Quasiresonant processes in slow collisions

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Collisions between slow atomic particles involving a small change in electron energy in the transition are examined. Asymptotic methods are presented for calculating the parameters of interaction potentials for atomic particles at large separations. Different models describing electron transitions during collisions between atomic particles are analyzed. The simultaneous use of the asymptotic method for the calculation of the interaction potentials between colliding particles and of the generalized two-level approximation for the quasiresonant particle collision results in reliable calculations of transition cross sections for a broad range of processes. This is demonstrated by considering examples of resonant charge transfer, spin exchange, and also some quasiresonant processes.

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CONTENTS

INTRODUCTION

Quasiresonant processes during atomic collisions are, by definition, connected with transitions in which the electron energy of the particles changes very little (or not at all). Quasiresonant processes therefore take place with high cross sections, comparable with or exceeding the gas-kinetic cross sections, and play an important role in phenomena occurring in ionized or excited gases under different conditions. For slow collisions, when the relative velocity of the colliding particles is small in comparison with the characteristic velocity of valence electrons in their orbits, the natural theoretical description of quasiresonant transitions expresses the properties of the system of colliding particles in terms of the parameters of the quasimolecule, i.e., the system consisting of the same particles but with fixed nuclei.

Calculations of cross sections for quasiresonant transitions can be substantially simplified for two reasons. Firstly, the transition energy is small and the collision itself is slow, so that a restricted number of states of the quasimolecule participates in the transitions. Secondly, the quasiresonant transitions themselves occur at large separations between the colliding particles as compared with their dimensions. This determines the smallness parameter of the theory and this, in turn, enables us to express the properties of the quasimolecule in which we are interested in terms of the parameters of the colliding particles. The cross section for the quasiresonant transition can therefore be expressed in terms of the parameters of the colliding particles and the collision velocity by taking into account the nature of the transition for each particular quasireso-

nant process and by considering the possible collision paths.

This approach to the theory of atomic collisions was developed in the sixties by Soviet scientists and has been reviewed in a number of monographs.[1–6] It has been called the asymptotic theory of atomic collisions. The idea of the asymptotic method is to expand the cross section in terms of a small parameter which is essentially equal to the ratio of the geometrical cross sections of the colliding particles to the cross section for the process under investigation. Since, for the processes which we are reviewing, this ratio is small, we can not only calculate the transition cross section but also estimate the precision of the calculation. This is the fundamental difference between the asymptotic theory, on the one hand, and model and semiempirical approaches, on the other. Moreover, despite the fundamental difficulties in obtaining the intermediate result, the asymptotic theory does yield the final result in relatively simple form (analytic or semianalytic), which establishes a simple relationship between the cross section for a particular process and the parameters of the colliding particles as well as the collision velocity. This is a natural consequence of the expansion in terms of the small parameter, and may be regarded as the advantage of the asymptotic theory.

Our aim is to review the asymptotic theory of quasiresonant processes and to illustrate it by simple examples of interactions and collisions between atomic particles. Experience has confirmed the advantages of the asymptotic theory of atomic collisions as compared with other approaches, and many new results have been obtained, some of which are included in this paper. More-

over, the idea of the asymptotic approach to the theory of atomic collisions, which enables us to present the result of the theory in terms of an expansion in a small parameter, has itself turned out to be fruitful in adjacent branches of physics as well. The authors hope that the principles of the asymptotic methods presented here will also be useful in other branches of physics.

1. INTERACTION BETWEEN ATOMIC PARTICLES AT LARGE SEPARATIONS

The probability of transition between quasiresonant states during a slow collision between atomic particles can be expressed in terms of the parameters of the interaction potential between these particles. Since such transitions are found to occur mainly at large separations between the particles as compared with their dimensions, we shall, in this chapter, confine our attention to the interaction potential at large separations between the particles. This type of information is important not only for the particular problems with which we shall be concerned, but also in determinations of the elastic scattering cross sections and the associated transport coefficients of gases at moderate temperatures, as well as in determinations of the parameters of molecules with low dissociation energies and the parameters of condensed media consisting of weakly interacting atoms and molecules.

Calculations of the atomic interaction potential at large separations are a part of the general problem of evaluating the adiabatic electron terms of quasimolecules (the adiabatic electron term of a quasimolecule is the electron energy as a function of the distance between the nuclei when the latter are treated as being held fixed). The "direct" method of evaluating these terms, which has recently been widely used, is based on the variational procedure which cannot be successfully employed without the use of powerful modern computers.[35] This, of course, restricts the application of the variational method to the many particular problems of collision theory in which we have to know the behavior of the potential curves over relatively large intervals of interatomic distance R. However, computational difficulties and the high cost of variational calculations are not the main impediment to the broad application of this procedure to collision problems. The basic problem is that, as the interatomic distance increases and the interaction between the atoms is reduced, the precision of the variational method for a given basic set of electronic functions becomes lower. This is connected simply with the fact that the interatomic energy is a small part of the total energy of the system of atoms, and decreases with increasing R. Moreover, the variational method is suitable in practice only for the simplest systems.

Perturbation theory, based on the electron states of free atoms, is an alternative approach to this problem. It is well known[7] that this method can be used to obtain relatively simply the first and second order terms for the interaction energy when this energy can be expressed in the form of a multipole expansion and the overlap between the functions associated with different atoms can be neglected. The interaction energy can then

be written as a series in the reciprocal powers of R and, depending on the electron and charge states of the atomic particles, the first term of the expansion R^{-n} will correspond to different values of n. In particular, $n=4$ corresponds to the interaction of an ion and an atom in the S state (this is the interaction between a point charge and an induced dipole, i.e., the so-called polarization interaction) and $n=6$ corresponds to the interaction of two atoms, one of which is in an S state (this is the interaction of mutually induced dipoles, i.e., the so-called van der Waals interaction). We note that the basic methods for calculating the potentials corresponding to the long-range interaction were developed quite early on in the history of quantum mechanics.[8-15]

However, a serious shortcoming of the above variant of perturbation theory is that it has a restricted range of application. In particular, the representation of the long-range interaction potential U_{lr} by a series in powers of $1/R$ is asymptotic in character (i.e., it diverges, beginning with a certain term) and is already invalid at distances considerably greater than could have been expected on the basis of the general criterion for the interaction U_{lr} to be small in comparison with the characteristic energies ΔE associated with the electronic excitation of atoms. This defect can be removed only by taking into account the overlap of electron wave functions.

On the other hand, if one attempts to take into account the overlap effect within the framework of the usual Heitler-London method,[35] it turns out that the more stringent criterion for the validity of perturbation theory (namely, that the first-order corrections to the zero-order functions must be small) is not satisfied for the range of electron coordinates which provides the main contribution to overlap, i.e., for the "tails" of the electron functions. The consequence of the violation of this criterion is that calculations of the overlap integrals, or of the related exchange and resonance integrals, with unperturbed atomic state functions yield an incorrect result for the exponentially decreasing part (sometimes called the short-range or exchange part) of the interaction $\Delta(R)$.

We thus have the problem of finding the correct procedure for evaluating the wave functions of "almost free" atoms, i.e., of taking into account the small distortions of the atomic state functions that are important for the overlap calculation at large separations between the atoms. When this is done, one can, of course, confine one's attention to the classically forbidden region of motion of the electron, where the electron density is appreciably smaller than the maximum density. All this collectively forms the foundation for the asymptotic method of determining the exchange interaction potentials for atomic particles. In the final analysis, this approach will yield an analytic expression for the exchange interaction potential in the limit of large separations.

There are several types of exchange interaction between atomic particles (Fig. 1). The first corresponds to the transition of a valence electron from the field of the remaining ion to the field of another, and the second
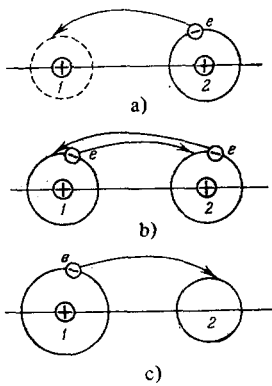
FIG. 1. Three types of exchange interaction: a) electron transferred from the field of one ion (atom) to the field of another; b) exchange of two electrons between two different atomic particles; c) the wave-function "tail" of the valence electron in the field of its own atomic residue reaches another atomic particle and thereby interacts with it.

corresponds to the simultaneous exchange of two electrons. The third type is determined by the distribution of the valence electron in the field of a neighboring "foreign" atom. In the ensuing discussion, we shall examine in detail the interaction of an ion with a corresponding atom, which belongs to the first type of exchange interaction. We shall use this simple example, which retains all the main features of the problem of calculating the asymptotically exact expression for the exchange interaction potential, to demonstrate the special features and possibilities of the asymptotic method.

We begin with the case where the electron shell of the ion is full and the valence electron of the atom is in an s state. We shall analyze the behavior of the electron terms of the quasimolecule consisting of the ion and the corresponding atom in the limit of large separation between them. We shall use the symmetry of the quasimolecule, which is such that the Hamiltonian describing the electron is invariant under reflection of the electrons in the plane of symmetry. This plane is perpendicular to the line joining the nuclei and bisects it. A double reflection in this plane returns the system to its initial state. The electron eigenstates can therefore be divided into even and odd ones, depending on whether their wave functions retain their sign or change it on reflection in the symmetry plane. These wave functions satisfy the Schroedinger equations

$$-\frac{\hbar^2}{2m}\Delta\psi_g + V_1\psi_g + V_2\psi_g + \frac{e^2}{R}\psi_g = \varepsilon_g\psi_g, \qquad (1.1a)$$

$$-\frac{\hbar^2}{2m}\Delta\psi_u + V_1\psi_u + V_2\psi_u + \frac{e^2}{R}\psi_u = \varepsilon_u\psi_u, \qquad (1.1b)$$

where V_1, V_2 are the effective interaction potentials between the electron and the corresponding atomic residue, $\varepsilon_g, \varepsilon_u$ are the energy levels of the states under consideration, which depend on the separation between the nuclei, and the term e^2/R represents the Coulomb repulsion between the nuclei. In the limit of infinite separation between the nuclei, the energies $\varepsilon_g, \varepsilon_u$ are equal and correspond to the electron energy level in the atom.

Let us consider the region of large separations between the nuclei, when the even-odd energy difference between the electron states is small in comparison with the ionization potential of the atom. In accordance with Fig. 2, the wave functions of the even and odd states can then be expressed in terms of the same functions, and

the even-odd energy difference can be found by using the following device.[16] We multiply (1.1a) by ψ_u and (1.1b) by ψ_g. We then subtract one from the other and integrate over the half-space to the left of the symmetry plane. The result is

$$\frac{\hbar^2}{2m}\int_V \nabla\,(\psi_g\nabla\psi_u - \psi_u\nabla\psi_g)\,d\mathbf{r} = (\varepsilon_g - \varepsilon_u)\int_V \psi_g\psi_u\,d\mathbf{r}.$$

Next, we transform the left-hand integral into a surface integral and express the wave functions of the even and odd states in terms of the wave functions centered on the corresponding ion (see Fig. 2): $\psi_{g,u} = (\psi_1 \pm \psi_2)/\sqrt{2}$. Finally, since the separation between the nuclei is large,

$$\int_V |\psi_2|^2\,d\mathbf{r} = 1 - \int_V |\psi_1|^2\,d\mathbf{r} \ll 1.$$

This yields

$$\varepsilon_g - \varepsilon_u = \frac{\hbar^2}{m}\int_S \left(\psi_2\frac{\partial\psi_1}{\partial z} - \psi_1\frac{\partial\psi_2}{\partial z}\right)\,ds, \qquad (1.2)$$

where the surface S coincides with the symmetry plane, and the z axis lies along the line joining the nuclei.

We now introduce a cylindrical coordinate system with the origin at the midpoint of the line joining the nuclei, the z axis lying along this line, and the ρ axis perpendicular to it. Since the electron is in an s state, the wave functions ψ_1 and ψ_2 depend only on the distance to the given nucleus. In the above coordinate system they are therefore given by

$$\psi_1 = \psi\left(\sqrt{\left(z + \frac{R}{2}\right)^2 + \rho^2}\right), \qquad \psi_2 = \psi\left(\sqrt{\left(z - \frac{R}{2}\right)^2 + \rho^2}\right),$$

where R is the separation between the nuclei and $\psi(r)$ is the electron wave function with r being the distance from the nucleus in the neighborhood of which the electron is largely concentrated. We now use this to transform (1.2) to the form

$$\varepsilon_g - \varepsilon_u = \frac{\hbar^2}{m}\int_0^\infty 2\pi\rho\,d\rho\,\Big\{\psi\Big[\sqrt{\left(z - \frac{R}{2}\right)^2 + \rho^2}\Big]\frac{\partial}{\partial z}\,\psi\Big[\sqrt{\left(z + \frac{R}{2}\right)^2 + \rho^2}\Big]$$

$$-\psi\Big[\sqrt{\left(z + \frac{R}{2}\right)^2 + \rho^2}\Big]\frac{\partial}{\partial z}\,\psi\Big[\sqrt{\left(z - \frac{R}{2}\right)^2 + \rho^2}\Big]\Big\}\Big|_{z=0}$$

$$= \frac{\hbar^2}{m}\int_0^\infty \pi\,d\rho^2 R\frac{\partial}{\partial\rho^2}\,\psi^2\left(\sqrt{\frac{R^2}{4} + \rho^2}\right) = \frac{\pi\hbar^2}{m}R\psi^2\left(\frac{R}{2}\right). \qquad (1.3)$$
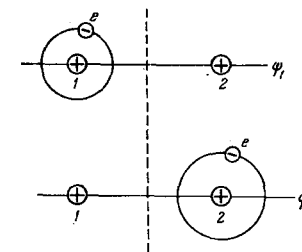
In doing this, we use the obvious relation

FIG. 2. Electron in the field of two identical centers. Reflection in the symmetry plane corresponding to the transformation $\psi_1 \to \psi_2$, $\psi_2 \to \psi_1$. Correspondingly, the even electron wave function which retains its sign under reflection is given by $\psi_g = (\psi_1 + \psi_2)/\sqrt{2}$, and the odd wave function is $\psi_u = (\psi_1 - \psi_2)/\sqrt{2}$.
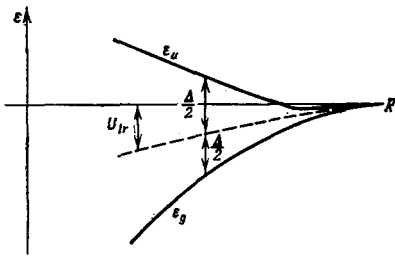
FIG. 3. Electron terms for the quasimolecule $A^+ + A$ with one valence s electron at large separations between the nuclei. U_{lr} is the long-range interaction potential between the ion and atom and Δ is the exchange interaction potential.

$$\frac{\partial}{\partial z} \psi \left[\sqrt{\left(\frac{R}{2}+z\right)^2 + \rho^2} \right]\Big|_{z=0} = R\frac{\partial}{\partial \rho^2} \psi \left(\sqrt{\frac{R^2}{4} + \rho^2} \right)$$

and assume, for simplicity, that the electron wave function is real.

The function given by (1.3) relates the difference between the energies of the states of the molecular ion under consideration to its parameters in the limit of large separations between the nuclei. Before we analyze this formula in detail, let us consider the expression for the state energy. In this case, the long-range interaction between the ion and the atom is the same for both states, so that the energy of each of the states can be written in the form

$$\varepsilon_{g,u} = \varepsilon_0 + U_{lr}(R) \pm \frac{1}{2}\Delta(R),$$

where ε_0 is the electron energy for an infinite separation between the nuclei, U_{lr} is the long-range and mainly polarization interaction, and Δ is the exchange interaction potential due to the overlap of the electron shells (Fig. 3). The exchange interaction potential between the ion and its own atom is, by definition,

$$\Delta = \varepsilon_g - \varepsilon_u = \frac{\langle \psi_g \mathcal{H} \psi_g \rangle}{\langle \psi_g \psi_g \rangle} - \frac{\langle \psi_u \mathcal{H} \psi_n \rangle}{\langle \psi_u \psi_n \rangle} = 2\langle \psi_1 \mathcal{H} \psi_2 \rangle - 2\langle \psi_1 \mathcal{H} \psi_1 \rangle \langle \psi_1 \psi_2 \rangle,$$

(1.4)

where the wave functions ψ_1 and ψ_2 correspond to finding the electron in the field of the respective atomic residues. The exchange interaction potential is assumed small in comparison with the characteristic energy of the electron in the atom, so that $|\langle \psi_1 | \psi_2 \rangle| \ll 1.$[1]

We now determine the resonance interaction between the ion and the atom in the above case. This means that we must determine the wave function of the electron in the quasimolecule, which is centered on one of the nuclei and is present in this form in the expression for the exchange interaction potential given by (1.3). We shall do this by using the Schroedinger equation (1.1) but, since the separation between the nuclei is large, we shall neglect the long-range and exchange interactions in the expression for the energy. The result is the following Schroedinger equation for the wave function centered on the first nucleus:

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[1] The two definitions given by (1.2) and (1.4) for the exchange interaction potential become identical when the exact wave functions are used.

$$-\frac{\hbar^2}{2m}\Delta\psi + V_1\psi + V_2\psi = \left(-\frac{\hbar^2\gamma^2}{2m} - \frac{e^2}{R}\right)\psi,$$

(1.5a)

where $\hbar^2\gamma^2/2m$ is the ionization potential of the atom. At the same time, in the range of coordinates for which the electron does not enter the "interior" of the atomic residues, the potential representing the interaction between the electron and the ion is a Coulomb potential, so that this equation becomes

$$-\frac{\hbar^2}{2m}\Delta\psi - \frac{e^2}{r_1}\psi - \frac{e^2}{r_2}\psi = \left(-\frac{\hbar^2\gamma^2}{2m} - \frac{e^2}{R}\right)\psi,$$

(1.5b)

where $r_{1,2}$ is the distance of the electron from the corresponding nucleus.

The wave function of the electron in the quasimolecule can be conveniently expressed in terms of the wave function of the electron in the atom which, well away from the atomic residue, satisfies the Schroedinger equation

$$-\frac{\hbar^2}{2m}\Delta\psi_{at} + \frac{e^2}{r}\psi_{at} = -\frac{\hbar^2\gamma^2}{2m}\psi_{at}.$$

(1.6)

The solution of this equation at large distances r from the nucleus is

$$\psi_{at} = Ar^{(1/\gamma a_0)-1} e^{-r\gamma}, \quad r\gamma^2 \gg a_0,$$

(1.7)

where a_0 is the Bohr radius and A is an asymptotic coefficient determined by the behavior of the electron in the interior of the atom.

Assuming that the atomic parameters A and γ are known, we shall determine the wave function of the electron in the quasimolecule in the region between the nuclei as follows. In the neighborhood of the first nucleus, where $r_1 \ll R$, we can neglect the effect of the second ion on the electron, so that the wave function of the quasimolecule is identical with the atomic wave function. This region also includes $r_1\gamma^2 \gg a_0$, where the asymptotic expression (1.7) is valid for the atomic wave function. Next, we move the electron along the line joining the nuclei toward the region between the nuclei, where the interaction potentials between the electron and each of the nuclei are comparable. Here, we have $r_1\gamma^2 \gg a_0$, so that the Coulomb interaction potential between the electron and each of the nuclei is small in comparison with $\hbar^2\gamma^2/2m$, and the main change in the wave function is connected specifically with this term. In view of this, we write the electron wave function in the form[18]

$$\psi(\mathbf{r}) = \psi_{at}(r_1)\,\chi(\mathbf{r}).$$

(1.8)

Substituting this into the Schroedinger equation, and neglecting the second derivative with respect to χ, we obtain

$$\frac{\hbar^2}{m}\nabla\frac{\partial\chi}{\partial r_1}\psi_{at} + \left(\frac{e^2}{R} - \frac{e^2}{r_2}\right)\psi_{at}\chi = 0,$$

where, along the axis, $r_1 + r_2 = R$. Hence, we have

$$\chi = \left(\frac{R}{r_2}\right)^{1/\gamma a_0} e^{-r_1/R\gamma a_0}.$$

(1.9)

In particular, the electron wave function at the midpoint of the line joining the nuclei is

$$\psi\left(\frac{R}{2}\right) = \left(\frac{4}{e}\right)^{1/2\gamma a_0}\psi_{at}\left(\frac{R}{2}\right).$$

(1.10)

Accordingly, if we use the asymptotic expression given by (1.7) for the radial wave function of the electron in the atom, we obtain the following expression for the resonant exchange interaction (1.3)[17]:

$$\Delta = A^2 \frac{\hbar^2}{m} e^{-1/\gamma a_0} R^{(2/\gamma a_0)-1} e^{-R\gamma}. \qquad (1.11)$$

This expression was obtained for the interaction between the ion and the one-electron atom containing the valence s electron, but it can be extended to the more general case. Let us begin with the one-electron atom with electron angular momentum l and component μ of this momentum along the line joining the nuclei. The wave function of the valence electron can be written in the form of the product of the radial and angular wave functions $\Phi(r)$ and $Y_{lm}(\theta, \varphi)$ (r, θ, φ are the spherical coordinates of the electron relative to the nucleus in the field of which it is mainly concentrated):

$$\Psi(r) = \Phi(r) Y_{l_\mu}(\theta, \varphi).$$

The main variation of the radial wave function (1.7) is then exponential, i.e., $\Phi(r) \sim e^{-r\gamma}$, so that the exchange interaction potential given by (1.2)[2] now becomes:

$$\Delta = \varepsilon_g - \varepsilon_u = \frac{2\hbar^2}{m} \gamma \int |Y_{l_\mu}(\theta, \varphi)|^2 \Phi^2(r) \, d\varphi \rho \, d\rho.$$

Because of the exponential form $\Phi \sim e^{-r\gamma}$, this integral converges for small ρ ($\rho \sim \sqrt{R/\gamma} \ll R$, since $R\gamma \gg 1$), where $\Phi(r) = \Phi(R/2) e^{-\gamma\rho^2/R}$. This corresponds to small angles $\theta = 2\rho/R$ and, since $Y_{l_\mu}(\theta, \varphi) \sim \theta^\mu$, for small θ, the evaluation of the above integral yields

$$\Delta_{l\mu} = \pi \frac{\hbar^2}{m} R\Phi^2 \left(\frac{R}{2}\right) |\mu|! \left(\frac{2}{R\gamma}\right)^{|\mu|} \lim_{\theta \to 0} |Y_{l_\mu}(\theta, \varphi)|^2/\theta^{2|\mu|},$$

or, using the explicit form of the spherical harmonics Y_{l_μ} for small angles and the asymptotic expressions given by (1.7) and (1.10) for the radial wave functions, we obtain the following expression for the exchange interaction potential[19]:

$$\Delta_{l\mu} = A^2 \frac{\hbar^2}{m} R^{(2/\gamma a_0)-1-|\mu|} e^{-R\gamma-(1/\gamma a_0)} \frac{(2l+1)(l+|\mu|)!}{(l-|\mu|)! |\mu|! \gamma^{|\mu|}}. \qquad (1.12)$$

This expression can be generalized to the case where the atom and the ion contain a number of valence electrons. As in the preceding case, the transition to the new result involves a change in the wave function for electrons in the interior of the atom. Neglecting relativistic effects, let us represent the atomic wave function by the sum of products of wave functions of one of the electrons by the wave function of one of the atomic residues. In accordance with the Racah fractional parentage scheme, the wave function of an atom containing n valence electrons is given by[20,21]

$$\Psi_{LM_L SM_S}(1, 2, \ldots, n) = \frac{1}{\sqrt{n!}} \hat{P} \sum_{lM_l sm_s} (l_e\mu; lM_l | LM_L)$$

$$\times \left(\frac{1}{2}\sigma; sm_s \Big| SM_S\right) G_{LS}^{l's} \psi_{l_e\mu \frac{1}{2}\sigma}(1) \Psi_{lM_l sm_s}(2, 3, \ldots, n), \qquad (1.13)$$

where Ψ, ψ, and Ψ' are the wave functions of the atom,

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[2] We use this formula in this case with allowance for the fact that we are dealing with complex angular wave functions.

the valence electron, and the atomic residue, respectively; the numbers in parentheses are the numbers of electrons on which these functions depend; $LM_L SM_S$ are, respectively, the orbital angular momentum of the atom and its component along the line joining the nuclei, S is the spin of the atom, M_S is the spin component along the line joining the nuclei, $lM_l sm_s$ are the same quantum numbers for the atomic residue, and $l_e\mu\frac{1}{2}\sigma$ are the quantum numbers of the valence electrons. The quantities $(j_1m_1; j_2m_2 jm)$ are the Clebsch-Gordan coefficients corresponding to the addition of the orbital and spin angular momenta of the electron and of the atomic residue to give the corresponding angular momentum of the atom, and $\hat{P}$ is the electron permutation operator.

The state of the quasimolecule consisting of the ion and the atom is characterized by its total spin J. Accordingly, the wave function of the quasimolecule corresponding to the atom being near the first nucleus is

$$\Psi_1 = \sqrt{\frac{n!(n-1)!}{(2n-1)!}} \hat{P} \sum_{m_s, M_S} (sm_s; SM_S | JM_J)$$

$$\times \Psi_{LM_L SM_S}^{(1)}(1, \ldots, n) \Psi_{lm_l sm_s}^{(2)}(n+1, \ldots, 2n-1), \qquad (1.14)$$

where the operator $\hat{P}$ permutes the electrons situated in the field of different atomic residues, and the wave function superscript indicates the number of the nucleus in neighborhood of which the electron is located. The Clebsch-Gordan coefficient corresponds to the addition of the spins of the ion and of the atom giving the resultant spin of the quasimolecule. The remaining notation is the same as in the previous formula.

We now substitute the wave functions given by (1.14) and (1.13) for Ψ_1 and the analogous expressions for Ψ_2 into the expression for the exchange interaction potential given by (1.4). If we extract from the complete Hamiltonian for the system of electrons the Hamiltonian for the electron undergoing the transition, and at the same time neglect the simultaneous exchange of two electrons, we can express the exchange interaction potential of the many-electron system in terms of the one-electron potential. These operations yield the following expression for the exchange interaction potential[22]:

$$\Delta = \frac{n\left(J+\frac{1}{2}\right)}{2s+1} |G_{SL}^{sl}|^2 \sum_\mu (l_e\mu; lM_l | L, M_l+\mu)(l_e\mu; l, M_L-\mu | LM_L) \Delta_\mu; \qquad (1.15)$$

where J is the total spin of the quasimolecule and Δ_μ is the exchange interaction potential when only one valence electron is present with angular momentum component μ along the line joining the nuclei. We can thus replace the calculation of the exchange interaction potential between an atom with n valence electrons in the state with quantum numbers $LM_L S$ and the atomic residue in the state with quantum numbers $lM_l S$ to the problem of one valence electron described by the same wave function in the field of the two atomic residues.

The above detailed analysis of the interaction potential between the ion and the corresponding atom illustrates the possibilities of the asymptotic method in calculations of interaction potentials. The exchange inter-

action potential between the ion and the atom is represented by the first term of the expansion of this quantity in powers of $1/R$. This means that, by taking the neglected terms into account, we can estimate the precision of the asymptotic method. Moreover, the exchange interaction potential itself is calculated in the asymptotic method with allowance for all the structural features of the interacting atom and ion without the use of models.

The dependence of the exchange interaction potential between the ion and its own atom on the separation between them can be obtained without taking into account the distortion of the electron wave function due to the interaction with the other atomic residue. For example, in the case of the valence s electron, the use of the undistorted atomic wave function (1.7) in (1.4) or (1.3) leads to the correct result $\Delta \sim R^{(2/\gamma a_0)-1} e^{-R\gamma}$ [see (1.11)]. A different situation obtains in the case of the exchange interaction between two atoms, which is determined by the simultaneous exchange of two electrons. In this case, in the region which determines the exchange interaction, the potential for the interaction between the electrons is much greater than the potential for their interaction with the atomic residues. For this reason, the wave function for the electrons in the quasimolecule becomes essentially a two-electron function, and this gives a different dependence of the potential for the exchange interaction between atoms on the distance between the nuclei as compared with the case where we use the undistorted atomic functions.[3]

The first correct evaluation of the exchange interaction potential between two atoms at large separations was performed by Gor'kov and Pitaevskiĭ[23] in the case of hydrogen atoms (see also the paper by Hering and Flicker[24]). The asymptotic method was subsequently extended[25] to the case of the interaction of two alkali metal atoms and the interaction of arbitrary atoms at large separations.[26-28] In the final analysis, the asymptotic theory enables us to express the interaction potential between distant atoms in terms of the parameters of these atoms, namely, the asymptotic parameters A, γ and the quantum numbers characterizing the states of the atom and the quasimolecule.

The character of the exchange interaction between atomic particles is such that it can be used as one of the elements in finding the electron terms of the quasimolecule in a more complex situation. In fact, the exchange interaction is determined by the "tails" of the electron wave functions, the long-range interaction is due to the region in which the electrons are mainly concentrated, and the spin-orbit interaction is governed by the inner region of the atom. Since these regions do not overlap, we can independently calculate the matrix elements of the Hamiltonian corresponding to the different types of interaction. The subsequent diagonalization of

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[3] For example, the exchange interaction potential between two hydrogen atoms for large separations R between them is $\Delta \sim R^{5/2} \exp(-2R/a_0)$, whereas the use of atomic wave functions in (1.4) leads to[15] $\Delta \sim R^3 \exp(-2R/a_0)$.

the energy matrix can be used to determine the electron terms of the quasimolecule at large separations between them. As an example, we shall determine the energy matrix for the interaction of an inert gas atom (in the ^1S state) and its ion (^2P state).[4,29]

The Hamiltonian for the system of electrons in this example can be conveniently written in the form

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 - \frac{2}{3} \varepsilon_T \hat{\mathbf{L}} \cdot \hat{\mathbf{S}},$$

where $\hat{\mathcal{H}}_0$ includes the electrostatic interaction between the electrons, $\hat{\mathbf{L}}, \hat{\mathbf{S}}$ are the orbital and spin angular momentum operators for the ion, and ε_T is the spin-orbital splitting of the ion levels. We shall expand the eigenfunctions of the quasimolecule under consideration in terms of the eigenfunctions of the Hamiltonian $\hat{\mathcal{H}}_0$. In the limit of infinite separation between the nuclei, $R \to \infty$ and the state of the quasimolecule described by $\hat{\mathcal{H}}_0$ is twelve-fold degenerate (three-fold in the component of the orbital angular momentum, two-fold in the spin component, and two-fold in the dependence on the number of the nucleus to which the atom is bound). For finite distances between the nuclei, the quantum number of the quasimolecule is the parity of its state under reflection in the plane of symmetry, i.e., the plane perpendicular to the line joining the nuclei and bisecting it. Because of this symmetry property, the energy matrix can be divided into two 6×6 blocks.

Moreover, according to the Kramers theorem, each of the states of the quasimolecule is doubly degenerate with respect to the simultaneous change in the signs of the components of orbital and spin angular momenta M_L and m_s. The energy matrix is therefore found to split into four independent 3×3 blocks. Table I gives two blocks of the required energy matrix with $M_L + m_s > 0$, where $u_M(R)$ corresponds to the long-range interaction with angular momentum component M along the line joining the nuclei and Δ_M is exchange interaction potential. The upper sign in front of the exchange interaction potential corresponds to the even state of the quasimolecule and the lower to the odd state; E_0 is the energy of the system for $R \to \infty$ and in the absence of the spin-orbit interaction.

Diagonalizing the above energy matrix, we can readily determine from the relation $|E - \mathcal{H}_{ik}| = 0$ the position of

TABLE I. Energy matrix $\mathcal{H}_{ik}$ for the quasimolecule consisting of an ion and an atom of an inert gas at large separations.

Quantum numbers	$M_L = 0.$ $m_s = \frac{1}{2}$	$M_L = 1.$ $m_s = -\frac{1}{2}$	$M_L = 1.$ $m_s = \frac{1}{2}$
$M_L = 0.$ $m_s = \frac{1}{2}$	$E_0 + u_0 \pm \frac{1}{2}\Delta_0$	$-\frac{\sqrt{2}}{3}\varepsilon_T$	0
$M_L = 1.$ $m_s = -\frac{1}{2}$	$-\frac{\sqrt{2}}{3}\varepsilon_T$	$E_0 + u_1 - \frac{\varepsilon_T}{3} \pm \frac{1}{2}\Delta_1$	0
$M_L = 1.$ $m_s = \frac{1}{2}$	0	0	$E_0 + u_1 + \frac{\varepsilon_T}{3} \pm \frac{1}{2}\Delta_1$

100   Sov. Phys. Usp. 21(2), Feb. 1978

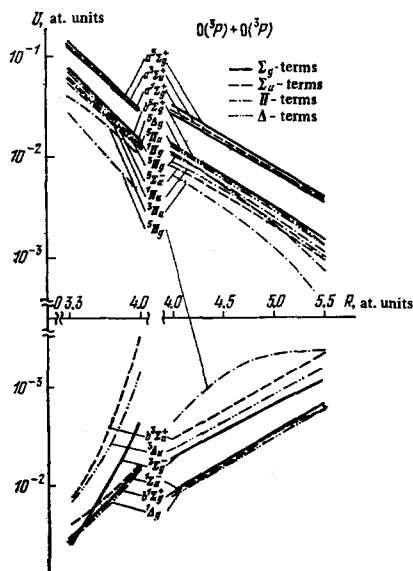E. E. Nikitin and B. M. Smirnov   100

FIG. 4. The $O(^3P)-O(^3P)$ potential[31]: left-hand side—variational calculation; right-hand side—results based on the asymptotic method.

Type	Ne	Ar	Kr	Xe
Separation between nearest neighbors	5.56 (6.05)	6.24 (7.25)	6.94 (7.5)	7.72 (8.2)
Sublimation energy, kcal/mole	0.50 (0.48)	2.3 (1.8)	2.6 (2.7)	3.1 (3.8)
Debye temperature, deg	71 (64)	91 (80)	62 (63)	49 (55)

*Results obtained by the asymptotic theory are shown without parentheses; figures in parentheses are experimental.

the six electron terms of the quasimolecule for any ratio between the types of interaction[7] ($|\ldots|$ represents a determinant).

Figure 4 shows another example of the exchange interaction, i.e., that involving two oxygen atoms (in the ^3P state). The spin-orbital interaction is now so small that it cannot be seen on the scale of the figure. To the left of the region of matching, we give the terms obtained by the variational method[30] which cannot be used for large R. On the right, we show the asymptotic terms.[31] It is clear that the matching between the two sets of data is satisfactory, and that the characteristic term energies in this region amount to about one-twentieth of the excitation energy corresponding to the next oxygen term (^1D). The asymptotic and variational methods give sharply differing results for only one Π_g term.

Figure 5 shows another case where the spin-orbital interaction is very large (the I_2 molecule). Comparison of the asymptotic (solid lines) and experimental (dashed curves) terms converging to the two fine-structure components of I (dissociation limits for $^2P_{1/2} + ^2P_{1/2}$ and $^2P_{3/2} + ^2P_{1/2}$, respectively) shows the high precision of the asymptotic method.[22]
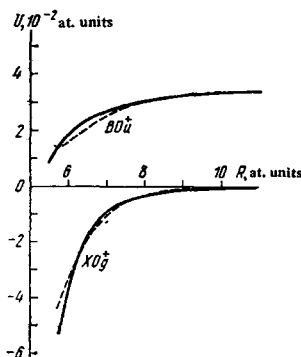

FIG. 5. Interaction potential for two iodine atoms[32]: dashed curve—experimental, solid curve—calculations by the asymptotic method.

It is important to note that in all the cases considered the exchange interaction plays an important, if not the dominant, role in the above range of distances. Even in the case of the interaction between alkali metal atoms in the ground and resonantly excited states, where the long-range interaction potential decreases as R^{-3}, calculations[33] of the exchange interaction show that this interaction is important for transitions between fine-structure components.

Finally, we mention the interesting possibility of using the above methods for term calculations at moderate distances by direct substitution of the exchange integrals tabulated in handbooks on quantum chemistry. A comparison of this method with the asymptotic method has been carried out in the literature[34] for a number of diatomic hydrides. As an example, Table II compares the parameters of an inert-gas crystal,[29] calculated on the basis of the exchange and long-ranged interactions, with results of measurement.

So far, we have confined our attention to the first two types of exchange interaction (Fig. 1), which involve a transition of the valence electron from the field of one atomic residue to the field of the other, or the simultaneous exchange of two electrons. The criterion for the validity of the asymptotic approach to the evaluation of the exchange interaction potential is that the separation between the nuclei must be large:

$$R \gg \frac{1}{\gamma}, \qquad R \gg \frac{a_0}{\gamma^2}, \qquad \gamma = \frac{\gamma_1 + \gamma_2}{2} \tag{1.16}$$

At the same time, the electron ionization potentials of both particles are similar but, if they do differ, the asymptotic approach used as indicated above is valid provided

$$R |\gamma_1 - \gamma_2| < 1. \tag{1.17}$$

It is only in this case that the exchange interaction potential is determined by the distributions of the electrons in the region between the nuclei.

If, on the other hand, the ionization potentials for the two atomic states are appreciably different, then the condition given by (1.17) is violated at large distances. Physically this means that the exchange interaction is determined by the region near the atom with the larger ionization potential. In the limiting case of a very large difference between the ionization potentials, the inter-

action picture can again be simplified. In particular, the effect of a perturbed "compact" atom on a weakly-bound valence electron in another atom is equivalent to the presence of the pseudopotential[36,37]

$$V = 2\pi L \frac{\hbar^2}{m} \delta(\mathbf{r} - \mathbf{R}), \qquad (1.18)$$

where L is the scattering length for the electron atom, $\mathbf{R}$ represents the position of the perturbing atom, and $\mathbf{r}$ is the position vector of the valence electron. Hence, according to perturbation theory, the interaction potential is given by

$$U = \langle \Psi | V | \Psi \rangle = 2\pi \frac{\hbar^2}{m} L \psi^2 (\mathbf{R}), \qquad (1.19)$$

where $\psi(\mathbf{R})$ is the wave function of the valence electron at the point occupied by the perturbing atom.

The above problem was first put forward by Fermi[38,39] in the course of an analysis of the shift of the spectral lines of alkali metal atoms in an inert gas. The Fermi formula for the spectral-line shift can be obtained by averaging (1.19) over the positions of the inert-gas atoms. Equation (1.19) was first derived by Ovchinnikova,[40] and the subsequent expansion terms of the interaction potential in terms of a small parameter were obtained by Alekseev and Sobel'man[41] for the case where the perturbing atom lies in the classically accessible region of motion of the valence electron. The opposite case has also been treated in the literature.[42]

The pseudopotential can be used as one of the elements in the energy matrix to determine the position of the electron terms for atoms of different sizes in a more complicated situation. The criterion for the validity of this approach demands that the size of one of the atomic particles should be small in comparison with the other. When this is so, this criterion enables us to investigate changes in the electron energy comparable with the electron binding energy. In particular, this method can be used to investigate the crossing between the electron term of the quasimolecule, consisting of the negative ion and the atom, and the continuous-spectrum limit.[5,43] We note that, when the asymptotic method is valid, the exchange interaction potential is much smaller than the binding energy of the valence electron.

The type of interaction which we have been considering characterizes the transition to a new type of bonding. Let us suppose that the perturbing atom can form a bound state with the electron, i.e., a negative ion. The scattering length L is then negative, and the interaction is attractive. This can also be understood in a different way; part of the electron is "located" in the well produced by the perturbing atom, and this leads to the appearance of charges on the interacting atoms. This is the so-called ionic bonding. It plays an important role in chemical bonds and in certain other elementary processes. The presence of ionic bonding and its influence on particle interaction is, however, more complicated than the above description would suggest.[44] Ionic states play an important role in the appearance of ionic bonding. As an example, Fig. 6 shows the potential curve for a system of interacting atoms in the presence
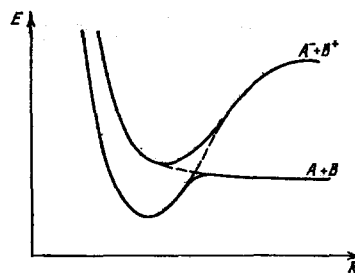

FIG. 6. Hypothetical behavior of the terms of a system subject to ionic bonding. Dashed curves show the potential curves in the absence of interaction between the ionic and covalent states, assuming that the covalent interaction is repulsive. The influence of the ionic states leads to the appearance of a well in the interaction potential between the atoms.

of ionic states.

In conclusion of this section, we note that our aim has been to provide a description of the exchange interaction between atomic particles and to demonstrate the value of the asymptotic approach to the determination of this interaction. The above material therefore uses only part of the existing information on the interaction potentials between atomic particles at large separations.

2. TRANSITIONS BETWEEN QUASIRESONANT STATES DURING COLLISIONS

We must now consider transitions between quasiresonant states in the course of slow collisions. The character of transitions between these states is determined by the size of the Massey parameter ξ, which is equal to the ratio of the effective collision time a/v to the transition time $\hbar/\Delta\varepsilon$:

$$\xi = \frac{\Delta \varepsilon a}{\hbar v}, \qquad (2.1)$$

where $\Delta\varepsilon$ is the transition energy, v is the relative collision velocity, and a is the characteristic length over which there is an appreciable change in the interaction. When $\xi \gg 1$, the transitions are adiabatically of low probability, and the transition probability is of the order of $e^{-\xi}$. We are interested in the case where the above process occurs efficiently enough to ensure that $\xi \lesssim 1$.

Under quasiclassical conditions, when the wavelength λ of relative motion is small in comparison with the characteristic size a, the nonadiabatic condition ($\xi \lesssim 1$) will automatically ensure that the transition energy is small in comparison with the kinetic energy E of the atoms:

$$\frac{\Delta\varepsilon}{E} = \xi \frac{\lambda}{a} \ll 1. \qquad (2.2)$$

If, in addition, we demand that the energy of the adiabatic electron states should be small in comparison with the kinetic energy for all interatomic distances that are significant for the process, i.e.,

$$\varepsilon(R) \ll E, \qquad (2.3)$$

then the system of quantum-mechanical equations de-

scribing the scattering process can be reduced to a semi-classical system, and the latter can be written down for rectilinear trajectories of the nuclei. In other words, complete information on the collision is provided by the scattering amplitudes $a_n(t)$ in the expansion of the time-dependent electron wave function of the quasimolecule in terms of the molecular wave functions:

$$\Psi(t) = \sum_n a_n \psi_n \exp\left(-\frac{i}{\hbar} \int^t \varepsilon_n \, dt'\right); \qquad (2.4)$$

where the sum is evaluated over the molecular states n that are adiabatically correlated with the initial and final states of the system, and it is assumed that there are no transitions to "distant" states. The equations for a_n that are equivalent to the time-dependent wave equation for $\Psi(t)$ in the restricted set of basis functions, have the form

$$i\hbar a_n = \sum_{n'} c_{nn'}(t) a_{n'}(t) \exp\left[-\frac{i}{\hbar} \int^t (\varepsilon_{n'} - \varepsilon_n) \, dt'\right]. \qquad (2.5)$$

The coupling between the equations in the adiabatic basis is provided by the matrix elements of the nonadiabatic coupling operator $c_{nn'}$, for which there are well-known general selection rules and methods for approximate calculation. Integration of the equations along rectilinear paths for different initial conditions gives a set of amplitudes completely defining the semiclassical scattering matrix which depends parametrically on the collision impact parameter ρ.

This formulation of the problem will, of course, substantially simplify the calculation of probabilities and cross sections, as compared with the rigorous quantum-mechanical approach but, nevertheless, the equations are still difficult to solve. Although such sets of equations, including tens or hundreds of channels, can be successfully solved by computers, the correlation between the interaction and the cross sections is lost in the solution, i.e., the information on the mechanism of the process in which we are specifically interested is lost. This is why approximate, but physically clear, methods, that can be used to follow all the details of the mechanism, continue to be important.

One of these methods is based on the transformation of the basis functions so that the interaction between the states in the new basis is localized within relatively small ranges of variation of ΔR. The particular form of the transformation depends on the physical picture of the process and is determined by the relative importance of the different interactions. A possible choice, based on the introduction of time-dependent Hund coupling is discussed in Sec. 4. Here, however, it is important to note that, if the nonadiabatic interaction is localized in a relatively small part of the overall domain of variation, the complete solution of the equations can be constructed by matching solutions obtained for different regions, and the set of equations can be substantially simplified in each region. At the same time, the solution of the equations in the intervals between the regions of nonadiabatic interaction can be obtained in explicit form as an independent evolution of the system over the individual terms.

The most probable of all the possible situations is the one in which two states are strongly coupled in a localized nonadiabatic region. We shall, therefore, confine our attention to this case. It is known in the literature as the two-state or two-level approximation. The time-dependent wave function in the basis of two adiabatic electron states of the quasimolecule, Ψ_1 and Ψ_2, can be written in the form

$$\Psi(t) = a_1(t) \psi_1 \exp\left(-\frac{i}{\hbar} \int^t \varepsilon_1 \, dt'\right) + a_2(t) \psi_2 \exp\left(-\frac{i}{\hbar} \int^t \varepsilon_2 \, dt'\right). \quad (2.6)$$

where the coefficients a_1 and a_2 satisfy the equations

$$i\hbar a_1 = c_{12} \exp\left[\frac{i}{\hbar} \int^t (\varepsilon_1 - \varepsilon_2) \, dt'\right] a_2,$$
$$i\hbar a_2 = c_{21} \exp\left[\frac{i}{\hbar} \int^t (\varepsilon_2 - \varepsilon_1) \, dt'\right] a_1, \qquad (2.7)$$

where $\varepsilon_1, \varepsilon_2$ are the adiabatic electron terms of the quasimolecule, which contain the separation between the nuclei as a parameter, and $c_{12} = \langle \psi_1 - i\hbar \partial/\partial t | \psi_2 \rangle$ is the matrix element of the nonadiabatic coupling operator.

We shall now consider the case of resonant charge transfer between the ion and the atom (or some other similar resonant process), when the process takes place without a transition between the states of the quasi-molecules. The probability amplitudes $a_{1,2}$ in (2.6) are then time-independent, and the wave function (2.6) can be written in the form (see Fig. 2)

$$\Psi(t) = \frac{1}{2}(\psi_1 + \psi_2) \exp\left(-\frac{i}{\hbar} \int_{-\infty}^t \varepsilon_g \, dt'\right) + \frac{1}{2}(\psi_1 - \psi_2) \exp\left(-\frac{i}{\hbar} \int_{-\infty}^t \varepsilon_u \, dt'\right),$$
$$(2.8)$$

where ψ_1, ψ_2 correspond, in accordance with Fig. 2, to finding the electron in the field of the first or the second atomic residue, respectively, $\varepsilon_g, \varepsilon_u$ are the energies of the even and odd states of the quasimolecule, which contain the separation between the nuclei as a parameter, and the initial conditions are chosen so that the electron is located near the first nucleus prior to collision $(\Psi(-\infty) = \psi_1)$.

The particles approach each other during the collision process, and the energies of the even and odd states become different. Therefore after the encounter the interference between even and odd states of the quasimolecule will be different from the initial interference. In particular, according to (2.8), the electron transition probability [the square of the coefficient in front of ψ_2 in (2.8)] is given by[16]

$$w = |\langle \Psi(\infty) | \psi_2 \rangle|^2 = \sin^2 \int_{-\infty}^{+\infty} \frac{(\varepsilon_g - \varepsilon_u)}{2\hbar} \, dt. \qquad (2.9)$$

We now return to the two-level approximation described by (2.8). Nonadiabatic coupling is usually localized, i.e., $c_{12}(t)$ reaches its maximum value at some instant of time, which we take as the origin, and then falls to zero quite rapidly on either side of the maximum. The probability of a nonadiabatic transition between states for a single transit through the region of nonadiabatic coupling is given by

$$P_{12} = |a_2(+\infty)|^2 \qquad (2.10)$$

subject to the initial conditions

$$a_1(-\infty) = 1, \quad a_2(-\infty) = 0. \tag{2.11}$$

The limits $\pm\infty$ are taken in the sense that, both at the beginning and the end of the process, the system is far removed from the nonadiabatic region, so that, the coupling c_{12} can be neglected.

It is frequently convenient to formulate the problem not in the adiabatic but in the diabatic basis. If we introduce the function

$$\chi(t) = \int_{-\infty}^{t} \frac{c_{12}}{i\hbar} dt, \tag{2.12}$$

which tends adiabatically to the constant values

$$\chi(-\infty) = 0, \\ \chi(\infty) = \pi - \theta = \chi_\infty, \tag{2.13}$$

the adiabatic basis ψ_1, ψ_2 will uniquely determine the diabatic basis φ_1, φ_2, the functions of which are time-independent:

$$\psi_1(t) = \cos\frac{\chi(t)}{2} \cdot \varphi_1 + \sin\frac{\chi(t)}{2} \cdot \varphi_2, \\ \psi_2(t) = -\sin\frac{\chi(t)}{2} \cdot \varphi_1 + \cos\frac{\chi(t)}{2} \cdot \varphi_2. \tag{2.14}$$

Next, Ψ is expanded in terms of the diabatic functions:

$$\Psi(t) = b_1(t)\,\varphi_1 \exp\left(-\frac{i}{\hbar}\int^t H_{11} dt'\right) + b_2(t)\,\varphi_2 \exp\left(-\frac{i}{\hbar}\int^t H_{22} dt'\right), \tag{2.15}$$

and the coefficients b_1, b_2 satsify the following set of equations:

$$i\hbar\dot b_1 = H_{12}\exp\left(\frac{i}{\hbar}\int^t \Delta H\, dt'\right) b_2, \quad i\hbar\dot b_2 = H_{21}\exp\left(-\frac{i}{\hbar}\int^t \Delta H dt'\right) b_1, \tag{2.16}$$

where $\Delta H = H_{11} - H_{22}$ is the difference between the diabatic terms and H_{12} is the nondiagonal matrix element of the interaction, which can be expressed in terms of $\varepsilon_1 - \varepsilon_2$ and χ:

$$\Delta H = (\varepsilon_1 - \varepsilon_2)\cos\chi(t), \tag{2.17}$$
$$2H_{12} = (\varepsilon_1 - \varepsilon_2)\sin\chi(t). \tag{2.18}$$

The transition probability P_{12}, given by (2.10), can be calculated in the diabatic basis from

$$P_{12} = \lim_{t\to\infty} |\langle\Psi(t)|\varphi_2\rangle|^2 = \lim_{t\to\infty}\left| -b_1(t)\sin\frac{\chi_\infty}{2}\exp\left(-\frac{i}{\hbar}\int^t H_{11}dt'\right)\right.$$
$$\left. + b_2(t)\cos\frac{\chi_\infty}{2}\exp\left(-\frac{i}{\hbar}\int^t H_{22}dt'\right)\right|^2 \tag{2.19}$$

if (2.16) are integrated subject to the initial conditions

$$b_1(-\infty) = 1, \quad b_2(-\infty) = 0. \tag{2.20}$$

We note that the initial conditions for a_1 in (2.11) and for b_1 in (2.20) are the same since, in the limit as $t \to -\infty$, the diabatic basis, constructed taking into account the definition of χ in accordance with (2.13), becomes identical with the adiabatic basis.

It is clear from (2.13) and (2.17) that the conditions for localized adiabatic coupling do not mean that coupling between the diabatic terms vanishes in the limit as t

$\to +\infty$. In fact, the ratio $H_{12}/\Delta H$, which vanishes in the limit as $t \to -\infty$ by virtue of the particular choice of the diabatic basis, tends to the constant value $H_{12}/\Delta H = (1/2)\tan\chi_\infty$ in the limit as $t \to +\infty$.

The calculation of the transition probability can, of course, be carried out in any basis, but the adiabatic basis is frequently the most natural because it arises in the course of choosing an approximate basis of electron functions, the weak dependence of which on the internuclear coordinates can be neglected.

We now consider the simple gyroscopic interpretation of (2.5) or (2.16). If we look upon $b_1 b_1^* - b_2 b_2^*$, $b_1 b_2^*$, $b_1^* b_2$ as the spherical components of a unit vector $\mathbf{m}$, the two equations in (2.16) for the four complex quantities satisfying a single normalization condition is equivalent to the following set of three equations for the components of the precessing unit vector $\mathbf{m}$:

$$\dot{\mathbf{m}} = \frac{1}{\hbar}[\nu \times \mathbf{m}], \tag{2.21}$$

where the vector ν is defined by the components

$$v_x = 2\,\mathrm{Re}\,H_{12}, \quad v_z = 2\,\mathrm{Im}\,H_{12}, \quad v_y = \Delta H. \tag{2.22}$$

For the case under consideration when H_{12} is real, i.e., for $v_z = 0$, the time dependence of $\nu(t)$ can be represented by the curve in the x, y plane, traced out by the end-point of the vector ν. It is clear that the length of the vector ν is equal to the adiabatic term splitting, and the matrix element of the nonadiabatic coupling is equal to the rate at which it rotates relative to the axes.

The adopted diabatic basis and the initial conditions correspond to the fact that the vectors ν and $\mathbf{m}$ are parallel to the z axis when $t \to -\infty$. Next, the vector $\nu(t)$ rotates, and $\mathbf{m}$ follows ν with a certain lag, and precesses. In the limit as $t \to \infty$, the vector ν tends to a constant ν_∞, and the vector $\mathbf{m}$ precesses around ν_∞ with a frequency determined by the magnitude of ν_∞ and the angle β which characterizes the degree of departure from the adiabatic situation as $\mathbf{m}$ follows ν. It is readily verified that P_{12} is given by

$$P_{21} = \frac{1}{2}(1 - \cos\beta) = \frac{1}{2}\left[1 - \frac{\mathbf{m}(\infty)\,\mathbf{v}(\infty)}{\mathbf{v}(\infty)}\right]. \tag{2.23}$$

Other initial conditions for (2.21) correspond to the fact that the vector $\mathbf{m}$ has an arbitrary orientation relative to the y axis for $t \to -\infty$, and its precession around ν with a constant angle between $\mathbf{m}$ and ν corresponds to the adiabatic development of the system.

This gyroscopic interpretation of the two-level system provides a particularly simple characterization of the various available models, ascribing to them certain lines in the x, y, t space, which in turn characterize the evolution of the vector $\nu(t)$. The projection of these lines onto the x, y plane gives curves which no longer contain information on the rate of variation of $\nu(t)$, but they nevertheless provide a characterization of the particular model employed. Figure 7 shows loci of the vector ν for which the solutions of (2.7) and (2.16) have been adequately investigated. These equations are widely used in the interpretation of quasiresonant processes.[53,54]
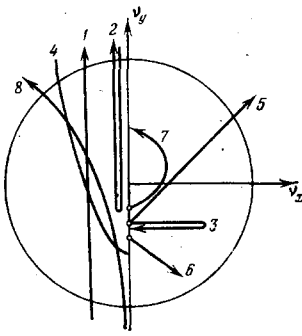
E. E. Nikitin and B. M. Smirnov

FIG. 7. Loci ν_x, ν_y of the end-point of the vector ν for which the two-level approximation leads to an analytic solution: 1—Landau-Zener case[7]; 2—generalization of this model obtained by taking into account the influence of the turning point[45]; 3—Rosen-Zener-Demkov case[46]; 4,5—exponential models[47,49]; 6,7—hypergeometric models[50]; 8—linear-exponential model. [52]

Some of these models have recently been generalized to the case of complex terms describing both the non-adiabatic interaction and the adiabatic decay of states.[53,54]

The solution of the two-level problem (2.7) in the case of localized nonadiabatic coupling and sufficient separation between the turning point and the transition region, is completely characterized by the nonadiabatic transition matrix which depends on transition probability P_{12} for a single crossing of the nonadiabatic region and on the so-called dynamic phases which originate in a nonadiabatic crossing. If the matrices N are known for different nonadiabatic coupling regions, the scattering matrix is obtained by multiplying the adiabatic matrices A, which are diagonal in the chosen basis, by the transition matrices N. We emphasize once again that this method can be used to construct the multichannel S-matrix although two states (different in each case) are coupled in each region.[105]

To elucidate the foregoing, consider the case where there are only two terms and one nonadiabatic coupling region. We shall define its position by the distance R_p at which the matrix element of the nonadiabatic interaction is a maximum, i.e., $c_{12}(R_p) \equiv c_p$. In this case,

$$S = A N^* A^* N A, \qquad (2.24)$$

where A^* and A are diagonal matrices describing the advance of phase during adiabatic motion over terms for $R > R_p$ and $R < R_p$. The transition probability $\mathcal{P}_{12}$ for a double crossing of the nonadiabatic region resulting from a collision between the atoms [in contrast to the transition probability P_{12} for a single crossing defined by (2.10)] can be expressed in terms of the nondiagonal element of the S-matrix and, consequently, in terms of the parameters contained in the N and A matrices:

$$\mathcal{P}_{12} = |S_{12}|^2 = 4P_{12}(1 - P_{12})\sin^2(\Phi + \varphi), \qquad (2.25)$$

where Φ is the so-called Stuckelberg phase which is determined only by the character of the adiabatic terms for $R < R_p$, and φ is the dynamic phase. In this procedure, $\Phi \gg 1$ and represents the fact that the transition

region must be far removed from the turning point.

As an example, we reproduce the expression for P_{12} in the case of the exponential model,[47,48] of which the Landau-Zener and Rosen-Zener models are limiting cases. The probability P_{12} and the phase φ in this model are functions of two parameters. These can be conveniently taken to be the ratio of the maximum value of the matrix element of the nonadiabatic coupling U_p to the splitting Δ of the adiabatic terms at $R = R_p$, and the adiabatic mixing parameter χ.

If we define ξ by

$$\frac{U_p}{\Delta} = \frac{\operatorname{ctg}\bar{\chi}}{2\xi}, \qquad (2.26)$$

then the probability P_{12} will be given by

$$P_{12} = \exp\left[-\frac{\pi\xi}{2}(1 + \cos\bar{\chi})\right] \frac{\operatorname{sh}[(\pi\xi/2)(1 - \cos\bar{\chi})]}{\operatorname{sh}\pi\xi}. \qquad (2.27)$$

We note that the parameter ξ in (2.26) and (2.27) has the same interpretation as the Massey parameter given by (2.1), and this justifies the use of this notation here.

The expression for the dynamic phase φ in terms of ξ and $\bar{\chi}$ is also known.[55] As regards the phase Φ, this remains a free parameter, subject only to the condition $\Phi \gg 1$ and determined by the behavior of the terms for $R < R_p$.

We must now briefly consider the applications of model solutions.

The Landau-Zener model [Eq. (2.27) in the limit of $\bar{\chi} \to \pi$ and U_p/Δ finite] has frequently been used to calculate the total and differential cross sections in the case of quasicrossing terms (see, for example, the reviews given by Nikitin and Ovchinnikova[135] and by Lavrov[136]). Its generalizations to cases where the condition $\Phi \gg 1$ can be removed were found to be essential in the evaluation of the total and differential cross sections near the threshold in energy[52] and angle,[56] and even at the maximum of the total cross section, because of the appreciable contribution of nonadiabatic tunneling transitions for trajectories with large impact parameters.[137] It was also found that the sharp dependence of the non-diagonal interaction element in the diabatic basis on the interatomic distance, which is exhibited by the linear-exponential model, has a substantial influence on the cross section at low energies and may lead to two maxima in the velocity dependence of the cross section.[51,52]

The special case of the exponential model [formula (2.27) in the limit as $\bar{\chi} = \pi/2$], initially put forward to describe nonresonant charge transfer,[151,152] is being successfully used at present both for processes with large energy transfers (transitions between inner shells of atoms[85]) and with very small energy transfers (transitions between states displaced as a result of the isotopic shift[95]). We also note that the general case of the exponential model (arbitrary $\bar{\chi}$) is being used to describe transitions between quasimolecular terms correlated with different fine-structure components of atoms. The relative flexibility of this model suggests that it may be applicable for describing effects associated with the coherent population of atomic states where

it is known that the results depend to a significant extent not only on the probability but also on the phase.[197] So far, the transition probability has been calculated for model processes of this type only for special cases of the exponential model.[198]

Thus, the availability of different model solutions enables us to consider a broad class of problems subject to the condition that only pairs of states interact strongly in localized regions. As regards weak interactions between this pair and other states, it is found that their inclusion presents no difficulties within the framework of this or some other variant of perturbation theory. Certain resonant and quasiresonant processes are discussed below from this point of view.

3. RESONANT CHARGE EXCHANGE BETWEEN AN ION AND AN ATOM OR A MOLECULE

We shall now consider the simplest resonant process, namely, resonant charge exchange between an ion and an atom or a molecule. This process proceeds in accordance with the scheme

$$A^+ + \tilde{A} \to A + \tilde{A}^+, \qquad (3.1)$$

where the tilde labels one of the nuclei. Resonant charge exchange occurs with large cross sections, much greater than the elastic cross section for the collision between an ion and an atom, even at thermal collision energies. Resonant charge exchange between an ion and an atom will therefore determine processes associated with the motion of an ion in its own gas and, in particular, quantities such as the mobility and the diffusion coefficients of the ion in its own gas. As an example, Fig. 8 shows the "relay" type of charge exchange during the motion of an ion in its own gas (this is the Sena effect). Henceforth, we shall confine our attention to the cross section for the resonant charge exchange.

We begin by considering resonant charge exchange corresponding to the transition of an s electron when the transition takes place only between two states. Using (2.3) for the probability of resonant charge exchange we
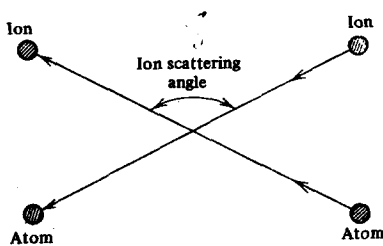

FIG. 8. "Relay" charge transfer (Sena effect[57]) during resonant charge exchange between an ion and a neutral atom of the same kind. Since the resonant charge exchange occurs in distant encounters, there is no elastic scattering and particles move along rectilinear trajectories. As a result of resonant charge exchange an initially neutral particle becomes an ion. This means that charge exchange results in a change in both the direction and magnitude of the velocity, and the ion assumes the parameters of the initially neutral particle, so that the scattering of the ion is due to resonant charge exchange.

obtain the following expression for the resonant charge exchange cross section[16,62]

$$\sigma = \int_0^\infty 2\pi\rho \, d\rho \, \sin^2 \int_{-\infty}^{+\infty} \frac{\Delta(R)\,dt}{2\hbar}. \qquad (3.2)$$

The main contribution to this cross section is due to large impact parameters $\rho \sim R_0$. Bearing this in mind, we shall evaluate (3.2) on the basis that the exchange interaction potential $\Delta(R)$ is largely an exponential function of the distance R between the nuclei [see (1.11)], i.e., $\Delta(R) = \Delta(R_0) e^{-\gamma(R-R_0)}$ for $R \sim R_0$. This means that our calculation will be equivalent to the expansion of the integral (3.2) in powers of $1/\gamma R_0 \ll 1$. Accordingly, we divide the integral (3.2) into two parts so that, in the first, the phase is

$$\zeta = \int_{-\infty}^{+\infty} \frac{\Delta \, dt}{2\hbar} \gg 1,$$

and, in the second, we can use the exponential approximation for this quantity. In the first region, the integrand oscillates rapidly around the value of 1/2 and can be replaced by this value, and, in the second, the integral can be evaluated exactly, bearing in mind the small range of the impact parameters that define it. To within terms of the order of $1/\gamma^2$, we have

$$\sigma = \frac{\pi R_0^2}{2} + \int_{R_0}^\infty 2\pi\rho \, d\rho \, \sin^2 \zeta(R_0) \, e^{-\gamma(\rho-R_0)}$$

$$= \frac{\pi R_0^2}{2} + \frac{\pi}{\gamma^2}(\ln\zeta + \gamma R_0)(C + \ln 2\zeta) - \frac{\pi}{2\gamma^2}\ln^2\zeta + \frac{\pi}{2\gamma^2}(C + \ln 2) - \frac{\pi^3}{24\gamma^2},$$

where $C = 0.577$ is the Euler constant. The quantity R_0 can be obtained from the condition that the terms linear in R_0 in the cross section for the resonant charge-exchange process must vanish. As a result, we obtain[58]

$$\sigma = \frac{\pi R_0^2}{2} - \frac{\pi^3}{24\gamma^2} + O\left(\frac{1}{\gamma^3 R_0}\right), \qquad (3.3)$$

where $\zeta(R_0) = e^{-C}/2 = 0.28$.

Let us examine this result in detail. The very idea of the asymptotic approach consists of the expansion of the transition cross section in terms of a small parameter. This enables us to estimate the magnitude of the neglected terms and hence the precision of the calculation. Let us estimate the precision first. In the evaluation of the integral (3.2), the main error is connected with the fact that we have excluded all information about the behavior of the system at distances comparable with the dimensions of the atom. This means that we use asymptotic expressions for the exchange interaction potential, and that inelastic transitions may occur at these distances and the two-level approximation will be violated.[4] It follows that the uncertainty in the calculated cross section turns out to be of the order of the cross

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[4] The behavior of the exchange interaction potential at distances comparable with the atomic dimensions, and the appearance of inelastic channels in close encounters, result in oscillations of the total cross section for the resonance charge exchange process (see for example, Smirnov[4]). The amplitude of the oscillations of the cross section, which characterizes the precision of our calculations, turns out to be of the order of $1/\gamma^2$.

106   Sov. Phys. Usp. 21(2), Feb. 1978

E. E. Nikitin and B. M. Smirnov   106

section of the atoms, i.e., of the order of $1/\gamma^2$.

Let us now examine the expression given by (3.3) for the resonant charge exchange cross section. Assuming that both the ion and the atom move along straight paths, and using the exponential dependence of the exchange interaction potential Δ on the separation between the nuclei, we obtain the following expression in the limit under consideration:

$$\sigma = \frac{\pi R_0^2}{2}, \quad \text{where } \frac{1}{v}\sqrt{\frac{\pi R_0}{2\gamma}}\,\Delta(R_0) = 0.28. \qquad (3.4)$$

This formula, together with the expression given by (1.11) for the exchange interaction potential, enables us to calculate the resonant charge exchange cross section connected with an s-electron transition. Some of the results[59] are listed in Table III. Let us examine them in detail.

We begin by considering the dependence of the resonant charge exchange cross section on the collision velocity. Since the exchange interaction potential is an exponential function of distance, we can write (3.4) in the form $\sigma = \pi R_0^2/2$, where $(1/v)f(R_0)e^{-\gamma R_0} = 1$ and $f(R)$ is a power-law function of the separation between the nuclei. The final result turns out to be[60–62]

$$\sigma = \frac{\pi}{2\gamma^2}\ln^2\frac{v_0}{v}, \qquad (3.5)$$

where v_0 is a slowly-varying (logarithmic) function of velocity. The resonant charge exchange cross section thus turns out to be a function of the logarithm of the relative collision velocity.

The formulas given by (3.4) and (1.11) enable us to calculate the resonant charge exchange cross section. Let us estimate the uncertainty introduced by this procedure. Experience shows that the maximum uncertainty is due to an incomplete knowledge of the exchange interaction potential because of the uncertainty in the asymptotic coefficient A. Let us suppose that the uncertainty in A is ΔA. Since $\Delta \sim A^2$, we can determine the uncertainty in the resonant charge exchange cross section. The replacement of A by $A + \Delta A$ is equivalent to the replacement of v_0 by $v_0[1 + (\Delta A/A)]^2$ in (3.5). This leads to the following change $\Delta\sigma$ in the resonant charge exchange cross section (we are assuming that $\Delta A/A \ll 1$):

$$\frac{\Delta\sigma}{\sigma} = \frac{\Delta\sigma}{\pi R_0^2/2} = \frac{4\Delta A}{\gamma R_0}\frac{A}{A}.$$

It follows from Table I that, in realistic cases, the characteristic value of the small expansion parameter is $1/\gamma R_0 \sim 1/10$. Hence, we find that our relative uncertainty of $\Delta A/A = 20\text{–}30\%$. The uncertainty due to the use of the above asymptotic method is then shown by our earlier analysis to be of the order of $1/(\gamma R_0)^2$, which is of the order of 1% in realistic cases.

Now consider the collision between an ion and an atom with unfilled electron shells. The exchange interaction potential then depends on the complete set of quantum numbers of the ion and the atom [see (1.15)], and the states involved in the transition turn out to be degenerate in the components of the angular momenta, so that the

TABLE III. Parameters determining the resonant charge exchange cross section.

Type of ion and atom	State of ion	State of atom	γ	A	Resonant charge exchange cross section (10^{-15} cm^2) at the stated incident ion energy, eV			γR_0 *)
					0.1	1	10	
H	^1S	^2S	1.00	2.00	6.2	5.0	3.8	11.9
He	^2S	^1S	1.344	2.87	3.5	2.8	2.1	12.0
Li	^1S	^2S	0.629	0.82	26	22	18	15.3
C	^2P	^3P	0.910	1.30	6.2	5.0	3.8	10.8
N	^3P	^4S	1.033	1.49	4.9	3.8	2.9	10.9
O	^4S	^3P	1.000	1.32	5.2	4.3	3.5	10.9
F	^3P	^2P	1.132	1.59	3.6	2.9	2.2	10.2
Ne	^2P	^1S	1.259	1.75	3.2	2.5	1.9	10.7
Na	^1S	^2S	0.615	0.74	31	26	22	16.3
Mg	^2S	^1S	0.749	1.32	19	16	13	15.6
Al	^1S	^2P	0.663	0.61	16	13	10	12.6
Si	^2P	^3P	0.774	1.10	9.8	7.7	6.0	11.6
P	^3P	^4S	0.878	1.65	8.1	6.5	5.0	11.9
S	^4S	^3P	0.873	1.11	8.7	6.7	5.5	12.3
Cl	^3P	^2P	0.978	1.78	5.8	4.6	3.6	11.2
Ar	^2P	^1S	1.070	2.11	5.5	4.5	3.5	12.0
K	^1S	^2S	0.565	0.52	41	35	29	17.2
Ca	^2S	^1S	0.670	0.95	26	21	18	16.3
Cr	^6S	^7S	0.705	1.13	21	18	14	15.4
Fe	^6D	^5D	0.762	1.40	21	18	14	16.6
Cu	^1S	^2S	0.753	1.29	19	16	13	15.6
Br	^3P	^2P	0.933	1.83	6.8	5.5	4.5	11.6
Kr	^2P	^1S	1.014	2.22	4.8	3.9	3.1	10.6
Pb	^1S	^2S	0.555	0.48	45	39	32	17.8
Ag	^1S	^2S	0.746	1.18	20	17	14	15.9
Cd	^2S	^1S	0.813	1.59	17	14	12	16.0
In	^1S	^2P	0.652	1.58	19	16	13	13.6
J	^3P	^2P	0.876	1.94	8.0	6.8	5.3	11.8
Xe	^2P	^1S	0.944	2.37	9.1	7.5	6.0	13.6
Cs	^1S	^2S	0.535	0.39	53	45	38	18.6
Ba	^2S	^1S	0.649	0.72	35	30	25	17.5
Au	^1S	^2S	0.823	1.41	17	14	11	16.2
Hg	^2S	^1S	0.876	1.82	15	12	10	16.2
Tl	^2P	^1S	0.670	0.65	19	15	12	13.9

*) At 0.1 eV ion energy.

two-level approximation can no longer be used. This means that the charge exchange process is accompanied in the course of collision by processes involving the rotation of the angular momenta of the atom and the ion, and, since the exchange interaction potentials between the ion and atom are functions of the components of the angular momenta of the ion and the atom, these processes are coupled. Nevertheless, if we use the small parameter of the theory, namely, $1/\gamma R_0 \ll 1$, we can separate these processes and present the results for the general case in the form of an expansion in terms of this parameter.

In fact, the transition occurs for large impact parameters for which the angle of rotation of the line joining the nuclei is small (see Fig. 9) and is of the order of $1/\sqrt{\gamma R_0}$. This enables us to separate the charge exchange process from the process involving the rotation of the angular momenta, and to use this to carry out an expansion of
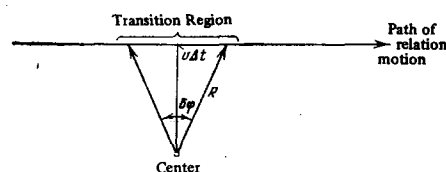

FIG. 9. Region of electron transition during resonant charge exchange. Because of the exponential interaction $\Delta \sim e^{-\gamma R}$, the transition occurs in the region $\Delta R \sim 1/\gamma$. The relative motion of the particles is such that $R^2 = \rho^2 + v^2 t^2$ and this is used to obtain the following result for the characteristic time interval of the transition: $(v\Delta t)^2 \approx R\Delta R \sim R/\gamma$ and the angle of rotation of the line joining the nuclei is $\delta\varphi \sim v\Delta t/R \sim 1/\sqrt{R\gamma} \ll 1$.
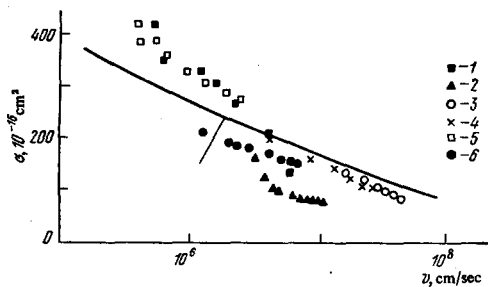
FIG. 10. Cross section for resonant charge exchange between an ion and an atom of potassium: solid curve—asymptotic theory[17]; 1, 2, 3, 4, 5, 6—experiment. [63,64,65,66,67,68]
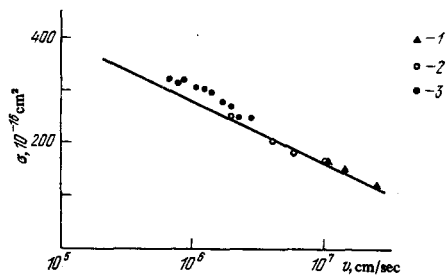

FIG. 11. Cross section for resonant charge exchange between an ion and an atom of rubidium: solid curve—asymptotic theory[17]; 1, 2, 3—experiment. [65,69,68]

the resonant charge exchange cross section in terms of the small parameter of the theory.

The asymptotic theory thus enables us to calculate the resonant charge exchange cross section with the inclusion of all the features of the real situation. Table III lists the resonant charge exchange cross sections for different pairs, together with the parameters which determine them and the values of the small expansion parameter of the asymptotic theory.[5] Figures 10–13 illustrate the comparison between theory and experiment for the charge exchange cross sections in some specific cases.

So far, we have confined our attention to the case where the relative collision velocity was small in comparison with the characteristic velocity of an electron in the atom, so that the nuclei could be assumed to be stationary during the electron transition. The main assumption of the theory is then connected with the fact that the electron transition proceeds from the "tail" of its wave function. Within the framework of this assumption, we can extend the results of the asymptotic theory to the case of high velocities as well.

Indeed, following Demkov et al.,[78] we find that, when the nuclei are allowed to move, the exponential $e^{-\gamma r}$ in the asymptotic expression for the wave function of the electron, given by (1.11), is replaced by $\exp[-\gamma r + (imvr/2\hbar)]$, where r is the separation between the electron and the nucleus, v is the relative velocity of the nuclei, and m is the electron mass. The inclusion of this factor corresponds to the replacement of γ in the resonant charge exchange cross section (3.5) by $\sqrt{\gamma^2 + (m^2 v^2/4\hbar^2)}$, so that (3.5) now assumes the form

$$\sigma = \frac{\pi}{2\left[\gamma^2 + (m^2 v^2/4\hbar^2)\right]}\ln^2\frac{v_0}{v}. \tag{3.6}$$

This is a generalization of (3.5) and is valid as long as the resonant charge exchange cross section is large in comparison with the characteristic atomic cross section, i.e., $\sigma \gg 1/\gamma^2$. This leads to the following restriction on the velocity:

$$v \ll \frac{\hbar\gamma}{m}R_0\gamma, \tag{3.7}$$

where R_0 is given by (3.4) and is a slowly-varying function of velocity. Since $R_0\gamma \gg 1$, the formula given by (3.6) is valid even when the velocity substantially exceeds the velocity of the electron in an atomic orbit $(\hbar\gamma/m)$.

We note that (3.6) describes the case of charge exchange that is the precise opposite of the classical case of Brinkman and Kramers[79–81] which, in turn, corresponds to charge exchange in the limit of very high collision velocities. In the Brinkman-Kramers case, the charge exchange process involves the participation of the electron-distribution region near the nucleus, where the electron velocity is comparable with the relative collision velocity. In our case, on the other hand, the transition takes place from the "tail" of the electron wave function.

The entire foregoing analysis was concerned with resonant charge exchange between an atomic ion and a neutral atom of the same kind. The theory encounters additional difficulties in the case of resonant charge exchange between a molecular ion and a diatomic molecule. These are connected both with the complexity of the system and the presence of vibrational and rotational transitions both in the molecule and the ion. The theory becomes much more unwieldy and, since the parameters of the electron distribution in the molecule are known
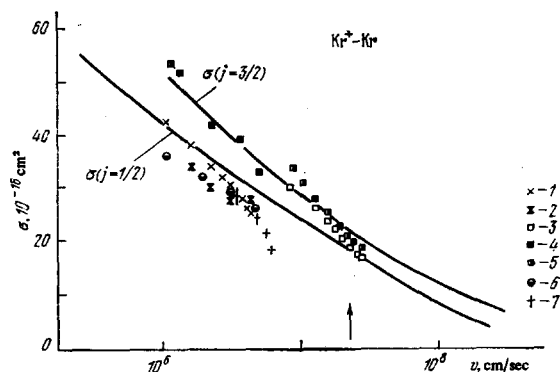

FIG. 12. Cross section for resonant charge exchange between an ion and an atom of krypton: solid curve—asymptotic theory[29]; 1, 2, 3, 4, 5, 6, 7—experiment. [70,71,72,63,73,74,75]

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[5]Asymptotic methods for calculating the resonant charge exchange cross sections have been used in recent years by Bardsley et al.,[168,169] whose results differ only slightly from those presented here.
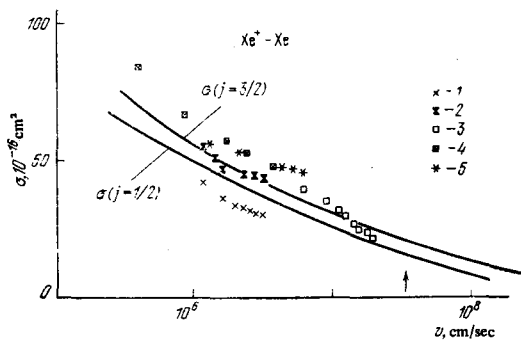
FIG. 13. Cross section for resonant charge exchange between an ion and an atom of xenon: solid curve—asymptotic theory[29]; 1, 2, 3, 4, 5—experiment. [76,71,72,63,77]

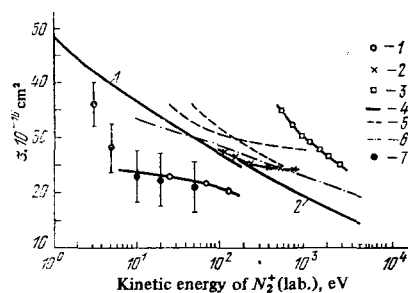FIG. 14. Cross section for resonant charge exchange between a molecular nitrogen ion and a nitrogen molecule: curves 1, 2—asymptotic theory[82] in the limit of large and small collision velocities relative to the excitation of vibrational states; points 1, 2, 3, 4, 5, 6, 7—experiment. [83,71,84,85,74,86,87]

with lower precision compared with the atom, the uncertainty in the results obtained from the asymptotic theory is then greater than in the case of resonant charge exchange involving atomic ions. Without dwelling on the special features of the asymptotic theory of resonant charge exchange involving molecular ions we demonstrate its possibilities in Fig. 14, which gives a comparison between theory and experiment in the case of the cross section for the resonant charge exchange between a molecular ion of nitrogen and a nitrogen molecule. It is clear that also in this case, the possibilities of the theory exceed those of current experiments.

4. QUASIRESONANT PROCESSES IN COLLISIONS BETWEEN ATOMS

Table IV summarizes quasiresonant collision processes between atoms that can be accompanied by small changes in the electron energy and that occur with cross sections large compared with the geometrical cross section of the atom. The above asymptotic methods of analyzing theoretically the cross sections for these processes are, therefore, valid. Let us briefly consider each of these processes.

Spin exchange is physically analogous to resonant charge exchange. Indeed, consider a collision between two atoms with spin 1/2 and suppose that the atomic spins are oppositely directed, i.e., that the component

of the resultant spin along a particular direction is zero. The coordinate eigenfunctions of the quasimolecule consisting of the colliding atoms will then have the form

$$\Psi = \frac{1}{\sqrt{2}} [\psi_a(1)\,\psi_b(2) \pm \psi_b(1)\,\psi_a(2)], \qquad (4.1)$$

where a and b label the atomic residues with which the corresponding electron forms a bond, and the numbers in parentheses label the electrons. Positive signs correspond to zero resultant spin and negative signs to unit resultant spin.

The wave function of the system of atoms prior to collision corresponds to the situation where the first electron is in the atomic residue a and the second in the atomic residue b. It is a combination of the wave functions in (4.1). Interference between the two states in the course of collision between the atoms may lead to electron exchange, i.e., to the transition of the first electron to the field of the atomic residue b and of the second electron to the field of the atomic residue a. Using the complete analogy with the process of resonant charge exchange, we have, in accordance with (2.9), the following expression for the probability of spin exchange:

$$W = \sin^2 \int_{-\infty}^{+\infty} \frac{\Delta\,dt}{2\hbar}, \qquad (4.2)$$

where the exchange interaction potential Δ is equal to

TABLE IV.

Process	Scheme	Notes
1. Spin exchange	$A\uparrow + B\downarrow \rightarrow A\downarrow + B\uparrow$	Arrow shows spin direction for each of the colliding particles
2. Excitation transfer	$A^* + B \rightarrow A + B^*$	Asterisk shows the electronically excited particle
3. Depolarization of atoms	$A(m) + B \rightarrow A(m') + B$	m is the component of the angular momentum of the atom along a particular direction
4. Transitions between fine structure states of atoms	$A(J) + B \rightarrow A(J') + B$	J is the total angular momentum of the atom and is equal to the sum of the orbital and spin angular momenta.

E. E. Nikitin and B. M. Smirnov

TABLE V.

Colliding particles	Spin exchange cross section, 10^{-16} cm^2		Small expansion parameter of the theory, $1/2\gamma R_0$
	Theory	Experiment *)	
H — H	2.0	2.4[89-95]	0.074
Na — Na	11	10[96,97]	0.051
K — K	15	21[97,98]	0.048
Rb — Rb	17	19[97,99-107]	0.046
Rb — Cs	18	24[106-108]	0.045
Cs — Cs	19	22[97,103,108,109]	0.045

*) Table includes averaged experimental cross sections, reported in the references, as indicated.

the difference between the energies of the states described by the wave functions (4.1). Thus, by calculating Δ within the framework of the asymptotic method, we can determine the spin exchange cross section in complete analogy with resonant charge exchange. The corresponding comparison between the asymptotic theory and experiment is given in Table V.

Spin exchange governs possible changes in the hyperfine structure of an atom. Indeed, suppose we have a gas consisting of atoms with electron spin 1/2 and nuclear spin J, so that the hyperfine states are characterized by resultant spin of the atom $F = J \pm (1/2)$. Suppose that the two colliding atoms are in a state with resultant spin F. The effective cross section for the transition of one of the atoms to a state with resultant spin F' is then given by

$$\sigma(F \to F') = 2 \cdot \frac{1}{2} \cdot \frac{2F'+1}{4J+2} \sigma_{\text{exch}},$$

where σ_{exch} is the spin exchange cross section, the first factor represents the fact that there are two identical atoms, and the second factor represents the probability that the spins of the valence electrons are oppositely directed. After the spin exchange process, the atom "forgets" its hyperfine state and the factor $(2F'+1)/(4J+2)$ is the probability that it will be in the new spin state. The spin exchange process is important for masers whose operation is based on hyperfine structure transitions. Spin exchange affects the maser parameters.

The transfer of excitation during collisions between excited and unexcited atoms may be of two types. In one of them, the spin conservation laws require that the transfer of excitation be accompanied by electron exchange. For example, when transfer of excitation occurs in the process $\bar{\text{H}}\text{e}(2\,^3S) + \bar{\text{H}}\text{e}(1\,^1S) \to \text{He}(1\,^1S) + \text{He}(2\,^3S)$, the electric interaction does not lead to a transition between the ground and metastable states of the helium atom, so that electron exchange is essential for this process to proceed. In this case, we can readily estimate the upper limit for the excitation transfer cross section if we suppose that the electrons are not equivalent. The process is complicated by the transition of the unexcited electron. It follows that, if we suppose that the size of the orbit of the excited electron is sufficiently large, the cross section for the process will be determined by the transition of the unexcited electron and will be equal to the resonant charge exchange cross section. When this condition is violated, the resonant charge exchange

cross section will be the upper limit for the excitation transfer cross section.

When the transfer of excitations can proceed without electron exchange, the excitation transfer cross section may turn out to be very large. The largest value occurs in the case of a collision between an atom and a resonantly excited atom, when the splitting of the levels of the quasimolecule formed by the colliding atoms for large R is $\Delta \sim d^2/R^3$, where d is the matrix element of the dipole moment operator taken between the ground and excited states of the atom. According to (3.3),[6] the excitation transfer cross section is, in this case, given by

$$\sigma \sim \frac{d^2}{\hbar v} \qquad (4.3)$$

and its order of magnitude may reach 10^{-12} cm^2 at thermal energies. Because of the large cross sections, this process will affect the shape and width of the resonance emission line.

Collisions between an atom and a resonantly excited atom have been investigated in the literature in some detail.[110-124] Calculations have been reported of the total cross section for collisions between atoms in this case, which determines the emission linewidth, of the excitation transfer cross section, and also of the cross sections for the accompanying processes such as depolarization and transitions between fine and hyperfine states of atoms for different values of the orbital angular momenta of the atom in the ground and excited states. We shall confine our attention to transitions between fine-structure states of the atom in this type of collisions.

To be specific, we shall consider the change in the fine-structure state of atoms in the case of a collision between two alkali metal atoms, one of which is in the ground state and the other in a resonantly excited state. Figure 15 shows the level scheme[120] for the quasimolecule, where the distance $R_0 \sim (d^2/\varepsilon_T)^{1/3}$ (ε_T is the spin-orbital level splitting) corresponds to the crossing of two levels of the quasimolecule corresponding to the same symmetry of states and different fine-structure states of the atoms. This crossing is the feature responsible for the transition.

Let us estimate the cross section for the above process, assuming that $R_0 \ll \sqrt{\sigma}$, where σ is the excitation transfer cross section given by (4.3). This relation is well satisfied for alkali metal atoms. The transition under consideration occurs in the neighborhood of the crossing point, where the energy difference is less than or of the order of $\hbar\dot\theta$, and $\dot\theta \sim v/R$ is the angular velocity. Next, the transition is adiabatically of low probability, so that the range of distances ΔR within which the transition will take place can be estimated from

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[6] Like most of the resonant processes which we have considered, this process is very dependent on the interference between the states of the quasimolecule and, therefore, its cross section can be estimated from the formula $\sigma \sim R_0^2$, where R_0 is the impact parameter satisfying the condition $\int \Delta dt \sim \hbar$.
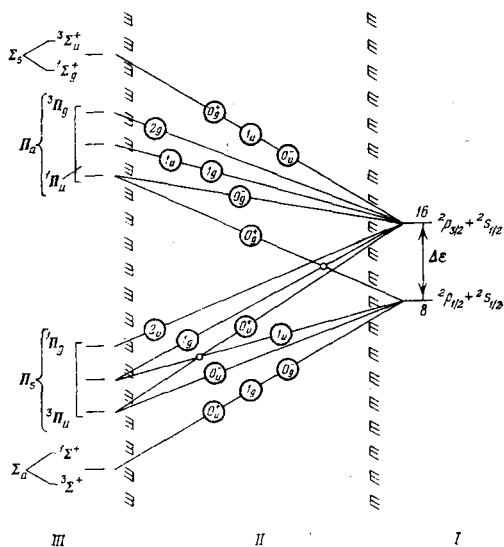
FIG. 15. Energy level scheme for the quasimolecule consisting of two alkali metal atoms in the ground and resontly excited states. [120]

$$\frac{\Delta R}{R_0} \frac{d^2}{R_0^3} \sim \frac{\hbar v}{R_0} \, .$$

The transition probability corresponds to a rotation of the molecular axis in this region, given by $\Delta\theta \sim \Delta R/R_0$ $\sim R_0^2/\sigma \ll 1$, where σ is the cross section given by (4.3). Hence, we obtain the following estimate for the cross section for the transition between the fine-structure states[119]:

$$\sigma \sim \frac{\Delta R}{R_0} R_0^2 \sim \frac{\hbar v d^{2/3}}{\varepsilon_T^{4/3}} \, . \tag{4.4}$$

This compact expression has a restricted range of validity because, in practice, exchange interaction between the alkali metal atoms is important at distances of the order of R_0.[125] The inclusion of this factor[120,125,126] complicates the overall picture of the process and permits only numerical calculations of the cross section. These results are not, at present, in good agreement with experimental data,[127–134] and there also are appreciable discrepancies among the experimental data themselves.

Transitions between fine-structure states of alkali metal atoms colliding with inert gas atoms have been examined in sufficient detail both theoretically[138–150] and experimentally.[153–166] Below, we shall formulate some general results relating to the change in the fine-structure state of an atom on collision.

The reason for the transitions between the components of atomic fine-structure during collisions is the temporary breaking of the spin-orbital coupling due to the polarization of the orbital angular momentum of the electrons L along the axis of the quasimolecule, which competes with the Coriolis interaction impeding this polarization. It follows that in order to elucidate the mechanism responsible for intra-multiplet transitions and to calculate the cross sections we must take into account three types of interaction, namely, the electrostatic interaction between the electrons in the colliding atoms

TABLE VI. Cases of Hund coupling.

Hund case	V_e, L, n coupling	V_m, S, L coupling	V_r, effect of rotation	Electron quantum numbers
a	Strong	Intermediate	Weak	Λ, S, S_n
b	"	Weak	Intermediate	Λ, S, S_N
c	Intermediate	Strong	Weak	Ω
d	Weak	Intermediate	Strong	L, S, L_N, S_N
e	"	Strong	Intermediate	J, J_N

V_e (the so-called interaction between the electron angular momentum L and the molecular axis n), the spin-orbital interaction V_M (the L, S interaction), and the Coriolis interaction of the spin and orbital angular momenta of the electrons in the quasimolecule with the rotation of the molecular axis V_r (this is the interaction of L and S with the angular momentum of the nuclei).

An analogous problem of the competition between the three types of interaction arises also when one tries to construct the wave functions for rotating stable diatomic molecules. The corresponding solutions for the various limiting cases are known as Hund coupling rules.[170,171] The various types of Hund coupling are summarized in Table VI together with an indication of good quantum numbers when the quasiclassical conditions are satisfied, i.e., when the total angular momentum of the quasimolecule is assumed to coincide with the classical relative angular momentum of the atoms.

For stable diatomic molecules, transition from one type of coupling to another occurs either as a result of vibrational excitation (increase in the mean separation between the atoms leading to a reduction in V_e) or of rotational excitation (increase in the Coriolis interaction), and the transition is characterized by a definite intermediate type of coupling.

A similar classification of states can be used in the case of atomic collisions. One then has time-dependent Hund coupling, i.e., a successive variation in coupling types along the path of the relative motion. If this type of time-dependent basis is used to describe the electron state of the quasimolecule, it is found that the nonadiabatic transitions are localized in relatively small regions of variation in the coupling type. As a result, the complete scattering problem becomes much simpler, as indicated at the beginning of Sec. 2, and the scattering matrix can be constructed with the aid of the matrices for nonadiabatic transitions.

For a qualitative description of time-dependent Hund coupling in the system of colliding atoms, it will be useful to introduce the characteristic distance R_0 at which the electrostatic interaction becomes comparable with the magnetic interaction. It will also be useful to introduce the dimensionless parameters $\beta = \rho/R_0$ and $\xi = z/R_0$, the first of which is proportional to the impact parameter ρ and the second to the linear coordinate z determined by the rectilinear trajectory. Finally, we introduce the dimensionless velocity $\nu = \omega/vR_0$, where ω is the characteristic frequency of fine-structure transitions. We can then construct different regions in the space (β, ξ, ω) in which there will be preserved a definite
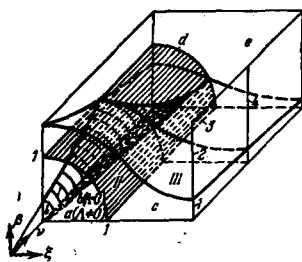
FIG. 16. Dependence of Hund coupling types on the ratios of different interaction potentials.

hierarchy of interactions, i.e., definite Hund coupling types. These regions will be separated by surfaces across which one type of coupling will be replaced by another. Figure 16 shows the separating surfaces for $\Lambda \neq 0$, $S \neq 0$ and $\Lambda \neq 0$, $S = 0$. When $\Lambda \neq 0$ but $S = 0$, we have only one surface (III) which separates cases b and d. The sectioning of the surfaces by the ξ plane produces different regions of Hund coupling for stable diatomic molecules. However, other sections are of greater interest for collision processes.

For slow atomic collisions, when the overlap of electron wave functions for the atoms is small, the interaction between L and S can be assumed to be independent of R. This means that, for fixed v, the parameter ν will be independent of R, i.e., the collision will be described by the motion of the representative point in the $\nu = $const plane. Along any trajectory (which need not necessarily be rectilinear), the coupling type will vary only near the boundaries of the regions. Consequently, the determination of the scattering matrix reduces to the determination of the nonadiabatic transition matrices N_{kl} on the boundary across which the $k \to l$ coupling change takes place. Hence, it is clear that the dominant parameter determining the transition probability is the rate at which the type of coupling changes. When this rate is high, the matrix N_{kl} is determined simply by the projection of the basis $|k\rangle$ onto the basis $|l\rangle$, so that we can use the well-known results relating to basis transformation (Chang and Fano[172] for $d \to b$ and Chin[173] for $a \to b$). If, on the other hand, this rate is low, we must solve the nonadiabatic transition problem in a small region near a boundary. Let us illustrate this by the simplest example of a collision between a resonantly excited sodium atom and a helium atom.

Figure 17 gives a qualitative picture of the terms of the Na-He system with a highly exaggerated spin-orbital
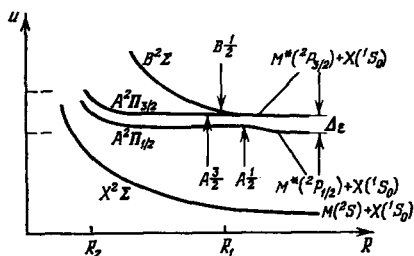

FIG. 17. Electron terms of the quasimolecule consisting of a helium atom and a sodium atom in ground and resonantly excited states.

interaction. The radius R_0, defined qualitatively above by the condition $V_e(R_0) = \varepsilon_T$ (ε_T is the fine structure splitting of the ^2P term) or, more precisely, as the distance corresponding to the maximum of the matrix element of the nonadiabatic interaction between terms of the same symmetry with $\Omega = 1/2$, will be in the range 12–14 atomic units, depending on the method of calculation. For trajectories with impact parameter $\rho > R_0$, the vibration in the Hund coupling types is described by $e \to c \to e$, and, for $\rho < R_0$, by the general scheme $e \to c \to a$ or $b \to c \to e$. However, this general scheme can be substantially simplified for the Na-He system. In particular, since the Massey parameter (2.1) defined as $\varepsilon_T R_0 / \hbar v$ turns out to be less than unity for thermal collision velocities, and since the splitting is relatively slight ($\varepsilon_T = 17$ cm^{-1}), coupling type b predominates for $\rho < R_0$. Moreover, the size of the region of type c turns out to be small in comparison with R_0, and this is a direct consequence of the condition $R_0 \gamma \gg 1$. As a result, approximate calculations of the probabilities for $\rho < R_0$ can be based on the simplified scheme $e \to b \to e$. Moreover, the same simplified scheme can be extended to all impact parameters in the calculation of the total cross sections if we neglect relative uncertainties of the order of $1/R\gamma$.

The use of this rough approximation which, in practice, means complete and instantaneous breaking of the spin-orbital coupling for $R < R_0$, along with the use of rectilinear trajectories for the relative motion, leads to cross sections that are already in satisfactory agreement with experimental data. In particular, the cross section for the transition between fine-structure states of the sodium atom at thermal energies, calculated in accordance with this scheme,[172] is practically in agreement with the experimental results.[153,159] Figure 16 illustrates the sequence in which the coupling types vary as a result of the variation of the impact parameter and of the collision velocity.

If for certain reasons the contribution of some particular ranges of impact parameters can be neglected in the calculation of the total cross section, then the number of coupling types becomes smaller still and this, of course, simplifies the problem still further.

Depolarization of the angular momentum of the atom may accompany the processes considered above when the angular momenta of the colliding atoms are nonzero, and is of independent interest when these processes are absent. The depolarization of atoms affects the polarization of the radiation emitted by an excited gas, and determines the various optical effects associated with the propagation or emission of polarized radiation in a gas (Hanle effect,[174,175] double and parametric resonance,[176–181] optical pumping in gas magnetometers,[182–187] nonlinear effects associated with the passage of laser radiation through a gas,[188] and so on).

Without going into the details of this process (this has been discussed in the literature[4,189–196]), we note that, from the physical standpoint, the nature of the process of depolarization of atoms in collisions is analogous to other resonance processes involving a set of states that are degenerate when the colliding particles

112   Sov. Phys. Usp. 21(2), Feb. 1978

E. E. Nikitin and B. M. Smirnov   112

are separated. Interference between these states during the collision process leads to these transitions.[197-199]

CONCLUSIONS

Successful applications of the theory of quasiresonant processes have relied on the development of asymptotic methods in collision theory. Calculations of cross sections for the different quasiresonant processes have been based on two types of asymptotic approach, which use two "large parameters" of the problem, namely, large interatomic distance R_0 compared with the mean radius $1/\gamma$ of the electron shell, and large Massey parameter $\Delta E/\hbar\gamma v$, characterizing a weak nonadiabatic coupling between most of the electron terms with a characteristic separation of the order of 1 eV or more.

Large values of $R_0\gamma$ are used in determining the exchange interaction potentials at large distances. For an essentially quantum-mechanical system for which the effect under consideration is determined by the "tails" of the electron wave functions, it is possible to use quasiclassical methods. This permits the inclusion of all the real features of the object without the use of models. The atomic interaction potentials themselves are relevant to a broader range of problems extending beyond atomic collision theory. They have been used to calculate kinetic transport coefficients[200-202] and parameters of noble-gas crystals at low temperatures[203,204] and may be useful in calculations of parameters of molecular crystals of the biological type.[205] The general approach used above can be applied to different problems connected with interactions and sub-barrier transitions in condensed media and on their surfaces.

The fact that $\Delta E/\hbar\gamma v$ is large results in a substantial simplification of the general dynamic problem of collision between atoms. It is precisely in this case that one can investigate transitions in a quantum-mechanical system under the action of a slowly-varying perturbation (in comparison with the characteristic times of motion of the electrons), the magnitude of which can be large.

Nonadiabatic transitions between the states of a quasimolecule will, under these conditions, occur only during small intervals of time corresponding to a sharp rearrangement of the wave functions of the quasimolecule. The characteristic parameter of this process, which determines the transition probability, is the product of the electron transition frequency and the characteristic time of the external perturbation. When these regions are excluded, i.e., during the main interval of time, the quantum-mechanical system develops adiabatically, but even such development of the system may lead to transitions because of interference between states. Methods for the solution of this type of problem in the theory of atomic collisions have been successfully extended to the theory of chemical reactions.[206] The methods developed so far may find applications in the theory of nuclear collisions and nuclear reactions, and also in problems involving interactions between quantum-mechanical systems and time-dependent external fields.

Finally, we note that, although the possibilities of the asymptotic method are, by definition, restricted to a definite range of variation of the interatomic distances and of the Massey parameters, nevertheless, the method can be used to calculate total collision cross sections which, formally, require extensive information about the transition probabilities. This can be done by using additional "small parameters" of the system. In particular, the asymptotic method can frequently be used to obtain the probabilities providing the main contribution to the total cross section as was done in the above example of resonant charge exchange.

An example demonstrating the wide range of applicability of the asymptotic method is also provided by its application in the theory of intramultiplet mixing in the case of a large spin-orbital interaction. In these cases, the transition cross section is small (smaller than the gas-kinetic cross section) because the collisions are adiabatic even though transitions between the terms of the quasimolecule occur at large separations. The possible contribution of other channels with transitions at small separations must, of course, be considered in such calculations.

Another example of this type is the asymptotic theory of transport coefficients,[200-202,207] where a small parameter can be introduced by using the rapid variation in the interaction potential between the atomic particles. The above devices can be used to present the results in the same form as for the simplest model, i.e., the hard sphere model, but without introducing model assumptions. Another example is the theory of transfer of infrared radiation in a molecular medium,[208] which involves vibrational-rotational transitions in linear molecules. In this problem, the optical density of the gas layer at the center of the line emitted as a result of a transition with a given rotational quantum number is strongly dependent on the rotational quantum number so that, as in the previously considered cases, the situation is substantially simplified.

The asymptotic methods developed within the framework of the theory of atomic collisions are of a general character and extend beyond the framework of the present review. The authors hope that the asymptotic methods of the theory of atomic collisions presented here, including both the general ideas and the individual elements of the theory, will be found useful in other branches of physics.

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115   Sov. Phys. Usp. 21(2), Feb. 1978

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116   Sov. Phys. Usp. 21(2), Feb. 1978

E. E. Nikitin and B. M. Smirnov   116