma^+) + S(^3P)$ , in which a considerable fraction of the translational energy (in accordance with the momentum limit  $E_v/E_t \sim 0.88$  [32]) is transformed into the vibrational energy of the CO molecule [14, 32]. Such a reaction also occurs without the formation of an intermediate complex. The results of this calculation present in Fig.7. Naturally, many reactions exist in which a long-lived intermediate complex is formed in the course of the reaction (see [5-11, 14, 15, 17] for details). However, for some processes like those described above, a preliminary analysis of experimental data for a given processes required for analyzing various collisions; the absence of such an analysis often leads to erroneous interpretation of experimental data.



**Figure 7:** Cross sections of the  $O(^3P) + CS(X^1\Sigma^+) \rightarrow CO(X^1\Sigma^+; v = n) + S(^3P)$  reaction: (+++) calculated results of this work, (ooo) results of calculations based on classical mechanics [2-4,10-12],

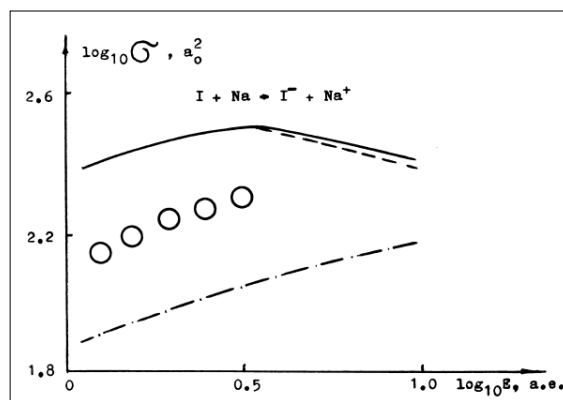
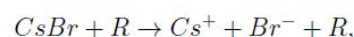
Thus, a class of processes existing in atomic, chemical, and biological physics can be referred to as direct processes in analogy with nuclear physics. The main feature of these processes is that no intermediate long-lived complex is formed in the course of scattering.

Consequently, the most adequate methods for interpreting such direct processes and reaction occurring with the formation of an intermediate complex are those proposed by Faddeev, Yakubovskii, and Merkur'ev, who developed a quantum theory of scattering in few-body systems without model assumptions concerning the formation an intermediate complex during a collision [13]. This method can be applied for describing direct processes as well as processes occurring with the formation of intermediate long-lived states. Thus, we can state that quantum transparency effects for various barriers and peculiarities of chemical reaction mechanisms described above can take place in various branches of physics, chemistry, and biology and can be interpreted in the framework of nonrelativ-istic quantum mechanics with the help of the formalism proposed in [13-15].

It is especially important for molecular biology, in which a consistent and mathematically correct explanation of fermentation reactions has not been obtained as yet [28]. The contemporary description of these reactions based on the assumption that a part of the free energy liberated as a result of a reaction is used for accelerating catalysis, i.e., penetration through a barrier (recuperation of energy), does not permit to quantitatively analyze the reaction energy. For this reason, it is extremely difficult to experimentally confirm or reject the proposed model.

On the contrary, the above substantiation of the transparency of potential barriers for structural complexes with a size commensurate with the barrier width provides an explanation for such reactions based on the well-known physical principles in the framework of ordinary quantum theory for a few-body system.

Figure 8 presents the cross sections of reaction  $Na + I \rightarrow Na^+ + I^-$  – calculated with the aid of the quantum scattering theory in a system of three particles ( $Na^+$ ,  $e$  and  $I^-$ ). In this case, differential equations with the corresponding boundary conditions are used. We employ the quantum scattering theory in a system of several particles in the calculations of the following molecular reactions:



**Figure 8:** Cross sections of the  $Na + I \rightarrow Na^+ + I^-$  reaction: (dots) calculated results of this work, (solid line) results of calculations based on classical mechanics, (dashed line) results of calculations in the tight-binding approximation and (dashed-and-dotted line) results of calculations in the quasi-classical approximation [2-4,10-12].

where  $R = Xe, Hg$  (Figures. 9 and 10). Note that the calculations are performed in the approximation in which the  $CsBr$  molecule is considered as the  $Cs^+Br^-$  system owing to a relatively high electron affinity of the halogen atom. Thus, the calculations of such a reaction are reduced to the solution of a problem in the system of three bodies (negative ion of halogen atom  $Br^-$ , positive ion  $Cs^+$ , and atom  $R$ ). The pairwise interaction potentials are written as [14, 15]

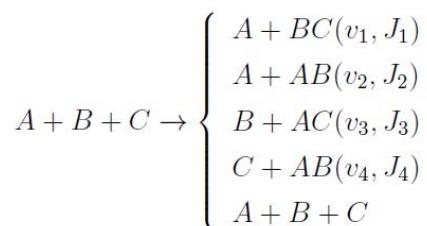
$$V_{RCs^+, RBr^-}(r) = A_i \exp(-r/\rho_i) - \alpha_{Ri}/2r^4 - C_i/r^6$$

$$V_{Cs^+Br^-}(r) = A_i \exp(-r/\rho_i) - 1/r - (\alpha_{Cs^+} + \alpha_{Br^-})/\sqrt{2}r^4 - C_i/r^6$$

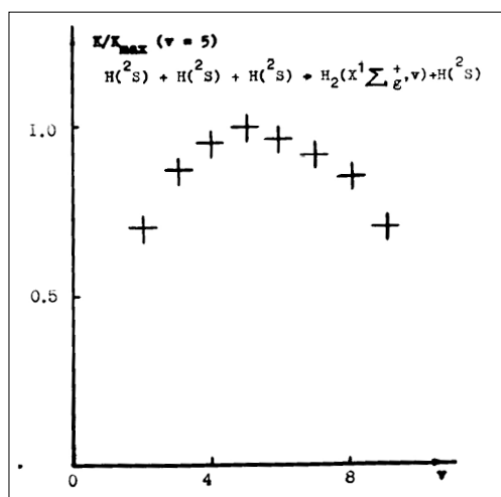
where  $C_i, A_i, \rho_i, \alpha_i$  determinates from experimental data [2-5,10-15].



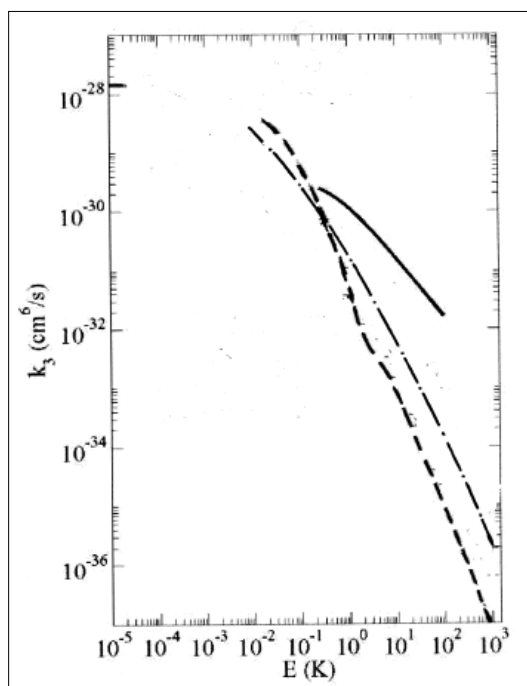
To prove the universal character of the proposed method in the calculations of cross sections of the following chemical reactions in which three (initially free) atoms are involved:



Figures. 11 and 12 present the calculated results for vibrational excitation of the reaction products in reactions  $H+H+H \rightarrow H_2(v=n)+H$  and  $He+He+He \rightarrow He_2(v=n)+He$ .



**Figure 11:** Plot of the rate of reaction  $H+H+H \rightarrow H_2(v=n)+H$  vs. vibrational quantum number (calculated results of this work).



**Figure 12:** Plot of the rate of reaction  $He+He+He \rightarrow He_2+He$  vs. energy: (solid line) experimental data of [3, 4], (dashed line) calculated results of [9, 12, 14], and (dashed- and-dotted line) calculated results of this work.

Note that the above models allow qualitative estimation of the experimental data and are not aimed at exact approximation of the experimental results. This circumstance can be interpreted as the main advantage of the above calculations, which make it possible to qualitatively reproduce the experimental data using rough approximations (approximation of the problem of several bodies, application of the Morse pair potentials, etc.). The calculated results of Figs. 2–4 and 8-11 provide the supporting evidence.

To study the scattering processes occurring during the collision of an atom with a helium molecule and to determine the role of pair interaction potentials, we calculated the amplitudes of elastic scattering and decay as well as phase shifts with and without taking into account the hard core. The results of these calculations are present in [13-17]. The results are almost independent of the form of pair interaction potentials and on whether or not the hard core was taken into account both for bound states and for scattering state. Thus, it can be concluded that the form of pair interaction potentials and allowance for a hard core in the boundary-condition model in the given approximation does not substantially affect the results of calculations.

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