Nonadiabatic transitions in atomic collisions

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The adiabatic approximation is used in the physics of atomic collisions to calculate the parameters of inelastic (nonadiabatic) transitions between electronic states of colliding atoms (excitation, charge transfer, ionization) when, on the one hand, the motion of nuclei can be treated classically and, on the other, their relative velocities are low. The problem then reduces to solution of the secular Schrödinger equation for electrons with a Hamiltonian dependent on the internuclear distance and varying slowly with time. The review presents an asymptotic theory of nonadiabatic transitions between bound states as well as from bound states to a continuous spectrum without any limitations on the nature of the electron Hamiltonian of the kind encountered in exactly soluble models, except that a low value of the relative velocity of the nuclei is assumed. In addition to a general theory, the review deals with the various mechanisms of one-electron nonadiabatic transitions in the specific case of the simplest three-particle quasimolecular system (two nuclei and an electron). The concluding section deals with some modifications of the adiabatic approximation necessary for matching to the physical boundary conditions and calculation of the isotopic effects.

I. INTRODUCTION

The adiabatic approximation¹⁾ is one of the most widely used in physics and it involves approximate separation of the "fast" and "slow" motion of a dynamic system. Historically it dates back to the adiabatic principle of Ehrenfest¹ which has served as the basis (at least indirectly) of the Bohr-Sommerfeld quantization conditions in the old Bohr theory. The development of quantum mechanics was followed immediately by the adiabatic approximation, initially used by Born and Oppenheimer² for the approximate separation of the electronic, vibrational, and rotational degrees of freedom in molecules, where the adiabaticity is associated with the small value of the ratio of the electron and nuclear masses, and then by Born and Fock³ to solve the secular (time-dependent) Schrödinger equation with a Hamiltonian varying slowly with time.

There have been several monographs and reviews on the adiabatic approximation and particularly on its applications to the physics of atomic collisions⁴⁻⁸ where it is used in calculations dealing with the processes of excitation, charge transfer, and ionization in the course of slow collisions of atoms when the motion of the nuclei can be regarded as classical. The variant of the adiabatic approximation used in the theory of collisions is a further development of the approach of Born and Fock.³ Initially the following exactly soluble models were considered: two-level models of Landau and Zener,^{9,10} of Rosen, Zener, and Demkov,^{11,12} and of Nikitin¹³ for transitions between bound electronic states, and the model of Demkov and Osherov¹⁴⁻¹⁶ for transitions from a bound state to a continuous spectrum (ionization). These models made it possible not only to calculate the parameters of a large number of specific physically important processes, but also to discover the basis for a more general asymptotic approach in which they are used as standard problems. The high degree of universality of the asymptotic approach is due to the fact that the set of standard problems is wider than the set of exactly soluble models on which a number of general restrictions (such as unitarity) is imposed. On the other hand, a standard problem is simply required to show a given behavior in small regions near certain special points.

An asymptotic theory formulated initially for two-level nonadiabatic transitions¹⁷⁻²⁰ has since been extended to transitions involving a large number of levels^{21,22} and transitions terminating in a continuous spectrum.²³ The restrictions on the electron Hamiltonian of the kind needed in exactly soluble models are not required in this asymptotic theory and use is made simply of a low relative velocity of the nuclei. This helps to understand better the nature of nonadiabatic transitions and makes it possible to calculate the parameters of the processes in those cases when the model approaches are unsuitable. There is as yet no sufficiently comprehensive and systematic account of the asymptotic theory of nonadiabatic transitions. Usually attention is concentrated on the twolevel approximation, on analysis of exactly soluble models, and on semiphenomenological methods in calculations dealing with specific physical processes, whereas the general asymptotic theory which provides a more complete and logically self-consistent picture has been ignored. The purpose of the present review is to fill as much as possible this gap using the recently obtained results. The review is designed for a knowledgeable reader. It should be regarded as a supplement to the well-known monograph of Nikitin and Umanskii⁸ so that some of the topics already discussed in detail in Ref. 8 will be omitted and citations will be given only of those papers which relate directly to the content of the present review. We shall use the terminology adopted in the theory of atomic collisions, but the general theory discussed in the next three sections applies equally well to the physics of plasmas and gases, as well as to the physics of solids, wave propagation, mesoatomic physics, etc.

General formulation of the problem

In the case of classical motion of nuclei the transitions between electronic states of colliding atoms are described by the secular Schrödinger equation²

$$H(\mathbf{R}) \psi(\mathbf{r}, t) = i \frac{\partial \psi(\mathbf{r}, t)}{\partial t}, \qquad (1.1)$$

where r is a set of electron coordinates; $H(\mathbf{R})$ is the electron Hamiltonian of a diatomic quasimolecule, which depends on

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time only via the internuclear distance $\mathbf{R} = \mathbf{R}(vt)$ (v is the initial relative velocity of the nuclei), assumed to be a known function of time. The most general form of the adiabatic approximation is an asymptotic expansion of the solution of Eq. (1.1) in terms of a small parameter v. In this approximation the electronic wave function $\psi(\mathbf{r},t)$ is sought in the form of an expansion

$$\psi(\mathbf{r}, t) = \sum_{p} g_{p}(t) \varphi_{p}(\mathbf{r}, R) \exp\left(-i \int E_{p}(R(vt')) dt'\right)$$
(1.2)

in terms of the eigenfunctions of the instantaneous electron Hamiltonian

$$H(R) \varphi_p(\mathbf{r}, R) = E_p(R) \varphi_p(\mathbf{r}, R),$$

which depend on R as a parameter occurring in the Hamiltonian. The eigenvalues $E_p(R)$ are called in a number of different ways in the physics of atomic collisions: molecular potential curves, adiabatic terms, or simply terms or levels; for brevity, we shall use only the last names. In the representation of Eq. (1.2) the adiabatic approximation reduces to calculation of the main terms in the asymptotic expressions for the expansions $g_p(t)$ in the limit $v \rightarrow 0$. Selection of the expansion $\psi(\mathbf{r},t)$ in terms of the adiabatic basis $\varphi_p(\mathbf{r},R)$ is accounted for by the fact that, according to the Born-Fock theorem,³ the population of the adiabatic states does not change during a collision in the limit $v \rightarrow 0[g_p(t) = \text{const}]$, i.e., the functions $\varphi_p(\mathbf{r},R)$ are the "correct wave functions of the zeroth order approximation" in this limit.

The boundary conditions are formulated in the adiabatic representation as follows. In the limit $R \to \infty$, the terms $E_p(R)$ reduce to energy levels of isolated atoms at rest, whereas $\varphi_p(\mathbf{r}, R)$ reduce to the corresponding atomic wave functions $\varphi_p^{(a)}$. Consequently, if we ignore the momentum transfer effect,³⁾ the population of the atomic states $\varphi_p^{(a)}$ before and after a collision is identical with $g_p(t = \pm \infty)$ and the probability of a transition from an initial atomic state $\varphi_q^{(a)}$ to a final state $\varphi_p^{(a)}$ is

$$P_{pq} = \lim_{t \to \infty} |g_p(t)|^2$$

on condition that

$$\lim_{t \to \infty} g_p(t) = \delta_{pq}. \tag{1.3}$$

The probability of a transition depends on the impact parameter ρ , which specifies the trajectory of the nuclei $\mathbf{R}(t)$; having integrated with respect to ρ , we obtain the inelastic transition cross section

$$\sigma_{pq} = 2\pi \int_{0}^{\infty} P_{pq}(\rho) \rho \, \mathrm{d}\rho, \qquad (1.4)$$

which is the most important characteristic of a collision process.

The range of collision energies in which the adiabatic approximation is valid depends strongly on the actual process under consideration. It is limited from below by the condition of validity of the classical approach for the description of the motion of nuclei, whereas the upper limit is set by the condition of validity of an asymptotic expansion in terms of small values of v. There is no sufficiently rigorous but general quantitative criterion of the validity of asymptotic expansions. Usually the main term of the expansion gives a satisfactory result even in the region where the first correction begins to exceed it (in this case the first correction should be dropped, because it is known to cause deterioration of the results). In the case of the adiabatic approximation this means that we can extrapolate it toward higher values of v right up to those at which the transition probability P_{pq} becomes comparable with unity, i.e., to the maximum of the cross section defined by Eq. (1.4).

A general feature of the asymptotic theory of nonadiabatic transitions is that use is made not so much of the terms for real internuclear distances as of some local characteristics in the complex plane of R. Naturally, during collisions the real transitions occur for real values of R and the characteristics of the terms with complex values of R appear as a result of an approximate (asymptotic) solution of the dynamic problem represented by Eq. (1.1).⁴⁾ These terms concentrate all the information necessary for an asymptotic calculation and in each case they are readily linked to physically clear features of the adiabatic basis on the real axis of R, which lead to transitions. For example, in calculating the probability of a transition between two terms we have to know only the position of the common complex branching point $R_{\rm c}$ and the difference between these terms on a line joining R_c to the real R axis. In this case the branching point appears always on the real R axis as a maximum of the matrix element of the interaction between adiabatic states.

2. ANALYTIC PROPERTIES OF TERMS AND ADIABATIC WAVE FUNCTIONS

In the theory of nonadiabatic transitions the property of analyticity of the Hamiltonian with respect to R is of fundamental importance, because it provides the basis for the use of asymptotic methods. This is a natural property. In the theory of atomic collisions it follows from the analyticity, with respect to R, of the Coulomb interaction of electrons with nuclei. It follows from the analyticity of the Hamiltonian H(R) that all the terms $E_p(R)$ of a given symmetry are branches of sheets of the same analytic function E(R), which is specified over the whole complex plane of R. This can be illustrated by considering the example of the approximation postulating a finite number of states in which the Hamiltonian is a finite matrix and its eigenvalues $E_p(R)$ are found by equating to zero the determinant

$$\Delta (E, R) = \det (H(R) - EI),$$

where I is a unit matrix. Since $\Delta(E,R)$ is an analytic function of E and R, the solution of the transcendental equation $\Delta(E,R) = 0$ can only be, as is known from the theory of functions of the complex variable, one analytic function E(R) which naturally has many sheets also in the approximation of N states, i.e., in the case of the matrix H(R) of size $N \times N$, there are N branches of $E_p(R)$ (p = 1, 2, ..., N). This property of the terms will be demonstrated more clearly in the fifth section by considering the example of the terms of the problem of two Coulomb centers.

In the asymptototic approach the nonadiabatic transitions are associated with singular points of the terms in the complex plane of R. There are two types of singularities: complex-conjugate pairs of branching points in the quasicrossing region,⁵⁾ which match the terms of the system to a single analytic function, and branching points at the boundary of the complex spectrum, where the term acquires a finite width and the state becomes quasistationary. Singularities of the first type give rise to transitions between bound states, whereas those of the second type induce transitions from a bound state to a continuous spectrum (ionization).

2.1. Level quasicrossing region

At low velocities v the nonadiabatic transitions between terms (levels) occur in the regions of their closest approach. According to the theorem of Neumann and Wigner,²⁴ the exact crossing of two levels or terms of the same symmetry for real values of R is an exception, so that the most frequent case is that of a quasicrossing shown in Fig. 1. A quasicrossing of two levels $E_1(R)$ and $E_2(R)$ reflects their exact crossing at complex-conjugate points R_c and R_c^* , which are located near the real axis of R. Degeneracy of the terms at the points R_c and R_c^* has an important special feature. Away from the real axis of R the Hamiltonian is no longer selfadjoint because the parameter R occurring in it is complex, so that when two eigenvalues are identical $[E_1(R_c)]$ $= E_2(R_c) \equiv E_c$] it is reduced not to the diagonal form but to the Jordan form²⁵

$$H(R_{\rm c}) = \begin{pmatrix} E_{\rm c} & \mathbf{1} \\ 0 & E_{\rm c} \end{pmatrix}.$$

The values of $E_1(R)$ and $E_2(R)$ in the vicinity of the point R_c can be found using perturbation theory in terms of a small parameter $\Delta R = R - R_c$. In the most natural case of a perturbation linear with respect to ΔR

$$U(R) = \Delta R \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \quad (U_{ij} = \text{const}),$$

in the first approximation the terms are

$$E_{1,2}(R) = E_{c} \pm (U_{21}\Delta R)^{1/2}, \qquad (2.1)$$

i.e., instead of the usual linear dependence on a small parameter ΔR , we now have a square-root dependence. This is a consequence of the fact that the Hamiltonian $H(R_c)$ is no longer self-adjoint. The square-root branching point com-



FIG. 1. Quasicrossing of terms (energy levels). The dashed line shows the linearized diabatic terms.

bines the two terms into a single analytic function, so that when the point R_c is gone around once, the sign in front of the radical in Eq. (2.1) is reversed and the terms transform into one another. Obviously, the same property is exhibited also by the corresponding adiabatic wave functions.

Another special feature of the Jordan form is that it has just one eigenvector,²⁵ i.e., on approach to the point R_c we have not only $E_1 \rightarrow E_2$, but also $\varphi_1 \rightarrow \varphi_2$. At first sight this looks paradoxical, since the wave functions satisfy the orthonormalization condition⁶⁾

$$\int \varphi_{1}(\mathbf{r}, R) \varphi_{1}^{*}(\mathbf{r}, R^{*}) d\mathbf{r} = \int \varphi_{2}(\mathbf{r}, R) \varphi_{2}^{*}(\mathbf{r}, R^{*}) d\mathbf{r} = 1,$$
(2.2)
$$\int \varphi_{1}(\mathbf{r}, R) \varphi_{2}^{*}(\mathbf{r}, R^{*}) d\mathbf{r} = 0,$$
(2.3)

which is continued analytically to the complex plane of R and, in particular, to the point R_c . It is at this point that the wave functions φ_p are identical and so should be the integrals in Eqs. (2.2) and (2.3). This apparent contradiction can be explained as follows.¹⁹ We shall introduce adiabatic wave functions normalized by the condition

$$\chi_p(\mathbf{r}, R) \to A(\hat{\mathbf{r}}) \frac{\exp(-\kappa r)}{(2\pi\kappa)^{1/2} r} \quad \text{for} \quad r \to \infty,$$
$$\int |A(\hat{\mathbf{r}})|^2 d\hat{\mathbf{r}} = 1, \quad \hat{\mathbf{r}} = \frac{\mathbf{r}}{r}, \quad \varkappa = (-2E_p(R))^{1/2} r^{1/2}$$

The functions $\chi_p(\mathbf{r}, R)$ are bounded for all values of R (this is the property important at this moment) and differ from the functions $\varphi_p(\mathbf{r}, R)$ only by the normalization factor

$$\varphi_p(\mathbf{r}, R) = C_p(R) \chi_p(\mathbf{r}, R). \qquad (2.4)$$

At the point R_c we indeed have

$$\chi_1 (\mathbf{r}, R_c) = \chi_2 (\mathbf{r}, R_c).$$
 (2.5)

Moreover, the following relationship is obeyed:

$$\int \chi_p \left(\mathbf{r}, R_c \right) \chi_p^* \left(\mathbf{r}, R_c^* \right) d\mathbf{r} = 0, \qquad (2.6)$$

so that the normalization factors $C_{\rho}(R)$ occurring in the condition (2.2) become infinite. Consequently, the adiabatic wave function $\varphi_{\rho}(\mathbf{r}, R)$ represents a product of a bounded function $\chi_{\rho}(\mathbf{r}, R)$ and a normalization factor $C_{\rho}(R)$, which is singular at the point R_{c} (Fig. 2). Under orthonormalization conditions this singularity of $C_{\rho}(R)$ is superimposed on the zero of the matrix element of Eq. (2.6), and this gives rise to an indeterminacy which can be avoided by different procedures under normalization and orthonormalization conditions, so that unity is obtained in Eq. (2.2) and zero in Eq. (2.3).

The singularity of $C_{\rho}(R)$ at the points R_c and R_c^* creates a singularity in all the matrix elements (apart from the normalization elements) and this gives rise to a considerable increase for real values of R in the quasicrossing region (this behavior is illustrated qualitatively by curve A in Fig. 2). In particular, this explains a bell-shaped profile of the matrix element of the nonadiabatic coupling (see, for example, Fig. 6c below), which characterizes the interaction of adiabatic states and can be written in two equivalent forms⁶:

$$w_{pp\bullet}(R) = \left\langle \varphi_p \middle| \frac{\mathrm{d}}{\mathrm{d}R} \middle| \varphi_{p\bullet} \right\rangle = \frac{\left\langle \varphi_p \middle| (\mathrm{d}H/\mathrm{d}R) \middle| \varphi_{p'} \right\rangle}{E_{p'}(R) - E_p(R)}.$$
 (2.7)



FIG. 2. Singularities of the normalization coefficient C(R) in the complex R plane.

Therefore, we have a logic chain: a branching point R_c common for a pair of terms $E_1(R)$ and $E_2(R) \Rightarrow a$ singularity of normalization factors $C_{1,2}(R)$ at $R = R_c \Rightarrow a$ peak in the interaction $w_{12}(R)$ in the quasicrossing region $R \approx \text{Re } R_c$ \Rightarrow intensive transitions between states $\varphi_1(\mathbf{r}, R)$ and $\varphi_2(\mathbf{r}, R)$ in this region; such a chain links the branching points of the terms with nonadiabatic transitions and demonstrates more clearly that calculation of the probability of a transition on the asymptotic theory reduces to an analysis of the terms in the complex plane of R, i.e., to finding the point R_c and the difference between the terms on a line connecting R_c to the real axis R [see Eq. (3.8)].

We shall illustrate the properties of the adiabatic basis discussed above by considering the Demkov–Osherov model¹⁶ which is sufficiently general, because it contains an arbitrary number of states and nontrivial free parameters. The Hamiltonian of the Demkov–Osherov model represents a matrix of arbitrary size $N \times N$ and is given by^{16,26}

$$H(R) = \begin{pmatrix} \alpha R & h_1 & h_2 & h_3 & \dots \\ h_1 & \lambda_1 & 0 & 0 & \dots \\ h_2 & 0 & \lambda_2 & 0 & \dots \\ & & & \ddots & \ddots & \ddots & \ddots \end{pmatrix},$$

where α , h_i , and λ_i are real constants (i = 1, 2, ..., N - 1). The terms in this model can be found from the secular equation

$$\alpha R - E_p - \sum_{i=1}^{N-1} \frac{h_i^a}{\lambda_i - E_p} = 0, \qquad (2.8)$$

and the corresponding eigenvectors φ_p have components (*i* is the number of the component)

$$\varphi_p^{(0)} = C_p, \quad \varphi_p^{(i)} = C_p \frac{h_i}{E_p - \lambda_i} \quad (i \neq 0)$$

$$(2.9)$$

with a normalization factor

$$C_{p} = \left[1 + \sum_{i=1}^{N-1} \frac{h_{i}^{2}}{(E_{p} - \lambda_{i})_{i}^{2}}\right]^{-1/2}.$$
 (2.10)

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Differentiating Eq. (2.8) with respect to R and comparing the results with Eq. (2.10), we can write C_p in a different form:

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After substitution of Eq. (2.9) with the normalization factor (2.11) into Eq. (2.7), we obtain an explicit expression for the matrix element of the nonadiabatic relationship expressed in terms of the parameters of the problem:

$$w_{pp'}(R) = \frac{1}{E_{p'}(R) - E_{p}(R)} \left(\frac{dE_{p}(R)}{dR} - \frac{dE_{p'}(R)}{dR}\right)^{1/2}.$$
(2.12)

These simple and exact (for the model in question) expressions yield directly all the above-mentioned general analytic properties of the adiabatic basis in the quasicrossing region. In fact, at a branching point R_c shared by a pair of terms E_1 (R) and $E_2(R)$ the components (2.9) of the corresponding adiabatic wave functions φ_1 and φ_2 are clearly identical because of the equality $E_1(R_c) = E_2(R_c)$, i.e., "degeneracy" of the wave functions of Eq. (2.5) occurs. Using Eq. (2.1), we find directly from Eqs. (2.11) and (2.12) that the normalization coefficients $C_{1,2}$ become infinite at the point R_c and the matrix element of the nonadiabatic coupling between the states has a first-order pole at this point: $w_{12}(R) \approx (R - R_c)^{-1}$. The matrix elements containing only one state of this pair also have a singularity at $R = R_c$, but this singularity is much weaker:

$$w_{pp'}(R) \approx (R - R_c)^{-1/4} (p = 1, 2, p' \neq 1, 2).$$

2.2. Region of merging of a level with a continuous spectrum

The region near the boundary of a continuous spectrum is important not only from the point of view of a qualitative investigation of analytic properties of the terms, but also for practical reasons because it is here that the ionization of a quasimolecule occurs in the adiabatic limit $v \rightarrow 0$. If a change in the internuclear distance shifts a term to a continuous spectrum, a bound state is converted into a quasistationary or a virtual state⁷⁾ and we then face the problem of classification and calculation of the widths of energy levels. We shall consider this task within the framework of perturbation theory in which an unperturbed Hamiltonian $H_0 = H(R_0)$ corresponds to a distance R_0 where the term in question crosses the boundary of a continuous spectrum $[E_{\rho}(R_0) = 0]$ and the role of a perturbation is played by the difference

$$U = H(R) - H(R_0) \approx H'(R_0) (R - R_0)$$
$$H'(R_0) \equiv \frac{\mathrm{d}H(R)}{\mathrm{d}R} \Big|_{R = R_0}.$$

The conventional variants of perturbation theory are unsuitable at the boundary of a continuous spectrum because right from the beginning we have to allow for an infinite number of states in the continuum. Another specific feature of this problem is that we encounter three qualitatively different situations, depending on the type of interaction at large distances r (short-range, Coulomb repulsion, Coulomb attraction).

We shall first consider the case when there is no longrange Coulomb interaction in H(R). As shown in Ref. 27, under these conditions the process of low-energy scattering is similar to the scattering by spherical centers and then an orbital quantum number l can be assigned to a state at the

boundary of a continuous spectrum. This makes it possible to use the results of perturbation theory for the spherically symmetric case, based on the S-matrix formalism,²⁸ to deal with a nonspherical overall potential. In this formalism the eigenvalues of the Hamiltonian correspond to zeros of the Jost function $f_i(k)$ in the complex plane of the wave number $k = (2E)^{1/2}$. The Jost function depends also on R as a parameter, but the conditions of the problem ensure that it vanishes for $R = R_0$ at the point k = 0. A modified version of perturbation theory is constructed as an approximate solution of a transcendental equation

$$f_l(k, R) = 0 (2.13)$$

at low values of $\Delta R = R - R_0$. This is done as follows: we expand the left-hand side of Eq. (2.13) in the vicinity of $R = R_0$ and k = 0 as a double Taylor series:

$$\sum_{k=0}^{\infty} \frac{1}{s|t|} f_l^{st} \Delta R^t k^s = 0, \quad f_l^{st} \equiv \frac{\partial^{s+t} f_l(k, R)}{\partial k^s \partial R^t} \Big|_{k=0, R=R_0}.$$
(2.14)

The familiar representation of the Jost function²⁹ $f_l(k) = A(k) + k^{2l+1}B(k)$, where A(k) and B(k) are even functions of k, shows that $f_l^{st} = 0$ for odd s and s < 2l. Consequently, the solution of Eq. (2.14) in the form of a series in powers of ΔR acquires a structure dependent on l:

$$k(R) = \sum_{j=1}^{l} \alpha_j \Delta R^{j-(j/2)} + \sum_{j=2l}^{\infty} \beta_j \Delta R^{j/2}, \qquad (2.15)$$

which contains powers of ΔR with exponents which are integers of half-integers. The coefficients α_j and β_j of the expansion can be expressed, after substitution of Eq. (2.15) into Eq. (2.14), in terms of derivatives f_l^{st} and the problem reduces to derivation of explicit expressions for f_l^{st} in terms of the wave function of the unperturbed state. This is done using integral representations of the Jost function.²⁸ In the final expansion of $E_p(R) = \frac{1}{2}k^2(R)$ the coefficients up to the *l* th order are identical with the coefficients in an ordinary perturbation theory series, but they are followed by terms of order $\Delta R^{l+1/2}$, which for a suitable sign of ΔR become imaginary and give the width of an energy level. If $l \neq 0$, the principal terms of the expansion of the real part of the energy and width $\Gamma_p(R) = 2 \text{ Im } E_p(R)$ of a level are given by²⁸

$$\operatorname{Re} E_{p}(R) = \lambda \Delta R_{i}^{i}$$

$$\Gamma_{p}(R) = a_{l}^{2} (2\lambda \Delta R)^{l+(1/2)}; \qquad (2.16)$$

here and in Eq. (2.18) we have $\lambda = \langle \varphi_{\rho}(R_0) | H'(R_0) | \varphi_{\rho}(R_0) \rangle$ and a_l is a coefficient in the asymptotic form of the unperturbed wave function $(\hat{\mathbf{r}} = \mathbf{r}/r)$:

$$\varphi_p (\mathbf{r}, R_0) = (2l - 1)!!a_l r^{-l-1} Y_{lm} (\mathbf{r}) (1 + O(r^{-1})), (2l - 1)!! = 1 \text{ for } l = 0.$$
(2.17)

In the case of the s states (l = 0) the expansion $E_p(R)$ contains only integral powers of ΔR and differs from the usual expansion already in the first approximation²⁸:

$$E_p(R) = -2\left(\frac{\lambda \Delta R}{a_0}\right)^2. \tag{2.18}$$

We can see from Eq. (2.18) that in this case the term does

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FIG. 3. Different types of behavior of terms (energy levels) in the vicinity of the boundary of a continuous spectrum.

not cross the boundary of a continuous spectrum but simply touches it. Further evolution of an s level in the k plane occurs as follows.³⁰ Passing the point k = 0 at $R = R_0$, it moves downward along the imaginary axis of k, corresponding to virtual states. As a rule, another virtual s level rises toward the descending level and they merge at some value $R = R_m$, and then they diverge in opposite directions at right-angles to the imaginary axis of k (see Fig. 9 below, which describes the problem of the long-range Coulomb forces, but it does give only a qualitatively correct picture of the nature of the shift of the s levels in the k plane in the case of the short-range potentials). A subsequent increase in $|\Delta R|$ causes a level to intersect the bisector in the lower quadrant of the k plane and the level then emerges in the region of positive energies (i.e., it is converted from virtual into quasistationary) and it immediately has a finite width (Fig. 3a).

The nature of the dependence on l described by Eq. (2.16), $\Gamma_p(R) \propto \Delta R^{l+1/2}$, is explained by the fact that a centrifugal barrier preventing the ionization of a particle grows on increase in l and, consequently, the width of a level decreases. It is in fact a centrifugal barrier with a penetrability which approaches zero in the limit $E \rightarrow 0$ that ensures the stability of a state and determines the width of a level at the moment when it reaches the continuous spectrum. Therefore, an s state which does not have a centrifugal barrier is not converted into a quasistationary state immediately after passing through the point R_0 , but becomes virtual. The difference in the behavior of the terms (levels) in the region of merging with the continuous spectrum in the two cases l = 0 and $l \neq 0$ is illustrated in Figs. 3a and 3b.

In the Coulomb repulsion problems the situation is fundamentally different from that just discussed because in the range of large values of r, which dominates the contribution to the width of a level in the range $0 < E \leq 1$, a centrifugal barrier can be ignored against the background of a more slowly falling Coulomb interaction, but in the first approximation the level width is independent of *l*. Bearing in mind the power-law smallness of the width of Eq. (2.16) in terms of ΔR , we can see that in the presence of a Coulomb barrier the level width tends to zero for $R \rightarrow R_0$ faster than any power of ΔR , i.e., exponentially. We shall consider the quantitative side of the problem following Refs. 31 and 32 by assuming a Hamiltonian of sufficiently general nature:

$$H(R) = -\frac{1}{2}\Delta + \frac{1}{|\mathbf{r}-\mathbf{R}|} + V(\mathbf{r}).$$

In the vicinity of the boundary of a continuous spectrum where the wave function is strongly delocalized the shortrange potential $V(\mathbf{r})$ can be replaced by a zero-range potential. Then, the wave function $\varphi_p(\mathbf{r}, \mathbf{R})$ can be expressed in terms of the Coulomb Green's function and the terms $E_p(\mathbf{R})$ are found from a transcendental equation²⁶

$$\alpha = 2\Gamma(\nu) \left[\left(\frac{1}{4} + \frac{\nu^2}{2R} \right) M_{-\nu, 1/2} \left(\frac{2R}{\nu} \right) W_{-\nu, 1/2} \left(\frac{2R}{\nu} \right) - M'_{-\nu, 1/2} \left(\frac{2R}{\nu} \right) W'_{-\nu, 1/2} \left(\frac{2R}{\nu} \right) \right], \qquad (2.19)$$

where $v = (-2E)^{-1/2}$; $\Gamma(v)$ is the gamma function; $M_{-v,\downarrow}(x)$ and $W_{-v,1/2}(x)$ are the Whittaker functions; α is a parameter characterizing the potential $v(\mathbf{r})$ [the quantity $\varepsilon = -\alpha^2/2$ represents the binding energy in an isolated potential $v(\mathbf{r})$]. In the vicinity of the point κ_0 where a term merges with a continuous spectrum, this first-approximation solution of Eq. (2.19) is³²

Re
$$E_p(R) = \lambda \Delta R$$
,
 $\Gamma_p(R) = \frac{\lambda \pi \sigma^2 (I_0^2(\sigma) - I_1^2(\sigma))}{4K_1(\sigma) I_1(\sigma)} \exp\left[-\pi \left(\frac{2}{\lambda \Delta R}\right)^{1/2}\right]$,
(2.20)

where λ has the same meaning as in Eq. (2.16); $I_i(x)$ and $K_i(x)$ are Bessel functions with an imaginary argument, which originate from an asymptotic expansion of Whittaker's functions for $\nu \rightarrow \infty$ ($E \rightarrow 0$) and $\sigma = 2(2R_0)^{1/2}$. At high values of R_0 . Eq. (2.20) simplifies to^{31,32}

$$\operatorname{Re} E_{p}(R) = -\frac{\Delta R}{R_{0}^{2}}, \qquad (2.21)$$

$$\Gamma_{p}(R) = 2^{-1/2} R_{0}^{-3/2} \exp\left[4 (2R_{0})^{1/2} - \pi R_{0} \left(-\frac{2}{\Delta R}\right)^{1/2}\right].$$

In agreement with the above qualitative discussion, the level width in Eqs. (2.20) and (2.21) is exponentially small in the limit $\Delta R \rightarrow 0$. In fact, this means that decay of a level does not begin immediately when it merges with the continuous spectrum. Equating to zero the argument of the exponential function in Eq. (2.21), we can estimate ΔR_{eff} at which the width of a level becomes significant: $\Delta R_{\text{eff}} \approx R_0$. It follows from this estimate that even when a level merges with the continuous spectrum for very high values of R_0 (which is the usual case), the decay of a level can be expected realistically only in the range $R \approx R_0 - \Delta R_{\text{eff}} \approx 1$ and the ionization cross section should not exceed the gas-kinetic value.

In the physics of atomic collisions these variants of merging of a term or level with the continuous spectrum occur when negative ions become ionized (by detachment of

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an electron): Eqs. (2.16) and (2.18) describe the behavior of the terms in the reactions $A^- + B^- \rightarrow A + B^- + e$, whereas Eqs. (2.20) and (2.21) describe the reactions $A^- + B^- \rightarrow A + B^- + e$. Obviously, in the former case an electron which emerges is subject to the short-range potential of a neutral quasimolecule (AB)⁻, whereas in the latter case it is in a Coulomb field of a negatively charged quasimolecule $(AB)^{-}$. From the point of view of applications the of ionization of a neutral process atom. $A + B \rightarrow A^+ + B + e$, is more important. In this case, and also when one or both atoms A and B are replaced with positive ions, the electron Hamiltonian (e) includes the Coulomb attraction at large distances r. Consequently, in addition to a continuous spectrum there is also an infinite number of bound Rydberg states with an infinitesimally small binding energy. The presence of a Rydberg series of terms prevents the merging of the initial term with the continuous spectrum. This is a consequence of the Neumann-Wigner theorem, which forbids actual crossing of levels or terms. However, we can have a situation shown in Fig. 3c where the initial term is strongly shifted toward a continuous spectrum and creates an infinite chain of quasicrossings, which becomes denser at the boundary of the continuous spectrum. Consecutive passing through all such quasicrossings results in ionization. This ionization mechanism was first used in Ref. 33 to calculate the energy spectrum of electrons in terms of the Demkov-Osherov model. The problem of the possibility of existence of infinite quasicrossing chains in real quasimolecular systems has not yet been settled, because they have not yet been finally established in dealing with the problem of two Coulomb centers.³⁴ The effect is known as "superpromotion" and will be discussed in Sec. 5.1.

3. NONADIABATIC TRANSITIONS BETWEEN BOUND STATES

Nonadiabatic transitions between terms are described by a system of Born-Fock equations which is obtained from the secular Schrödinger equation (1.1) after expansion of the wave function $\psi(\mathbf{r},t)$ in terms of an adiabatic basis [expansion (1.2)] and is given by

$$\frac{\mathrm{d}g_{p}(\tau)}{\mathrm{d}\tau} = \sum_{p'}' w_{pp'}(\tau) \exp\left(\frac{i}{v} \int \Delta E_{pp'}(\tau') \,\mathrm{d}\tau'\right) g_{p'}(\tau),$$
(3.1)

where

$$\tau = vt, \ \Delta E_{pp'}(\tau) = E_p(\tau) - E_{p'}(\tau),$$
$$w_{pp'}(\tau) = \left\langle \varphi_p(\tau) \middle| \frac{\mathrm{d}}{\mathrm{d}\tau} \middle| \varphi_{p'}(\tau) \right\rangle$$

is a matrix element of the nonadiabatic coupling. The variable τ is introduced so as to separate clearly a small parameter v in the system of dynamic equations (3.1). It represents the internuclear coordinate and will be used later instead of the internuclear distance to which it is related functionally by $R(\tau) \leftrightarrow \tau(R)$. Differentiation with respect to τ in a matrix element $w_{pp'}$ can be reduced to differentiation with respect to R and an angle ϕ , which sets the orientation of the internuclear axis to the collision plane:

$$w_{pp'}(\tau) = \frac{\mathrm{d}R}{\mathrm{d}\tau} \left\langle \varphi_p \right| \frac{\mathrm{d}}{\mathrm{d}R} \left| \varphi_{p'} \right\rangle + \frac{\mathrm{d}\phi}{\mathrm{d}\tau} \left\langle \varphi_p \right| \frac{\mathrm{d}}{\mathrm{d}\phi} \left| \varphi_{p'} \right\rangle.$$
(3.2)

Such a separation of $w_{pp'}$ into radial and rotational parts is usually employed in specific numerical calculations, but there is no need to do this in an asymptotic approach and both types of coupling will be allowed for simultaneously in the results given below.

In the adiabatic limit the transitions between terms are not frequent and they are localized, as already mentioned, in the region of the closest approach (quasicrossing). The technique for asymptotic calculation of the probability of a transition from a term $E_q(\tau)$ to other terms $E_p(\tau)$ participating in a given quasicrossing can be described briefly as follows.⁸ In the limit $v \rightarrow 0$ the solution of the system of equations (3.1) has the following asymptotic form (accurate to within a preexponential factor) in the complex plane of τ :

$$g_p^{(\mathrm{ac})}(\tau) \approx \exp\left(\frac{i}{v}\int \Delta E_{pq}(\tau') \,\mathrm{d}\tau'\right),$$
 (3.3)

which is valid everywhere except for a small region Ω around a complex branching point $\tau_c = \tau(R_c)$. Inside Ω we have to separate and solve exactly a simplified standard system of equations allowing correctly for the nature of a singularity at the point τ_c . The amplitude of the transition probability is obtained by matching, at the boundary of the region Ω , the solution of the standard system to the asymptote given by Eq. (3.3) and satisfying the initial conditions of Eq. (1.3). This procedure is analogous to matching of a semiclassical wave function to the right and left of a turning point with the aid of the Airy function.³⁵

3.1. Generalized Landau–Zener transitions

A theory of two-level Landau-Zener transitions is usually discussed in detail in the literature and such transitions are most frequent in applications. However, this theory is invalid in the case of some processes. They include, for example, transitions occurring in the case of short internuclear distances between terms which are degenerate in the limit of a united atom (R = 0). Simultaneous crossing of more than two terms appears in multicenter (polyatomic) systems for certain special configurations of the centers. The general problem, in which there is no limit on the number of states or on the nature of their interaction in the quasicrossing region, was solved in Ref. 21.

Following Ref. 21, we shall consider nonadiabatic transitions involving simultaneous quasicrossing of a group of Nterms or levels, which is related to the exact crossing in the complex plane of τ at the point τ_c . First of all, we shall separate the standard system of equations in the region Ω near the singularity τ_c . At the point τ_c the eigenvalues of the Hamiltonian are N-fold degenerate and the Hamiltonian can be reduced, because of its nonself-adjoint nature (Im τ_c \neq 0), to a Jordan form of $N \times N$ size:

$$H(\tau_{c}) = \begin{pmatrix} E_{c} & 1 & 0 & 0 & \dots \\ 0 & E_{c} & 1 & 0 & \dots \\ 0 & 0 & E_{c} & 1 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}.$$

Near the point τ_c the Hamiltonian can be represented in the first approximation by

$$H(\tau) = H(\tau_c) + \Delta \tau^s U, \qquad (3.4)$$

where $\Delta \tau = \tau - \tau_{\rm e}$, s > 0, and U is an $N \times N$ matrix with constant matrix elements U_{ij} . It is assumed that $U_{N1} \neq 0$. This condition corresponds to the general case, so that it should not be regarded as a limitation.⁸⁾ The terms of the Hamiltonian (3.4) obtained in the first order of perturbation theory based on a small parameter $\Delta \tau$ are

$$E_{p}(\tau) = E_{c} + (\Delta \tau^{*} U_{N1})^{1/N} e^{2i\pi p/N} \quad (p = 1, 2, ..., N).$$
(3.5)

In the same approximation a matrix element for the nonadiabatic coupling reduces to

$$w_{pp'}(\tau) = \frac{i(-1)^{p-p'}s}{2N\Delta\tau\sin\left[(p-p')\pi/N\right]}.$$

After substitution of the approximate expressions for $E_p(\tau)$ and $w_{pp'}$ in Eq. (3.1), we obtain a system of equations

$$\vartheta \frac{\mathrm{d}}{\mathrm{d}\vartheta} G = \hat{M}G, \quad M_{pp} = 0, \quad (3.6)$$
is exp [fexp [2ix (p'-1)/N] - exp [2ix (p-1)/N]] \vartheta]

 $M_{pp'} = \frac{15 \exp \left[(\exp \left[2 \ln (p' - 1)/N \right] - \exp \left[2 \ln (p' - 1)/N \right] \right]}{2 (N+s) \sin \left[(p-p') \pi/N \right]}$

which is the standard system in the vicinity Ω of the point τ_c . In Eq. (3.6) the quantity τ is replaced by a more convenient variable

$$\boldsymbol{\vartheta} = -\frac{i}{v} \left(1 + \frac{s}{N} \right) \left(U_{Ni} \Delta \tau^{N+s} \right)^{1/N} e^{2i\pi/N}$$

and instead of the functions g_p we have introduced

$$G_p = (-1)^p \exp\left(-\frac{i}{v} \int_{\operatorname{Re} \tau_c}^{\tau_c} E_p(\tau') \,\mathrm{d}\tau'\right) g_p. \tag{3.7}$$

The size of the region Ω where the standard system (3.6) differs little from the Born-Fock system of equations (3.1) is determined by the validity of the approximation (3.5) for the energy terms (levels) and is obviously independent of v, because at the boundary of Ω the values of ϑ tend to infinity for $v \rightarrow 0$ and the solution of the standard system of equations here reaches its asymptotic form which is described functionally by Eq. (3.3). This makes it possible to relate the values of $g_p^{(ac)}$ to the right and left of the quasicrossing region and to calculate the transition probability amplitude. In the adiabatic approximation this amplitude splits into an exponential function, which is trivial and is already separated in Eq. (3.7), and a preexponential factor, which is the Stokes constant of the standard problem. Calculation of the Stokes constants is not always possible for a system of two equations, but in the case of the system (3.6) this can be done for any values of N and of the parameter s representing the type of interaction of terms in the quasicrossing region.²¹ The final expression for the transition probability amplitude is

$$A_{pq} = \frac{\sin \left[\pi s/(N+s)\right]}{\sin \left[\pi/(N+s)\right]} e^{-\Delta_{pq}/v},$$
(3.8)

where

$$\Delta_{pq} = \left| \operatorname{Im} \int_{\operatorname{Re} \tau_{c}}^{\tau_{c}} \Delta E_{pq} \left(\tau \right) \, \mathrm{d}\tau \right|$$

.

is the Massey parameter. It is interesting to point out that in the case of the most natural multilevel quasicrossings, when the perturbation in Eq. (3.4) is linear in $\Delta \tau$ (s = 1), the preexponential factor in Eq. (3.8) is independent of N and equal to unity.

3.2. Rotational transitions in close collisions

Nonadiabatic transitions in the case of close atomic collisions between quasimolecular states, which are degenerate in the united atom limit (R = 0), are of special interest from the theoretical point of view, because they represent an example of transitions which are not of the Landau–Zener type. We shall consider these transitions in the problem of two Coulomb centers Z_1eZ_2 with the Hamiltonian described by Eq. (5.1). For low values of $R = |\mathbf{R}_2 - \mathbf{R}_1|$ (\mathbf{R}_i is the radius vector of the *i*th Coulomb center), in the first approximation the terms of this problem are³⁶

$$E_{nlm}(R) = -\frac{Z^2}{2n^2} + \gamma \left[3m^2 - l\left(l+1\right)\right] R^2, \qquad (3.9)$$

where

$$\gamma = \frac{2Z_1Z_2Z^2}{n^{3}l(l+1)(2l-1)(2l+1)(2l+3)},$$

 $Z = Z_1 + Z_2$, and (n,l,m) are spherical quantum numbers of the united atom. In this approximation the adiabatic wave functions are expressed in terms of hydrogenic wave functions of the united atom

$$\varphi_{nlm}^{(\pm)}(\mathbf{r}, R) = \frac{1}{\sqrt{2}} F_{nl}(r) \left[Y_{lm}(\widehat{\mathbf{rR}}) \pm (-1)^m Y_{l, -m}(\widehat{\mathbf{rR}}) \right]$$
(3.10)

in a system of coordinates with its origin at the center of the charges

$$R_{\rm C.C.} = (Z_1 \mathbf{R}_1 + Z_2 \mathbf{R}_2) Z^{-1},$$

where the z axis is directed along the internuclear distance and the x axis is perpendicular to the collision plane. The functions described by Eq. (3.10) have a definite parity (\pm) relative to the change in the sign of x (the symmetry is exact) and these functions depend on τ only via an angle $\phi(\tau)$, which determines the orientation of the internuclear axis. As a result the nonadiabatic interaction of Eq. (3.2) reduces to a rotational interaction of states with identical quantum numbers *n* and *l* and with the parity³⁷

$$\left\langle \varphi_{nlm}^{\pm} \middle| \frac{d}{d\tau} \middle| \varphi_{nlm'}^{\pm} \right\rangle = \frac{1}{2} \frac{d\varphi}{d\tau} \left\{ \left[(l+m) (l-m+1) \right]^{1/2} \delta_{m', m-1} \right] \\ + \left[(l-m) (l+m+1) \right]^{1/2} \delta_{m', m+1} \right\},$$

$$(3.11)$$

whereas the Born-Fock system of equations splits into independent systems of N = l equations for odd states and N = l + 1 equations for even states.

The explicit time dependence can be found and analytic properties of the adiabatic wave functions of the Hamiltonian can be determined by introducing a fixed system of coordinates with the x' axis directed opposite to the flux of the incoming particles Z_2 and with the z' axis perpendicular to the collision plane. The adiabatic functions of Eq. (3.10) can be expressed in terms of spherical functions in a fixed coordinate system using the Wigner d functions:

$$\varphi_{nlm}^{\pm} = \frac{1}{\sqrt{2}} F_{nl}(r) \sum_{m'=-l}^{l} \left[d_{mm'}^{l} \left(\frac{\pi}{2} \right) \pm (-1)^{m} d_{-mm'}^{l} \left(\frac{\pi}{2} \right) \right] \times Y_{lm'}(\vartheta', \varphi') e^{im'\varphi(\tau)}.$$
(3.12)

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Since rotational transitions occur within the subspace of states with fixed values of n and l, instead of the exact Hamiltonian (5.1) we shall consider a simpler "equivalent" operator which has the eigenvalues of Eq. (3.9) and the eigenfunctions of Eq. (3.10) in this half-space:

$$H_{eq}(\tau) = hI + 3\gamma R^2 l_z^2$$
$$= hI + \frac{3}{4} \gamma R^2 (\tilde{l}_-^2 e^{2i\varphi} + \tilde{l}_+ \tilde{l}_- + \tilde{l}_- \tilde{l}_+ + \tilde{l}_+^2 e^{-2i\varphi}), \quad (3.13)$$

where $h = -Z^2/2n^2 - \gamma l(l+1)R^2$; *I* is a unit operator; l_z is the projection of the angular momentum onto the internuclear axis; $\tilde{l}_{\pm} = l_{x'} \pm i l_{y'}$ are the operators representing an increase and reduction in the azimuthal quantum number in a coordinate system at rest. In Eqs. (3.12) and (3.13) the time dependence appears explicitly in the form of powers of the exponential function $\exp(i\phi)$. We shall consider specifically the approximation of a rectilinear transit characterized by $R^2 = \rho^2 + v^2 t^2$ and $\tan \phi = \rho/vt$, where ρ is the impact parameter. We then have

 $\Delta E_{nlm, nlm'}(\tau) = 3\gamma (m^2 - m'^2) R^2 = 3\gamma (m^2 - m'^2) (\rho^2 + \tau^2),$

$$\frac{\mathrm{d}\varphi}{\mathrm{d}\tau} = \frac{P}{R^2} = \frac{P}{(\rho - i\tau)(\rho + i\tau)}, \qquad (3.15)$$

$$e^{\pm i\phi} = \cos\phi \pm i \sin\phi = \frac{vt \pm i\rho}{[(\rho - i\tau)(\rho + i\tau)]^{1/2}}.$$
 (3.16)

Equation (3.14) describes a quasicrossing of a group of parabolic levels with the minimum splitting

$$\Delta E_{\min} = 3\gamma \left(m^2 - m^{\prime 2} \right) \rho^2$$

at $\tau = 0$. The exact crossing of the levels occurs at complex points $\tau_c = \pm i\rho$, where R = 0. It follows from Eq. (3.15) that, in accordance with the general theory, a matrix element of the nonadiabatic coupling described by Eq. (3.11) has a first-order pole at the point τ_c . A divergence of the exponential function (3.16) at points τ_c creates a divergence of the terms in the wave function (3.12); the most singular of these is of the order of R^{-N+1} and exhibits the same dependence on the electron coordinates for all the interacting states. The Hamiltonian of Eq. (3.13) at the point τ_c is

$$H_{\rm eq}(\tau = \pm i\rho) = -\frac{Z^2}{2n^2}I - 3\gamma\rho^2 \tilde{l}_{\pm}^2$$

and, as can be demonstrated readily, can be reduced to the Jordan form in the basis of spherical functions $Y_{em}(\vartheta', \varphi')$. Therefore, although the levels of the problem cross exactly for a real internuclear distance $R \approx 0$ and a quasicrossing appears for kinematic reasons as a result of a change from R to $\tau(R)$, we nevertheless still have all the properties discussed in the first part of Sec. 2.

Rotational transitions between the states with l = 1 (σ - π transitions) were considered in the adiabatic approximation in Refs. 19 and 20. In this case there is one odd state which does not participate in the transitions and two even states, and the amplitude of the transition probability between these states is given by Eq. (3.8) with N = 2 and s = 2. The value s = 2 is obtained by comparing Eqs. (3.14) and (3.5) in the vicinity of the point τ_c . The preexponential factor in Eq. (3.8) amounts to $\sqrt{2}$ for these transitions and the cross section is twice as large as that obtained by the

formal application of the Landau-Zener model with the same Massey parameter as before.

If $l \ge 2$ for even states and $l \ge 3$ for odd states, the twolevel approximation becomes invalid. On the other hand, in view of the specific tridiagonal structure of the Hamiltonian (3.13) in the $Y_{em}(\vartheta', \varphi')$ basis, the matrix element U_{N1} in Eq. (3.4) vanishes so that strictly speaking it is not possible to use the result obtained in the general theory and given by Eq. (3.8). However, because of a large set of standard systems of the type described by Eq. (3.6), we can select that system which is closest to the situation under consideration. In the case of N-level rotational transitions (N = l + 1 for)even states and N = l for odd states) the closest is the system with s = N. This ensures the correct, linear in $\Delta \tau$, behavior of the splitting of the terms in the vicinity of the point $\tau_{\rm c}$ and is approximated optimally by the matrix elements of the nonadiabatic coupling of Eq. (3.11). Substituting s = N in Eq. (3.8), we find that the amplitude of the probability of rotational transitions is

$$A_{mm'} = \frac{1}{\sin(\pi/2N)} e^{-\Delta_{mm'}/v}.$$
 (3.17)

In the case of three-level $\sigma - \pi - \delta$ transitions this result is rigorous.²² At high values of l the preexponential factor is approximately equal to $2N/\pi$ and it affects strongly the magnitude of the cross section. For example, if l = 4, it increases the cross section by an order of magnitude.

Figure 4 shows, by way of example, the results of a calculation for the case of the charge transfer reaction C^{6+} $+ H(1s) \rightarrow C^{5+}(n') + H^+$. This reaction is due to a Landau-Zener transition between the terms $5g\sigma$ and $4f\sigma$ when $R \approx 8$ a.u., and also because of rotational transitions over short internuclear distances within multiplets (n = 4, l = 3)and (n = 5, l = 4). Figure 4 shows the charge-transfer cross sections for the C^{5+} state with the principal quantum numbers n' = 4 or 5, calculated in the adiabatic approximation ignoring the rotational transitions in question³⁸ and allowing for them in accordance with Eq. (3.17).³⁹ It is clear from this figure that the rotational transitions make a considerable contribution to the charge-transfer cross section and inclusion of these transitions within the adiabatic approximation framework ensures good agreement both with



FIG. 4. Dependences of the charge transfer cross section on the collision velocity for the C⁶⁺ + H(1s) \rightarrow C⁵⁺ (n') + H⁺. The continuous curves represent the adiabatic approximation allowing for rotational transitions,³⁹ the chain lines give the adiabatic approximation ignoring rotational transitions,³⁸ the dashed lines give the numerical calculations carried out by the tight-binding method,⁴¹ and the black dots are the experimental values.⁴⁰

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the experimental results⁴⁰ and with the currently most accurate numerical calculations by the strong coupling method in the basis of 33 states.⁴¹

We shall conclude this section with a brief analysis of two more cases, which have been discussed in detail in the literature, but require some additional explanations in the context of the general theory discussed here.

3.3. Quasiresonant charge transfer

A process of quasiresonant charge transfer $A + B^+ \rightarrow A^+ + B$, characterized by a small splitting of the energy levels of the initial and final atomic states, represents a special situation. In calculations dealing with charge transfer characterized by a small resonance defect we can use the exactly soluble two-level Rosen–Zener–Demkov model^{11,12} in which the splitting of the levels is

$$\Delta E(R) = (\delta^2 + u^2(R))^{1/2}, \qquad (3.18)$$

where δ is the splitting of the levels in the limit $R \to \infty$ (resonance defect) and the function $u(R) = \alpha \exp(-\beta R)$ models the exchange interaction. Nonadiabatic transitions occur for $\delta \approx |u(R)|$. In the region of these transitions the splitting of the levels given by Eq. (3.18) is in the form of an infinite equidistant chain of complex branching points

$$R_j^{\pm} = R_P \pm i\pi \left(j - \frac{1}{2}\right) \beta^{-1} \quad (j = 1, 2, \ldots)$$

with the same real part $R_P = \beta^{-1} \ln(\delta^{-1}\alpha)$ for all the points. The probability of transition in the Rosen-Zener-Demkov model is¹²

$$P = \frac{\exp(-\Delta/v)}{2 \operatorname{ch}(\Delta/v)} = \sum_{j=1}^{\infty} (-1)^{j} e^{-j\Delta/v}, \qquad (3.19)$$

where $\Delta = \pi \delta / 2\beta$ is the product $(i \cdot \Delta)$ identical with the Massey parameter of a branching point R_i . The probability series given by Eq. (3.19) is identical, with a precision which is exponential in terms of v^{-1} , with the probability of a Landau-Zener transition because of a branching point R_1 closest to the real axis of R and the difference from Eq. (3.8) is obviously associated with the fact that the Rosen-Zener-Demkov model has a more distant branching point R_i with $i \ge 2$. The question then arises: is an infinite regular chain of branching points R_i a specific feature of the exactly soluble model or does it indeed exist for real quasimolecular levels discussed in the case of quasiresonant charge transfer? The relevant procedure was applied in Ref. 39 to levels in the problem of two Coulomb centers with very similar charges. The results revealed regular chains of branching points of the relevant type (see Fig. 6b below), confirming the physical justification for the application of the Rosen-Zener-Demkov model in calculations relating to quasiresonant charge transfer.

3.4. Transitions due to level crossing

An exact crossing of levels for real values of τ_c usually occurs for states of different symmetry. If τ_c is real, the Hamiltonian $H(\tau_c)$ is self-adjoint, so that it is reduced not to the Jordan form but to the diagonal one. Adiabatic wave functions at the point τ_c are then linearly independent and do not have a singularity, like the matrix elements for the nonadiabatic coupling. This makes it possible to calculate the transition probability employing the adiabatic version of perturbation theory.⁸ This adiabatic version is based on the assumption of smallness of the changes in the populations of the levels in the course of a collision; the solutions $g_{\rho}(\tau)$ for the right-hand side of the Born–Fock equations [Eq. (3.1)] are replaced with the initial values of Eq. (1.3) and then the solution is obtained in a trivial manner:

$$A_{pq} = \lim_{\tau \to \infty} g_p(\tau) = \int_{-\infty}^{+\infty} w_{pq}(\tau) \exp\left(\frac{i}{v} \int \Delta E_{pq}(\tau') d\tau'\right)^{1/2} d\tau.$$

The integral with respect to τ can be calculated in the limit $v \rightarrow 0$ by the stationary phase method so that the probability of a transition from the initial level $E_q(\tau)$ to other levels participating in a given crossing is described by:⁹⁾

$$P_{pq} = 2\pi v |w_{pq}(\tau_c)|^2 \left(\frac{\mathrm{d}\Delta E_{pq}}{\mathrm{d}\tau} \Big|_{\tau=\tau_c} \right)^{-1} ,$$

which is valid for an arbitrary number of levels which cross at the point τ_c . The adiabatic version of perturbation theory cannot be applied to quasicrossings because in this case the change in the solutions $g_{\rho}(\tau)$ in the vicinity of the complex stationary phase point τ_c is not small and, moreover, the solutions and the matrix elements of the nonadiabatic coupling have a singularity at this point.

4. NONADIABATIC TRANSITIONS FROM A BOUND STATE TO A CONTINUOUS SPECTRUM

In dealing with ionization processes the theoretical task is to calculate the ionization cross sections and the energy distributions of the emitted electrons. The process of detachment of an electron, i.e., ionization of a negative ion, can be described quite simply in the adiabatic approximation. This process is associated with the evolution of a quasimolecule in respect of the level which merges with a continuous spectrum at some value of the internuclear distance R_0 (see Figs. 3a and 3b). After such merging the level in practice decays completely at low values of v, i.e., the ionization probability is unity if in the process of a collision the point R_0 is reached and the probability is zero in the opposite case. Obviously, the ionization cross section calculated in the approximation of rectilinear transit in accordance with Eq. (1.4) is independent of the velocity v in this approximation and its value is given by $\sigma = \pi R_0^2$. This expression can be refined allowing mainly for curved paths of the nuclei.42

The process of ionization of neutral atoms and positive ions is associated with a more subtle "superpromotion" effect (Fig. 3c) which is difficult to reveal in a general picture of real quasimolecular levels. In this case the ionization probability is equal to the product of the probabilities of Landau-Zener transitions via a sequence of quasicrossings which becomes denser at the boundary of a continuous spectrum:

$$P(\rho) = e^{-2\Delta(\rho)/\nu}, \qquad (4.1)$$

where

$$\Delta(\rho) = \sum_{p=q}^{\infty} \Delta_{p, p+1}(\rho)$$

is the total Massey parameter of a transition from a level

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 $E_q(R)$ to the continuous spectrum and $A_{p,p+1}$ is the Massey parameter for a single quasicrossing. It follows from Eq. (4.1) that the cross section for such a "subbarrier" ionization process tends exponentially to zero in the limit $v \rightarrow 0$ (see Fig. 11a below).

The task of calculation of the energy distribution of the emitted electrons is more difficult. This was tackled first using the adiabatic version of perturbation theory for subbarrier transitions to a continuous spectrum⁴³ and also within the framework of exactly soluble models, among which the most general is the Demkov–Osherov model.^{14–16} The range of validity has been extended by proposing a number of semi-phenomenological generalizations of the model results.^{44,45} A consistent asymptotic approach to the calculation of transitions to a continuous spectrum, which is not subject to the limitations on the nature of the Hamiltonian, is proposed in Ref. 23.

4.1. Adiabatic approximation for the ionization process

Inclusion in the adiabatic approximation of transitions to a continuous spectrum requires a radical review of the formalism employed earlier. In this case the selection of the basis for expansion of a nonstationary wave function $\psi(\mathbf{r},t)$ is no longer a trivial task. In the standard total basis of adiabatic functions in discrete and continuous spectra the secular Schrödinger equation of Eq. (1.1) reduces to the Born-Fock integrodifferential system. The shortcoming of this system of equations is that when one of the levels merges with a continuous spectrum, the system loses the corresponding equation and becomes meaningless. This shortcoming can be avoided if we select as the basis a set of wave functions of bound, quasistationary, and virtual states of an instantaneous Hamiltonian. Such a basis is purely discrete and complete in the sense of the Mittag-Leffler expansion.⁴⁶ However, fundamental difficulties are then encountered because of the breakdown of unitarity in the dynamic system of equations. Both bases are unsatisfactory also from the point of view of physics, because they ignore the delay of a nonstationary wave function relative to the eigenstates of the instantaneous Hamiltonian. This delay occurs because a wave packet of emitted electrons escaping to infinity in the limit $t \rightarrow \infty$ is causally related to the nature of the Hamiltonian not at a given moment of time but at the moment at which the ionization has taken place. When dealing with transitions between bound states the delay is unimportant because of the localization of a nonstationary wave function at the nuclei. This explains why the following expansion of a nonstationary wave function is selected in Ref. 23:

$$\Psi(\mathbf{r}, t) = \sum_{p} \int_{L} g_{p}(E) \varphi_{p}(\mathbf{r}, E) e^{-iEt} dE, \qquad (4.2)$$

where τ is replaced with E in the adiabatic functions φ_{ρ} with the aid of the functions $\tau_{\rho}(E)$ which are inverse to $E_{\rho}(\tau)$; the integration contour L has simply to satisfy the condition of vanishing of the integrand at its ends. Integration with respect to the energy in Eq. (4.2) makes it possible to allow in a natural manner, as shown below, for the delay of a wave packet of electrons formed as a result of ionization.

The secular Schrödinger equation of Eq. (1.1) assumes the following form ($\tau = vt$) after substitution of the expansion of Eq. (4.2):

$$\sum_{p} \int_{L} \left[H\left(\tau\right) - H\left(\tau_{p}\left(E\right)\right) \right] g_{p}\left(E\right) \varphi_{p}\left(\mathbf{r}, E\right) e^{-iEt} dE = 0.$$

$$(4.3)$$

This equation does not include the whole Hamiltonian but only its time-dependent part $V(\mathbf{r},\tau)$. Multiplying Eq. (4.3) by (*i* εt) and integrating with respect to time, we obtain

$$\sum_{\mathbf{p}} V(\mathbf{r}, \tau_{p}(\boldsymbol{\varepsilon})) g_{p}(\boldsymbol{\varepsilon}) \varphi_{p}(\mathbf{r}, \boldsymbol{\varepsilon})$$

$$= \sum_{p} \int_{L} \mathcal{V}(\mathbf{r}, v) g_{p}(\boldsymbol{\varepsilon} + vv) \varphi_{p}(\mathbf{r}, \boldsymbol{\varepsilon} + vv) dv, \qquad (4.4)$$

which can be used to find the functions $g_p(E)$ and is an analog of the Born-Fock system of equations [we have here $v = (E - \varepsilon)/v$ and $\mathscr{V}(\mathbf{r}, v)$ is a Fourier transform of the time-dependent interaction $V(\mathbf{r}, \tau)$]. The asymptotic forms of the solutions of this equation with respect to v, corresponding to the initial condition (1.3), are¹⁰

$$g_{p}(E) = \exp\left(\frac{i}{v}\int_{-\infty}^{E} \theta(\varepsilon) d\varepsilon\right), \quad p = q, \qquad (4.5)$$
$$= v\eta_{p}(E) \exp\left(\frac{i}{v}\int_{-\infty}^{E} \theta(\varepsilon) d\varepsilon\right), \quad p \neq q,$$

where $\theta(E)$ and $\eta_{\rho}(E)$ are the final functions in the limit $v \rightarrow 0$. The structure of the asymptotes in Eq. (4.5) is such that in the first and second approximation the states with $p \neq q$ make no contribution to the nonstationary wave function and the solution $g_q(E)$ obtained in this approximation is²³

$$g_q(E) = N\left(\frac{\mathrm{d}\tau_q}{\mathrm{d}E}\right)^{1/2} \exp\left(\frac{i}{v}\int_{E_q^{\infty}}^{E}\tau_q(\varepsilon)\,\mathrm{d}\varepsilon\right), \qquad (4.6)$$

so that the nonstationary wave function of Eq. (4.2) can be described by the following expression which is accurate to within corrections linear in v:

$$\psi(\mathbf{r}, t) = N \int_{L} \left(\frac{\mathrm{d}\tau_{q}}{\mathrm{d}E} \right)^{1/2} \varphi_{q}(\mathbf{r}, E)$$

$$\times \exp\left(\frac{i}{v} \int_{E_{q}^{\infty}}^{E} \tau_{q}(\varepsilon) \,\mathrm{d}\varepsilon - iEt \right) \mathrm{d}E; \qquad (4.7)$$

here, N is the normalization factor and E_q^{∞} = $\lim_{\tau \to -\infty} E_q(\tau)$.

The functions $\tau_q(E)$ and $\varphi_q(\mathbf{r},E)$ in Eq. (4.7) represent an analytic continuation throughout the complex plane of E and carry information not only on the state φ_q , but also on all the adiabatic states linked to this state by the branching points of Eq. (2.1), i.e., it carries information on all the states of a given symmetry. The limiting values of the level energies E_p^{∞} are real branching points of the integrand in Eq. (4.7). If we specify the rule for going around these points, we automatically specify the initial state. For example, if the integration contour $L(-\infty, +\infty)$ goes around above all the branching points (except E_q^{∞}) and below the point in question (Fig. 5), then in the limit $t \to -\infty$ this contour can be shifted to the upper half-plane (contour L' in Fig. 5) and the integral can be calculated by the saddle-point method. The saddle point \tilde{E} is found from the condition



FIG. 5. Contours of integration with respect to E in an expression for a nonstationary wave function given by Eq. (4.7).

$$\tau_q(\widetilde{E}) - vt = 0$$

and it tends to E_q^{∞} in the limit $t \to -\infty$. Consequently, the initial state for the solution of Eq. (4.7) selected in this way is

$$\psi(\mathbf{r}, t) \xrightarrow[t \to -\infty]{} N (2\pi\nu)^{1/2} \varphi_q(\mathbf{r}, E_q^{\infty}) e^{-iE_q^{\infty} t},$$

and hence the normalization factor is $N = (2\pi v)^{-1/2}$.

In the case of a nonstationary wave function of Eq. (4.7) a delay occurs in a natural manner for high values of r where in the limit $t \to +\infty$ there is a wave packet of the emitted electrons. In this case the large parameters in the integrand are r, v^{-1} , and t, and in calculation of the integral with respect to E by the saddle-point method the saddle point \tilde{E} is found from the equation

$$r (2\tilde{E})^{-1/2} + (\tau_q (\tilde{E}) - vt) v^{-1} = 0, \qquad (4.8)$$

in which the first term is taken from an asymptote for the adiabatic wave function $\varphi_q \propto \exp[i(2E)^{1/2}r]$. Interpretation of Eq. (4.8) is quite clear. It shows that a wave packet is formed from electrons that are created at a moment $\tilde{t} = \tau_q(\tilde{E})/v$ at a finite distance $\tilde{r} \sim 1$, when an adiabatic state φ_q (\mathbf{r}, \tilde{E}) is characterized by a momentum $\tilde{k} = (2\tilde{E})^{1/2}$ and as a result of free propagation with this momentum the packet travels to a distance $r = \tilde{k}(t - \tilde{t})$. Therefore, at a moment t the wave packet in question depends on the adiabatic state and on the nature of the Hamiltonian at the moment \tilde{t} of detachment of an electron with a momentum \tilde{k} .

4.2. Energy spectrum of electrons

The energy distribution of electrons formed as a result of ionization is obtained from Eq. (4.7) as follows. An integral with respect to E in Eq. (4.7) is divided into two parts: the first in the interval $-\infty < E < 0$ and the second in the interval $0 < E < \infty$. The first integral corresponds to that part of a nonstationary wave function which is localized near the nuclei and this follows from the exponential fall of the adiabatic wave function $\varphi_q(\mathbf{r}, E)$ away from the nuclei in this range of energies. In the limit $t \rightarrow \infty$ this integral can be calculated exactly by the saddle-point method and it is equal to the sum of the contributions of the saddle points E_p^{∞} corresponding to occupied atomic states. The probability of $q \rightarrow p$ transitions obtained in this way is identical with the Landau-Zener probability and, therefore, this approach includes, as a special case, nonadiabatic transitions between bound states. The second integral

$$\psi_{\text{w.p.}}(\mathbf{r},t) = \frac{1}{(2\pi\nu)^{1/2}} \int_{0}^{\infty} \left[\left(\frac{\mathrm{d}\tau_{q}}{\mathrm{d}E} \right)^{1/2} \varphi_{q}(\mathbf{r}, E) \right] \times \exp\left(\frac{i}{\nu} \int_{E_{q}^{\infty}}^{E} \tau_{q}(\varepsilon) \,\mathrm{d}\varepsilon - iEt \right) dE$$

$$(4.9)$$

represents in the limit $t \to \infty$ a wave packet (w.p.) of free electrons formed as a result of ionization. The adiabatic wave function in this integral describes a particle traveling to infinity with a momentum $k = (2E)^{1/2}$ and this function can be written in the form

$$\varphi_q (\mathbf{r}, E) = C_q (E) \chi_q (\mathbf{r}, E), \qquad (4.10)$$

where χ_q (**r**, *E*) is an adiabatic wave function normalized to the δ function on the energy scale *E* [see also Eq. (2.4)]. Substituting Eq. (4.10) into Eq. (4.9), we obtain $\psi_{w.p.}$ (**r**, *t*) in the form of an expansion in terms of the normalized functions of the continuous spectrum χ_q (**r**, *E*), and this leads directly to the following expression for the probability density of the electron energy distribution:

$$P_{q}(E) = \frac{1}{2\pi\nu} \left| \frac{\mathrm{d}\tau_{q}}{\mathrm{d}E} C_{q}^{2}(E) \exp\left(-\frac{2}{\nu} \int_{E_{q}^{\infty}}^{E} \tau_{q}(\varepsilon) \,\mathrm{d}\varepsilon\right) \right|. (4.11)$$

We can see from Eq. (4.11) that in calculating the energy spectrum we need to know the function $\tau_{q}(E)$, which is the inverse of $E_{a}(\tau)$ in the case when E > 0. In discussing the ionization process it is more usual to employ directly the function $E_{a}(\tau)$, which specifies the position and width of a quasistationary state as it merges with a continuous spectrum. Generally speaking, the two functions carry equivalent information about the system. However, the energy spectrum is not governed by the values of $E_{\mu}(\tau)$ with real τ , but by the values of $\tau_q(E)$ for real E > 0.¹¹⁾ Since Im τ_q $(E) \neq 0$ when E > 0, the two functionally related sets $\{E, \tau\}$ are different. The functions $\tau_q(E)$ describe the situation more satisfactorily than do $E_{q}(\tau)$. For example, in the case of real values of τ , the latter do not contain information on a continuous spectrum of virtual states of the system, where the energy is negative. In addition to $\tau_{a}(E)$, the distribution described by Eq. (4.11) includes also a factor $C_{\mu}^{2}(E)$ which represents the density of states. This is not a complication of fundamental importance, because both functions $\tau(E)$ and C(E) are found from the same spectral problem. In the case of short-range potentials the functions R(E) [which are used to describe $\tau(E)$ for given paths of the nuclei] and C(E) have low-energy asymptotes^{23,28}: if l = 0, then

$$\begin{split} R(E) &= R_0 + iE^{1/2} (\sqrt{2}\lambda)^{-1}, \quad C^2(E) = 8\pi E, \\ \text{if } l \neq 0, \text{ then} \\ R(E) &= R_0 + \left[E + \frac{i}{2} a_l^2 (2E)^{l + (1/2)}\right] \lambda^{-1}, \\ C^2(E) &= 2\pi a_l^2 (2E)^{l + (1/2)}, \end{split}$$

where λ and a_i are constants defined in Eqs. (2.16) and (2.17). The simple approximate expressions are very useful in practical calculations, since the spectrum of electrons corresponding to low values of v is concentrated at low energies. Among systems with the Coulomb long-range interaction

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the most detailed investigations have been made in the case of two Coulomb centers. This problem of two centers will be discussed in the next section, where we shall give both approximate expressions for the quantities governing the electron spectrum [Eqs. (5.7) and (5.8)] and the results of exact numerical calculation (see Figs. 9 and 10 below).

An example illustrating the application of this theory is shown in Fig. 11b, which gives the differential (in respect of the energy) ionization cross sections $\sigma'(E)$ for the $He + H^+ \rightarrow He^+ + H^+ + e$ reaction taken from Ref. 47. This ionization process occurs simultaneously in three channels (mechanisms of which will be discussed in the next section) and for each channel there is a certain range of energies E where a given mechanism predominates. A calculation of the cross section $\sigma'(E)$ was made using Eq. (1.4) with $P(E,\rho)$ of Eq. (4.11) in the rectilinear transit approximation. The functions C(E) and R(E) were taken from the solution of the problem of two Coulomb centers with effective charges for the appropriate one-electron molecular orbitals. It is clear from Fig. 11b that the total theoretical cross section is in good agreement with the experimental results (the experimentally observed oscillations in the region of 40 eV are related to the autoionization resonances of helium).

The asymptote of Eq. (4.7) breaks down in the vicinity of extremal points E_0 of the term $E_q(R)$, where $\tau_q(E) \approx \tau_0 + \text{const} \cdot (E - E_0)^{1/2}$ and the preexponential function in Eq. (4.7) becomes infinite. Here, we can separate and solve a standard equation which in this case is the Airy equation. Consequently, the uniform asymptote $g_q(E)$, which is valid in the vicinity of E_0 , can be expressed in terms of the Airy function Ai(x) and is of the form²³

$$g_{q}(E) = \left(\frac{2}{\pi v} \frac{\mathrm{d}\tau_{q}}{\mathrm{d}E}\right)^{1/2} \left(\frac{3}{2} \mu(E)\right)^{1/6}$$
$$\times \exp\left(-\mu(E_{q}^{\infty})\right) \operatorname{Ai}\left(\left(\frac{3}{2} \mu(E)\right)^{2/3}\right),$$

where

$$\mu(E) = \frac{i}{v} \int_{E_0}^E \tau_q(\varepsilon) \, \mathrm{d}\varepsilon$$

Away from the point E_0 the Airy function generally reduces to a superposition of two exponential asymptotes of the (4.6) type. This may give rise to oscillations in the energy spectrum, reflecting interference of electrons emitted as a result of approach and repulsion of nuclei. Similar oscillations, first discussed in a model approach,⁴⁵ have recently been observed experimentally.⁴⁸ In addition to extremal points E_0 , the asymptote of Eq. (4.7) breaks down in the vicinity of the limiting points E_q^{∞} , where $\tau_q(E)$ becomes infinite. In principle, the behavior of $g_q(E)$ in a small region of size ε surrounding a point E_q^{∞} can be obtained by comparing the known behavior, in the limit $t \to -\infty$, of a nonstationary wave function

$$\psi(\mathbf{r}, t) \approx \varphi_q(\mathbf{r}, E_q^{\infty}) \exp\left(-i \int_{-\infty}^{t} E_q(vt') dt'\right)$$

with the representation given by Eq. (4.2). However, there is no need for this refinement, because in an analysis of a nonstationary wave function after a collision it is sufficient to consider large but finite internuclear distances for which, on the one hand, there are no longer any transitions, and, on the other, the saddle points corresponding to populations of the term $E_p(\tau)$ do not fall within the region ε , the size of which tends to zero in the limit $v \rightarrow 0$.

5. LEVELS IN THE PROBLEM OF TWO COULOMB CENTERS

In the asymptotic theory adopted above the energy levels (terms) are assumed to be known and the problem of merging of these terms with the continuous spectrum and the reasons for quasicrossing are not discussed. We shall consider these reasons now in the specific case of two Coulomb centers as a problem of the same fundamental importance in the theory of atomic collisions as the problem of the hydrogen atom is in atomic physics. The levels and matrix elements of the nonadiabatic coupling are usually discussed by investigating their behavior for real values of R. Such information is sufficient in numerical integration of dynamic tight-binding equations in the adiabatic representation. However, in the asymptotic approach the probabilities of inelastic transitions are expressed in terms of the characteristics of the levels in the complex plane of R and one should rather speak of positions of branching points and of the general analytic structure of the levels. This is the approach which will be adopted here to deal with the problem of two Coulomb centers and an electron $(Z_1 e Z_2)$. A study of this system for real values of R has in the past led to the discouraging conclusion (see, for example, Ref. 36) that in the symmetric case $Z_1 = Z_2$ there should be no quasicrossing whatever, i.e., in such quasimolecules as H_2^+ the inelastic transitions cannot be described by the adiabatic approximation (apart from rotational transitions in the case of close collisions discussed in Sec. 3). Then only a direct numerical calculation of levels in the complex plane of R for the symmetric case gives a series of branching points, which can be regarded as a new type of quasicrossing called "latent" quasicrossing.^{34,49,50} Such quasicrossings explain not only the transitions between bound states, but also for the ionization process for which there has been no well-grounded mechanism in the one-electron approximation.

The nonsecular Schrödinger equation for two Coulomb centers

$$\left(-\frac{1}{2}\Delta - \frac{Z_1}{|\mathbf{r} - \mathbf{R}_1|} - \frac{Z_2}{|\mathbf{r} - \mathbf{R}_2|}\right) \varphi_{\mathbf{Q}} = E_{\mathbf{Q}}(\mathbf{R}) \varphi_{\mathbf{Q}} \quad (5.1)$$

admits, as is known, separation of variables in prolate spheroidal coordinates $(r_i = |\mathbf{r} - \mathbf{R}_i|)$:

$$\begin{split} \xi &= \frac{r_1 + r_2}{R} , \quad \eta = \frac{r_1 - r_2}{R} , \quad \varphi = \operatorname{arctg} \frac{x}{y} , \\ 1 &\leq \xi < \infty, \quad -1 \leq \eta \leq 1, \quad 0 \leq \varphi < 2\pi. \end{split}$$

Substitution of the wave function

$$\varphi_{0}(\mathbf{r}) = [(\xi^{2} - 1)(1 - \eta^{2})]^{-1/2} F(\xi) \Phi(\eta) e^{im\varphi}$$

in Eq. (5.1) yields the following equations for the functions $F(\xi)$ and $\Phi(\eta)$ (Ref. 36):

$$\frac{\frac{\mathrm{d}^{2}F\left(\xi\right)}{\mathrm{d}\xi^{2}} + \left[-p^{2} + \frac{a\xi - \lambda}{\xi^{2} - 1} + \frac{1 - m^{2}}{(\xi^{2} - 1)^{2}}\right]F\left(\xi\right) = 0, \quad (5.2)$$

$$\frac{\mathrm{d}^{2}\Phi\left(\eta\right)}{\mathrm{d}\eta^{2}} + \left[-p^{2} + \frac{b\eta - \lambda}{1 - \eta^{2}} + \frac{1 - m^{2}}{(1 - \eta^{2})^{2}}\right]\Phi\left(\eta\right) = 0, \quad (5.3)$$

where $p = (-2E)^{\frac{1}{2}}R/2; \quad a = (Z_1 + Z_2)R; \quad b = (Z_2)$

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 $-Z_1$) $R; \lambda$ is the separation constant. In the classification of levels it is usual to employ spherical quantum numbers Q = (n, l, m) of a compound hydrogenic atom with energy levels that reduce to terms in the problem of two Coulomb centers in the limit $R \to 0$. They are related to the number of zeros (k, q, and m) of the wave function in terms of the variables ξ , η , and φ (Ref. 36): n = k + q + m + 1, l = q + m. In the case of l and m we shall employ also the spectroscopic notation: $l = s, p, d, \dots$ instead of $l = 0, 1, 2, \dots$ and $m = \sigma, \pi, \delta, \dots$ instead of $m = 0, 1, 2, \dots$.

In the problem of two centers there are two nontrivial parameters which are the internuclear distance $R = |\mathbf{R}_2 - \mathbf{R}_1|$ and the ratio of the nuclear charges Z_1 / Z_2 . We shall consider first the symmetric problem $Z_1 = Z_2$. In this case the states are of specific parity relative to inversion in the system of coordinates with the origin in the middle of the internuclei axis and are divided into even (g states) and odd (u states). Clearly, the terms with different values of mor different parity do not have common branching points, since the exact symmetry of a state cannot change as a result of continuous variation of R. Figure 6a shows the branching points of the terms $1s\sigma_{g}$ (n = 1, l = 0, m = 0) and $2p\sigma_{u}$ (n = 2, l = 1, m = 0) of a molecular H_2^+ ion obtained as a result of direct numerical calculations.^{34,49} It is clear from this figure that all the branching points can be regarded as belonging to S and T series.



FIG. 6. Branching points of the terms $1s\sigma$ and $2p\sigma$ for $Z_1 = Z_2 = 1$ (a) and $Z_1 = 1$, $Z_2 = 1.001$ (b), and the matrix elements of the nonadiabatic coupling for the H_2^+ molecular ion (c). In Figs. 6a and 6b the expressions in parentheses give the quantum numbers of the terms associated with a given branching point. The black triangles in Fig. 6b identify approximate positions of the branching points of the P series calculated in the Rosen-Zener-Demkov model.



FIG. 7. The surface Re E(R) (a) and a system of adiabatic (continuous curves) and diabatic (dashed curves) terms (b) in the S series region of the H_2^+ ion. A rectangular box marked by a chain line represents the front cut of the energy surface in Fig. 7a.

5.1. S series of latent quasicrossings. Superpromotion of a diabatic level

The series S_{lm} consists of an infinite set of branching points R_n linking pairwise the terms $E_{nlm}(R)$ and $E_{n+1lm}(R)$ consecutively for all values of $n \ge l + 1$. The points in this series are localized in a small region Ω of the R plane (on the scale of Fig. 6 they merge) and have a limiting point

$$R_{\infty} = \lim_{n \to \infty} R_n$$

In the vicinity of the region Ω (but not inside it) the energy surface is in the form of a corkscrew with a pitch decreasing in proportion to n^{-3} (part of the corkscrew is shown in Fig. 7a for the S_{po} series). If in a given S series we assign a quasicrossing to each branching point and then replace such quasicrossings with the exact crossings, we obtain a system of what are known as the diabatic terms, which represent qualitatively possible directions of nonadiabatic transitions (Fig. 7b). It is clear from Fig. 7b that all the diabatic terms, except for one (W_{lm}), rise monotonically. The diabatic term W_{lm} is identical, at high values of R, with the lowest adiabatic term of a given series and then on reduction in R it bends steeply upward and joins a continuous spectrum at $R_s = \text{Re } R_{\infty}$.



The appearance of a series S_{lm} of latent quasicrossings is associated with the modification of the electron wave function in the vicinity of the point R_s , so that it changes from the one-center geometry of a united atom to the two-center geometry of a quasimolecule (Figs. 8a and 8b). An approximate analysis of the problem of two centers based on this representation yields a simple and fairly accurate analytic expression for the limiting point which sets the position of the S series⁵⁰:

$$R_{\infty} = Z^{-1} \left\{ \left(l + \frac{1}{2} \right)^2 - \frac{1}{2} (m+1)^2 \\ \pm i (m+1) \left[2 \left(l + \frac{1}{2} \right)^2 - \frac{1}{4} (m+1)^2 \right]^{1/2} \right\}.$$
 (5.4)

The complex quantity R_{∞} is of major practical importance. Its real part determines the range of the impact parameters for which we can expect nonadiabatic transitions involving S_{lm} latent quasicrossings, whereas the imaginary part gives the Massey parameter of the same transitions. Since the

FIG. 8. Qualitative representation of the regions of classically allowed motion of an electron (shown shaded) in the following ranges of the internuclear distance: a) $0 < R < R_s$; b) $R_s < R < R_1$; c) $R_1 < R < R_v$; d) $R_v < R < R_1$; e) $R_1 < R < \infty$.



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terms run almost parallel from the real axis R to the singularity R_{∞} (Ref. 34), the Massey parameter in Eq. (4.1) can be approximated quite accurately by

$$\Delta_{p,p+1} = \delta E_{p,p+1} \operatorname{Im} R_{\infty},$$

where $\delta E_{p,p+1}$ is the splitting of the corresponding pair of terms on the real axis when $R = R_s = \text{Re } R_{\infty}$.

The presence of the S_{lm} series can also be used to interpret the limits of validity of the compound atom approximation given by Eq. (3.9). The expansion postulated in this approximation is used widely in applications, but initially it has not been clear why in some cases it describes satisfactorily the real behavior of the terms (energy levels) at fairly large distances, whereas in other cases its range of validity is exceptionally narrow. As is known, this range of validity is governed by the distance to the nearest singularity. In the united atom approximation these singularities are in fact the S series and for them the distance to $|R_{\infty}|$ depends strongly on l [in accordance with Eq. (5.4)], so that in the case of the H_2^+ molecular ion it amounts to 17 a.u. for the h state (l = 5) and is only 0.5 a.u. for the s state. Another manifestation of the S series is the presence of a minimum in the case of the terms with $l > \sqrt{3m}$, when these series are quite close to the real axis of R. Figure 7a illustrates the formation of a minimum of the terms $3p\sigma$ and $4p\sigma$ under the influence of such a series, which makes the energy surface screw-like and displaces downward the terms in the interval $0 < R < 2R_s$.

5.2. T series of latent quasicrossings. Boundary of the quasimolecular region

Figure 6a shows not only the S series but also a series of branching points in the region of Re $R \approx 5$ a.u. Merging of the branching points of the $1s\sigma_g$ and $2p\sigma_u$ terms into one series is related to the exponential degeneracy of these terms in the limit $R \rightarrow \infty$. In the symmetric case $(Z_1 = Z_2)$ all the terms split into such (g,u) pairs for which the g state becomes a sum in the limit $R \rightarrow \infty$ and the u state becomes a difference between the hydrogenic states of isolated atoms (Z_1e) and (Z_2e) , which have the same set of quantum numbers $[n_1n_2m]$. The quantum numbers of the united atom introduced above are related to the latter by³⁶

$$q = 2n_2 - \frac{1}{2} [(-1)^m - 1],$$

$$n = q + n_1 + m + 1 \quad (g \text{ states}),$$

$$q = 2n_2 + \frac{1}{2} [(-1)^m + 1],$$

$$n = q + n_1 + m + 1 \quad (u \text{ states}).$$

Calculations reported in Ref. 49 indicate that for each pair there is a series of branching points $T_{n_in_jm}$ shared with higher terms. These series are described by approximate relationships illustrated in Fig. 6a. All the points of a given series are located on a straight line which is almost perpendicular to the real axis of R and they are separated by steps $\Delta R \approx 2\pi i n_{\infty}/Z$ ($n_{\infty} = n_1 + n_2 + m + 1$ is the principal quantum number of an isolated atom $Z_i e$). The branching points for the g and u terms alternate and they link states of the same parity with identical values of m and of the quasiradial quantum number k.

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The appearance of the $T_{n,n,m}$ series is due to the shift of a pair of the (g,u) terms to the top of the barrier in the effective potential of the quasiangular equation (5.3). The value of the internuclear distance R_T at which an energy level reaches the top of the barrier is given by the position of the T series on the real axis of R, so that we can obtain estimates using an expression

$$R_T = 8n_{\infty}Z^{-1} (2n_2 + m + 1), \qquad (5.5)$$

which is obtained in an approximation of high values of R. The presence of the T series reflects, as in the case of the S series, a qualitative modification of the adiabatic states: if $R < R_T$, an electron moves in a shared potential well of two centers and its wave function is essentially quasimolecular (Fig. 8b). If $R > R_T$, the ranges of classically allowed motion of an electron near its nucleus are separated from one another by a barrier and in this case the wave function can be represented approximately by a superposition (symmetric or antisymmetric) of the wave functions of two isolated atoms Z_1e and Z_2e (Fig. 8c). Therefore, R_T is the limit of the essentially quasimolecular region on the side of high values of R. On the other hand, R_T is the limit of validity of asymptotic expansions for energy levels expressed in terms of the reciprocals of R.

5.3. P series of latent quasicrossings. Rosen–Zener–Demkov interaction

If $Z_1 \neq Z_2$, we find that the exact (g,u) symmetry is lost and additional series of branching points appear. Figure 6b shows the branching points of the terms $1s\sigma$ and $2p\sigma$ in the case when $Z_1 = 1$ and $Z_2 = 1.001$. In addition to the $S_{s\sigma}$, $S_{p\sigma}$, and T_{000} series, we now have a new series of branching points (P_{000}) in the region where $R \approx 10$ a.u. It is related to the Rosen-Zener-Demkov interaction and it has been already discussed qualitatively in Sec. 3 in connection with quasiresonant charge transfer. Such series match pairs of terms given in the preceding subsection when dealing with the T series. However, in the present case these pairs are no longer degenerate in the limit $R \rightarrow \infty$, but have a resonance defect

$$\delta = (Z_2^2 - Z_1^2) (2n_{\infty}^2)^{-1}$$

and correspond in this limit to parabolic hydrogenic states localized at different nuclei. The branching points of the $P_{n,n,m}$ series can be found approximately by equating to zero the radicand in Eq. (3.18) if the exchange interaction w(R)is described by the asymptotic expression valid in the limit $R \to \infty$ for the problem of two centers with identical nuclear charges⁵¹:

$$w(R) = \frac{2(2R/n_{\infty})^{n_{\infty}-n_{1}+n_{2}} \exp\left[-n_{\infty}-(R/n_{\infty})\right]}{n_{\infty}^{2}n_{2}!(n_{2}+m)!}$$

The results of such a calculation are represented by triangles in Fig. 6b and we can see from this figure that they agree well with the exact values.

The series labeled P are related to breakdown of the approximate (g,u) symmetry. To the left of this series $(R < R_P)$ we can ignore the resonance defect compared with the exchange interaction so that the situation is close to the

symmetric case when $Z_1 = Z_2$, i.e., the adiabatic wave functions have an approximate (g,u) symmetry (Fig. 8c). To the right of the series ($R > R_P$) the dominant influence comes from the resonance defect while the approximate symmetry disappears and the state is localized at one of the nuclei (Fig. 8d). In the limit $Z_2 \rightarrow Z_1$ the P series shift along the real halfaxis of R to infinity and the (g,u) symmetry becomes exact.

When the difference between the charges increases, the S and T series are initially unaffected, but the P series shifts as a whole to the left and at some value $\Delta Z = Z_2 - Z_1$ it merges with the T series. This results in disappearance of a series of branching points characteristic of the Rosen-Zener-Demkov model and the model itself is no longer valid. For example,⁴⁹ in the case of a pair of the $1s\sigma$ and $2p\sigma$ terms this occurs for $Z_1 = 1$ and $Z_2 = 1.07$. It is worth noting the fact that the Rosen-Zener-Demkov coupling disappears when the resonance defect δ is very small, amounting to just 1/7th of the distance to the next multiplet.

5.4. Isolated Landau–Zener quasicrossings

In addition to the above-mentioned series of branching points, the problem of two centers is characterized by isolated pairs of conjugate branching points R_c and R_c^* in the case when $Z_2 \neq Z_1$ and $R > R_P$ (or $R > R_T$, when the T and P series merge); these isolated branching points are associated with the usual quasicrossings between adiabatic states located at different nuclei and are characterized by parabolic quantum numbers: n_1 , n_2 , m for the Z_1 nucleus and n'_1 , n'_2 , m' for the Z_2 nucleus; here, $n_1 = n'_1$, $n_2 \neq n'_2$, m = m'. These quasicrossings have long been known and are widely used in calculations dealing with specific processes.³⁶ The minimum separation between the terms ΔE_{\min} is then determined by a subbarrier exchange interaction so that quasicrossings are narrow and well defined (Fig. 1) and the Massey parameter can be calculated using the Landau-Zener approximation³⁵:

$$\Delta = \pi \Delta E_{\min}^2 \left(4\Delta F \right)^{-1}, \tag{5.6}$$

where $\Delta F = |F_2 - F_1|$ is the difference between the slopes of the corresponding diabatic terms at the point $R_1 = \text{Re } R_c$. In Eq. (5.6) we can replace ΔE_{\min} and ΔF by their asymptotic values corresponding to high values of R. The asymptotic expressions for ΔE_{\min} have been obtained by semiclassical^{52,53} and quantum^{54,55} approaches. They all ensure the same precision of the order of 10%. The most compact expression is of the form⁵³

$$\Delta E_{\min} = \frac{4E_{\mathrm{I}} (4p_{\mathrm{I}})^{n_{2}+n_{2}'+m+1} \exp\left(-2p_{\mathrm{I}}\right)}{\left[n_{\infty} n_{\infty}' n_{\infty}' n_{2}! n_{2}'! (n_{2}+m)! \left(n_{2}'+m\right)!\right]^{1/2}},$$

where

$$p_{\rm I} = \frac{1}{2} (-2E_{\rm I})^{4/2} R_{\rm I}, \quad n'_{\infty} = n'_{\rm I} + n'_{\rm 2} + m' + 1.$$

The values of E_1 , R_1 , and ΔF are usually obtained from an expansion of terms in reciprocal powers of R (Refs. 52–55):

$$E_{\rm I} = -\frac{(Z_2 - Z_1)^2}{2(n_2 - n_2')^2} , \quad R_{\rm I} = \frac{2(Z_2 - Z_1)}{(Z_2/n_{\infty}')^2 - (Z_1/n_{\infty})^2} ,$$
$$\Delta F = \frac{Z_2 - Z_1}{R_{\rm I}^2} .$$

The passage through an isolated quasicrossing is also

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accompanied by a qualitative change in the adiabatic states. For example, if $R < R_1$, a state is localized at the Z_2 nucleus (Fig. 8d), whereas for $R > R_1$ this adiabatic state is now located at the Z_1 nucleus (Fig. 8e) and vice versa.

Thus, the nonadiabatic transitions occur whenever a change in the internuclear distance causes a qualitative modification of the adiabatic state, i.e., when the topology of the range of classically allowed motion of electrons is modified. One may gain an impression that the S, T, and P series of branching points play no role in the theory of nonadiabatic transitions, because they are not manifested prominently in the behavior of the energy terms corresponding to real values of R. This is not true. According to the general asymptotic theory, any branching point is related to the transition probability of Eq. (3.8), which naturally can decrease on increase in the distance of a branching point from the real axis of R. The range of a strong interaction of adiabatic states may not be manifested in the pattern of terms corresponding to real values of R (as is true of terms in the Rosen-Zener-Demkov model). A more illuminating object is represented by the matrix elements of the nonadiabatic coupling $w_{QQ'}(R)$. Figure 6c shows the matrix elements $w_{QQ'}$ (R) obtained in Ref. 56 for the H_2^+ molecular ion. It is clear from this figure that they have clear maxima at the points where the S and T series are located (compare with Fig. 6a), although such regions are not distinguished in any particular case in the behavior of the terms themselves (Fig. 7b).

Latent quasicrossings are wide and are characterized by relatively large values of the Massey parameter Δ . Transitions due to these quasicrossings become noticeable when the collision velocity v is sufficiently high. This raises the problem of the limits of validity of the adiabatic approximation. There is no rigorous quantitative criterion, but the experience in using the adiabatic approximation makes it possible to hope that this is justified up to the maximum of the cross section of a given transition, i.e., $v < \Delta$.

5.5. Quasistationary and virtual states

Antibonding (quasistationary and virtual) states in the problem of two Coulomb centers have not been investigated until recently. This has been primarily due to the absence of an obvious effective barrier in the quasiradial equation (5.2)because quasistationary states are usually associated with the presence of a barrier. However, in calculations of the parameters of the ionization process in the adiabatic approximation the question of existence of such states appears unavoidably because the function R(E) in the range E > 0 is associated with these states; calculation of this function reduces to calculation of the function $\tau(E)$ governing the energy spectrum of electrons [Eq. (4.11)]. The results of such investigations are also of general theoretical interest since, because of the long-range Coulomb interaction, we cannot use the general ideas from the S-matrix theory and the situation is unclear even in the qualitative sense.

The antibonding terms were discovered in the problem of two centers and investigated in a study reported in Ref. 57. The following numerical calculation method was used to find these terms. Initially, a branching point R_c , which at this stage is common with the as yet unknown antibonding term $E_{ant}(R)$, is being sought on a discrete term $E_{nlm}(R)$. Then, going around this branching point results in a transi-



FIG. 9. Paths of the poles of the S matrix in the complex plane of the wave number k for antibonding states $\overline{2p\sigma}$, $\overline{3d\sigma}$, $\overline{4f\sigma}$, and $\overline{5g\sigma}$ of the H₂' molecular ion. The values in the parentheses give the internuclear distance.

tion to a sheet corresponding to the antibonding term [see the discussion of Eq. (2.1)] and on return to the real axis of R, we calculate the antibonding term $E_{ant}(R)$ for real values of R. Classification of antibonding terms is governed by the method of finding them: they are assigned spherical quantum numbers of the discrete term, with which they share a branching point R_c and they are identified by a bar above the quantum numbers: (nlm).

From the point of view of investigation of the ionization process it would be of interest to consider those antibonding terms which adjoin the series S_{lm} resulting from "superpromotion" of the diabatic term W_{lm} to a continuous spectrum. Figure 9 shows the results of a numerical calculation of such antibonding terms for the H_2^+ molecular ion in the form of a standard pattern of S-matrix poles in the complex plane of the wave number $k = (2E)^{1/2}$. They share the branching point R_c with the lowest, in the given S_{lm} series, discrete term $E_{n_alm}(R)$ ($n_0 = l + 1$). Moreover, they have a second branching point which coincides with the limiting point R_{∞} of the S series [Eq. (5.4)]. The positions of the poles depend on the internuclear distance and when R is varied, they shift along a path resembling a hyperbola with its vertex on the imaginary axis of k at a point

$$k_0 \approx i Z \left(l + \frac{1}{2} \right)^{-1}$$
.

A qualitative feature of this situation is that the symmetric poles merge for $k_0 \neq 0$. In the case of the short-range potential such a situation is possible only for the s states, whereas for $l \neq 0$ the poles always merge at the point k = 0 (Ref. 30). Such a deviation from the known behavior is due to the fact that the S matrix has a strongly singular point at k = 0 (associated with the Rydberg increase in the density of states) from which an isolated pole may split off as the parameters of the Hamiltonian are varied. In the limit $R \rightarrow 0$ the poles are displaced to infinity and eventually all the poles disappear from the lower half-plane of k, as expected for the one-center Coulomb potential.³⁵

As pointed out already in Sec. 4, in calculations of the energy spectrum of electrons we need not the antibonding terms $E_{nlm}(R)$ themselves, but the functions $R_{nlm}(E)$ which are inverse to them in the range E > 0. Figure 10 shows, by way of example, the results of rigorous calculation of the real and imaginary parts of R(E) and also the densities of states $C^2(E)$ for several ionization channels W_{lm} of the molecular ion H⁺. In the semiclassical approximation the following explicit analytic expressions⁵⁸ are obtained for these quantities.¹²

$$E_{n_0 lm}(R) = \frac{4}{R^2} \left\{ \left(l + \frac{1}{2} \right)^2 - ZR - \frac{7}{2} (m+1)^2 \right. \\ \left. \pm i (m+1) \left[8 \left(l + \frac{1}{2} \right)^2 - 6ZR - \frac{49}{4} (m+1)^2 \right]^{1/2} \right\},$$

$$(5.7)$$

$$C_{n_0 lm}^2(E) = 2\pi \left(\frac{dv}{dE} \right)^{-1} \exp \left\{ 2i \left[\delta + v \left(1 - \ln v \right) \right] \right\},$$

$$(5.8)$$

where

$$\delta = \lim_{\xi \to \infty} \left[\int_{\xi_1}^{\xi} \left(c^2 + \frac{a\xi - \lambda}{\xi^2 - 1} \right)^{1/2} d\xi - c \left(\xi - 1\right) - \frac{a}{2c} \ln 2c\xi \right]$$
$$v = \frac{1}{\pi} \int_{1}^{\xi_1} \left(\frac{\lambda - a\xi}{\xi^2 - 1} - c^2 \right)^{1/2} d\xi,$$
$$\xi_1 = -\frac{a}{2c^2} + \left(\frac{a^2}{4c^4} + 1 + \frac{\lambda}{c^2} \right)^{1/2}, \quad c = (2E)^{1/2} \frac{R}{2}.$$

Although these expressions are obtained in the approximation of large values of l, we can see from Fig. 10 that they agree satisfactorily with the results of a rigorous calculation even for l = 1 in the most important range of low values of E.

At high values of l the poles of the S matrix are located near the real axis of k (see Fig. 9) and, consequently, they correspond to quasistationary states. In this problem the quasistationary states are not subbarrier resonances, but are associated with the capture of a classical particle by an unstable equilibrium state on the internuclear axis, which occurs for m = 0 when the separation constant $\lambda(R)$ passes through the value $a \equiv ZR$ (Ref. 58). In this case the scattering occurs so that the path of a particle approaches asymptotically the internuclear axis and reaches this axis in the limit $t \to \infty$ after an infinite number of oscillations of the quasiangular variable η . Such paths, resulting in the capture of a particle, have been discussed for the problem of two centers in celestial mechanics back in the last century.

An example of a practical application of the results obtained in the present section is a calculation of the energy spectrum of electrons formed as a result of ionization of helium by protons, demonstrated in Fig. 11b. This figure had already been discussed at the end of the preceding section as an illustration of an asymptotic theory of transitions to a continuous spectrum. Here, we shall consider the mechanics of this process. In the approximation of one-electron orbitals the energy of the ground state of helium represents the limit of the $1s\sigma$ term of the (HeH) ⁺ quasimolecule in the limit $R \rightarrow \infty$. Nonadiabatic transitions from this term are possible only as a result of latent quasicrossings and, in particular, the ionization process proceeds as follows⁴⁷: as the nuclei approach, the terms $2p\sigma$ and $3d\sigma$ are populated first via the T series, which is located at $R \approx 2$ a.u., and then ionization of the quasimolecule occurs from the initial $1s\sigma$ term and it involves three diabatic terms $W_{s\sigma}$, $W_{p\sigma}$, and $W_{d\sigma}$, which



FIG. 10. Real (a) and imaginary (b) parts of R(E), and the density of states (c) for several antibonding states of the H_2^+ molecular ion. The dashed curves give approximate values of R(E) calculated using the inverted expression (5.7) and C(E) calculated from Eq. (5.8). In the case of Re R(E) the approximate and exact values merge on the scale of the figure for all values of l.

merge with the continuous spectrum. We can see from Fig. 11b that all three ionization channels have to be allowed for in explaining the experimental results. Figure 11a shows the total ionization cross section of hydrogen by protons. In this case the adiabatic basis of the problem Z_1eZ_2 discussed above is exact and the ionization process occurs from equally populated, in the initial state, terms $1s\sigma$ and $2p\sigma$ via the same latent quasicrossings as in the ionization of helium by protons. The cross section is calculated from Eqs. (1.4) and (4.1) using the exact numerical values of the Massey parameters.

An analysis of the problem of two centers not only makes it possible to reveal and understand different types of latent quasicrossings, but also to obtain approximate expressions¹³⁾ given by Eqs. (5.4) and (5.5) and relating the parameters of such quasicrossings to the characteristics of the quasimolecule and to the quantum numbers, which can then be used to calculate latent quasicrossings for many-electron quasimolecules in the approximation of one-electron orbitals. This applies also to the approximate expressions given by Eqs. (5.7) and (5.8) and describing antibonding states.

6. MODIFIED ADIABATIC BASES

Standard adiabatic wave functions are calculated on the assumption that the nuclei are fixed, so that they are not matched to physical boundary conditions in the limit $R \to \infty$. This lack of matching is manifested in different ways depending on whether the motion of nuclei in the full problem is tackled classically or quantum-mechanically. In the quantum approach these standard adiabatic functions suffer from the fact that, instead of the reduced mass, they contain simply the electron mass,¹⁴ whereas the defect of the classical approach is that the wave functions then do not contain the Galilean translation factor associated with the motion of nuclei. Consequently, the matrix element of the nonadiabatic coupling retains a constant component in the limit $R \to \infty$ (Fig. 6c), giving rise to undamped transitions between adia-



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FIG. 11. a) Dependence of the total ionization cross section on the collision energy in the $H + H^{+} \rightarrow H^{+} + H^{+}$ + e reaction; the continuous curve is the adiabatic approximation while the dashed curve is the contribution of the ionization channel $W_{p\sigma}$, and the points are the experimental values.⁵⁹ b) Differential (with respect to the energy) ionization cross section reduced to a unit solid angle for the He + H⁺ \rightarrow He⁺ + H⁺ + e reaction: 1) contribution of the $W_{\alpha\sigma}$ channel; 2) contribution of the $W_{p\sigma}$ channel; 3) contribution of the $W_{d\sigma}$ channel; the continuous curve is the total cross section in the adiabatic approximation⁴⁷; the dotted curve represents the experimental results.⁴⁸ batic states. The problem of removal of these physically meaningless transitions is most acute in numerical integration of the tight-binding equations in the adiabatic representation. When the asymptotic approach described above is employed, it is assumed implicitly that the problem in question has been solved and that there is no need to present the specific procedure as to how this had been accomplished.

Several methods are now available for constructing modified adiabatic bases, which are to a greater or lesser extent matched to the physical boundary conditions for nuclei separated by an infinite distance.⁶⁰⁻⁶⁷

6.1. Adiabatic basis matched to the boundary conditions in quantum motion of nuclei

Following Ref. 65, we shall consider the solution of the problem of the boundary conditions in the adiabatic representation taking as an example the quantum three-body problem (two nuclei A and B and an electron C). For simplicity, we shall consider only the case of zero total angular momentum (J = 0).

The boundary conditions in the three-body problem can be formulated naturally in terms of the Jacobi functions which are selected depending on which pair of particles remains in a bound state after removal of the third particle. Then, in the case of reactions with a redistribution of particles we have to construct such variables which in asymptotic regions of the configurational space corresponding to the reaction channels A + (BC), B + (AC), and C + (AB) reduce to the Jacobi coordinates of their own channel (Fig. 12). In the three-body problem considered in the adiabatic approximation it is usual to assume that the independent variables are the radius vector **R**, connecting the nuclei A and B, and the radius vector

$$\mathbf{r}' = \frac{1}{R} \quad , \tag{6.1}$$

where \mathbf{r} is the radius vector of an electron calculated from the center of mass of the nuclei.⁶⁸ These variables having the required property are obtained if in the coordinates \mathbf{R} and \mathbf{r}' we replace R with a new variable

$$\mathscr{R} = \varkappa^{1/2} R, \tag{6.2}$$

where

$$\kappa = 1 + \frac{mr'^2}{M}$$
, $M^{-1} = M_{\rm A}^{-1} + M_{\rm B}^{-1}$,
 $m^{-1} = M_{\rm C}^{-1} + (M_{\rm A} + M_{\rm B})^{-1}$;

 M_i is the mass of the *i*th particle. We can easily show⁶⁵ that in asymptotic regions of the configurational space the variables introduced in this way transform to the correct Jacobi coordinates in each channel. When these variables are used,

the Schrödinger equation obtained after separation of the motion of the center of mass and replacement of the threeparticle wave function F with a function

$$\mathcal{F} = \mathcal{R}^{3/2} \varkappa^{-1/2} F$$

reduces to the form (Ref. 65)¹⁵⁾

$$\left(-\frac{1}{2M}\frac{1}{\mathcal{R}^{2}}\frac{\partial}{\partial\mathcal{R}}\mathcal{R}^{2}\frac{\partial}{\partial\mathcal{R}}-\frac{1}{2m}\frac{x^{2}}{\mathcal{R}^{2}}\Delta_{r}\right)$$
$$+\frac{3}{8M\mathcal{R}^{2}}+V\left(\mathcal{F}=\mathcal{E}\mathcal{F}\right),$$
(6.3)

where $V = V_{AB} + V_{AC} + V_{BC}$; V_{ij} is the potential energy of the interaction of the *i*- and *j*th particles; \mathscr{C} is the total energy of the system of three particles after subtraction of the translational energy. Equation (6.3) retains all the specific features of the initial problem, justifying the adiabatic separation of variables. In contrast to the standard approach, the motion of the slow subsystem is described here by a variable \mathscr{R} and a modified Hamiltonian of the fast subsystem is

$$H_{\text{mod}}(\mathscr{R}) = -\frac{1}{2m} \frac{\varkappa^2}{\mathscr{R}^2} \Delta_{\mathbf{r}'} + V.$$
 (6.4)

In accordance with the above properties of the new variables \mathscr{R} and \mathbf{r}' the Hamiltonian of Eq. (6.4) reduces in the limit $R \to \infty$ to the exact Hamiltonian of an atomic complex in each reaction channel. We shall demonstrate it by considering the example of the $\mathbf{B} + (\mathbf{AC})$ channel, when the B nucleus moves to infinity and the particles A and C remain in the bound state. In this limit we have to separate the coefficient $\varkappa^2/(2m\mathscr{R}^2)$ in front of the Laplace operator in Eq. (6.4) into two factors. The first factor $\varkappa \mathscr{R}^{-2} = R^{-2}$, combined with a variable \mathbf{r}' in the Laplace operator, restores the initial length scale [see Eq. (6.1)] and the remaining factor gives the correct reduced mass m_A of the particles A and C (Fig. 12):

$$m \varkappa^{-1} = m \left[1 + \frac{m}{MR^2} \left(\mathbf{r}_{\rm A} - \frac{M_{\rm B}}{M_{\rm A} + M_{\rm B}} \mathbf{R} \right)^2 \right]^{-1}$$
$$\xrightarrow[R_{\rm A}^{-1} \to \infty]{} (M_{\rm C}^{-1} + M_{\rm A}^{-1})^{-1} = m_{\rm A}.$$

We then have $V \rightarrow V_{AC}$. Consequently, the Hamiltonian of Eq. (6.4) reduces to the exact Hamiltonian of the atomic complex (AC) so that the modified adiabatic functions $\tilde{\varphi}_{\rho}$ ($H_{mod}\tilde{\varphi}_{\rho} = \tilde{E}_{\rho}\tilde{\varphi}_{\rho}$) are matched to the physical boundary conditions, the matrix elements of the nonadiabatic interactions tend to zero in the limit $R \rightarrow \infty$, and the system of the tight-binding equations decouples in this limit.

The modified basis $\{\tilde{\varphi}_{\rho}\}$ is characterized, apart from the correct boundary behavior, by a number of additional useful properties. The variables \mathcal{R} and r' are closely related to hyperspherical coordinates.⁶⁹ In these coordinates the



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FIG. 12. Jacobi coordinates in the three-body problem. The radius vectors \mathbf{R}_A , \mathbf{r} , and \mathbf{R}_B are measured from the center of mass of a pair of particles (AC), (AB), and (BC), respectively. variable \mathscr{R} acts as a hyperradius and the Hamiltonian of the fast subsystem (6.4) corresponds to the angular part of the problem so that its spectrum is purely discrete. The advantages of a purely discrete basis, compared with a mixed one, are obvious in numerical calculations and this is exactly why the Sturm expansions are used extensively in atomic physics. Moreover, the modified basis makes it possible to allow simply for a logarithmic singularity at the triple collision point $(\mathscr{R} = 0)$.⁷⁰ This singularity is entirely due to the motion along the hyperradius, so that in the adiabatic separation of the variables in the coordinates \mathscr{R} and **r'** it does not affect the adiabatic basis itself, but is reproduced by the wave function of the slow subsystem already in the one-level approximation.

Some improvements in the approach described here, which are important in the case when $J \neq 0$ and there is degeneracy in the initial and final states, are discussed in Refs. 66 and 67.

6.2. Adiabatic basis matched to the boundary conditions in classical motion of nuclei

In the classical approach the path $\mathbf{R}(t)$ of the nuclei is assumed to be known *a priori* and the behavior of an electron is described by the secular Schrödinger equation in the center-of-mass system of two nuclei A and B:

$$\left(-\frac{1}{2}\Delta_{\mathbf{r}}+V_{\mathrm{AC}}\left(|\mathbf{r}+\boldsymbol{\gamma}_{\mathrm{A}}R|\right)+V_{\mathrm{BC}}\left(|\mathbf{r}+\boldsymbol{\gamma}_{\mathrm{B}}R|\right)\right)\psi=i\frac{\partial\psi}{\partial t},$$
(6.5)

where $\gamma_A = \hat{R}M_B/(M_A + M_B)$, $\gamma_B = -\hat{R}M_A/(M_A + M_B)$, $\hat{R} = \mathbf{R}/R$. The correct limiting states of the problem described by Eq. (6.5) represent the product of the wave function of a bound state $\varphi_q^{(a)}(r_j)$ at the *j*th isolated nucleus (j = A or B) and the Galilean translation factor, which allows for the motion of the nuclei⁶⁰:

$$\psi(\mathbf{r}, t) \xrightarrow[t \to -\infty]{} \phi_q^{(a)}(r_j) \exp\left[i\left(\mathbf{v}_j\mathbf{r}_j - \frac{1}{2}v_j^2t - E_q^\infty t\right)\right],$$
(6.6)

where $\mathbf{r}_j = \mathbf{r} + \gamma_j R$ and v_j is the velocity of the *j*th nucleus. In the usual adiabatic basis its translation factor is missing and this gives rise to serious computational difficulties in integration of the tight-binding equations, which is known as the momentum transfer problem. Several procedures have been suggested for the solution of this problem (see, for example, Refs. 60, 61, and 63). One of them, which we shall consider here in the approximation of rectilinear paths of the nuclei, is as follows.⁶¹ Instead of **r** we select a new variable

$$\mathbf{r}' = \frac{\mathbf{r}}{R(t)} \tag{6.7}$$

and represent the wave function in the form

$$\psi = R^{-3/2} \exp\left(i \frac{r^2 \dot{R}}{2R}\right) f(\mathbf{r}', t), \qquad (6.8)$$

where the dot represents the derivative with respect to time. The factor $R^{-3/2}$ in Eq. (6.8) ensures that the normalization is retained and the exponential function acts as a generalized translation factor that allows for the change in the kinematics on adoption of new coordinates in accordance with Eq. (6.7). Substitution of Eqs. (6.7) and (6.8) into Eq. (6.5) and the transition to a rotating reference system with the x' axis directed along the internuclear axis yields the modified Schrödinger equation for $f(\mathbf{r}',t)$:

$$\widetilde{H}f(\mathbf{r}', \tau) = i \frac{\partial f(\mathbf{r}', \tau)}{\partial \tau};$$

$$\widetilde{H} = -\frac{1}{2} \Delta_{\mathbf{r}'} + R^2 V_{\mathrm{AC}} \left(R |\mathbf{r}' + \boldsymbol{\gamma}_{\mathrm{A}} | \right)$$

$$+ R^2 V_{\mathrm{BC}} \left(R |\mathbf{r}' + \boldsymbol{\gamma}_{\mathrm{B}} | \right) + \omega l_z + \frac{\omega^2}{2} r'^2, \quad (6.9)$$

where $\omega = \rho v$ (ρ is the impact parameter and $\mathbf{v} = \text{const}$ is the relative velocity of the nuclei), whereas the variable

$$\tau = \int_{0}^{\tau} \frac{\mathrm{d}t'}{R^{2}(t')} = \frac{1}{\omega} \operatorname{arctg} \frac{vt}{\rho}$$

plays the role of time. In terms of the new coordinates the two potential centers are at rest and there is no momentum transfer effect. When we go back to the original wave function, the correct translation factor is obtained automatically from the exponential factor in Eq. (6.8). In fact, near a *j*th center when $R \to \infty$ we obtain the limiting expression

$$\exp \frac{ir^{2}\dot{R}}{2R}$$

$$= \exp \frac{i|\mathbf{r}_{j} - \mathbf{\gamma}_{j}R|^{2}\dot{R}}{2R} \xrightarrow{Rr_{j}^{-1} + \infty} \exp \left[i\left(\mathbf{v}_{j}\mathbf{r}_{j} - \frac{1}{2}v_{j}^{2}t\right)\right],$$
(6.10)

which is identical with the translation factor in Eq. (6.6).

The use of Eq. (6.9) solves another problem in the tight-binding method, namely the dependence of the transition probability on the selected coordinate system when a finite adiabatic basis is used (see, for example, Ref. 63). We can readily show that in a modified adiabatic basis $\tilde{\varphi}_p$ $(H\widetilde{\varphi}_p = \widetilde{E}_p \varphi_p)$ the transition probability is the same irrespective of whether it is calculated in the center-of-mass system, in the laboratory reference system, or in the reference system with a center at one of the nuclei, and this is true even in the two-level approximation. All these reference systems are distinguished, in terms of the new variables, by a shift amounting to a constant vector along the x' axis. Such a shift transforms \widetilde{H} and $\widetilde{\varphi}_{p}$ in a manner similar to the gauge transformation in the magnetic field (see § 111 in Ref. 35), which leaves unaltered the Born-Fock system of equations in the basis $\tilde{\varphi}_{p}$.

The transformations described by Eqs. (6.7) and (6.8) are a direct analog of the transformations (6.1) and (6.2). Representation of the wave function in the form of Eq. (6.8) has the same meaning as introduction of a variable \mathscr{R} instead of R in a quantum-mechanical analysis of the behavior of the nuclei. In both cases the electron part of the problem is corrected by explicit and exact allowance for the motion of the nuclei in the asymptotic range $R \to \infty$.

6.3. Isotope effects in the adiabatic approximation

One more case requiring modification of the adiabatic basis appears when we discuss isotope effects. In the case of diatomic quasimolecules, consisting of different isotopes of the same chemical element, the exact symmetry breaks down in the mutual transposition of the nuclei because their masses are different $(M_A \neq M_B)$. This gives rise to several new effects not encountered in the case of symmetric quasimolecules. They are associated entirely with the quantum nature of the motion of the nuclei so that at first sight they cannot be calculated quite simply in the adiabatic approximation. A direct numerical calculation of the isotope effects is far too time-consuming⁷¹ because of their smallness which in turn is due to the smallness of the parameter $\delta = M_{\rm A}^{-1} - M_{\rm B}^{-1}$, characterized by degree of departure from symmetry (for example, in the case of the HD molecule we have $\delta = 1.4 \times 10^{-4}$). On the other hand, this smallness shows that it is natural and necessary to develop approximate methods for the calculation of the isotope effects. Such a problem was first discussed in the theory of molecules in connection with calculations of the dipole moment induced by the isotopic asymmetry of the nuclei. 72-74 The asymmetry of the mass of the nuclei then reduces to the symmetry of the potentials by introduction of special coordinates. In the theory of collisions this approach has been used to calculate quasiresonant charge transfer between mesic atoms with an isotopic resonance defect.75

We shall consider introduction of the isotope effects in the adiabatic approximation by discussing the case of three charged particles with charges $Z_A = Z_B = Z_C = -1$ and the masses $M_{A,B} \gg M_C = 1$. We shall assume that \mathbf{R}_A , \mathbf{R}_B , and \mathbf{R}_C are the radius vectors of the particles in the laboratory reference system. We shall introduce coordinates of a special kind (Ref. 75)¹⁶)

$$\begin{aligned} \mathbf{R}_{cm} &= (\mathbf{R}_{C} + M_{A}\mathbf{R}_{A}^{*} + M_{B}\mathbf{R}_{B}) (\mathbf{1} + M_{A} + M_{B})^{-1}, \\ \mathbf{q} &= \frac{1}{2} (\mu_{A}^{1/2} + \mu_{B}^{1/2}) \mathbf{R}_{C} - \frac{1}{2} (\mu_{A}^{1/2}\mathbf{R}_{A} + \mu_{B}^{1/2}\mathbf{R}_{B}), \quad (6.11) \\ \mathbf{Q} &= (\mu_{A}^{1/2} - \mu_{B}^{1/2}) \mathbf{R}_{C} - (\mu_{A}^{1/2}\mathbf{R}_{A} - \mu_{B}^{1/2}\mathbf{R}_{B}), \end{aligned}$$

where $\mu_A^{-1} = 1 + M_A^{-1}$, $\mu_B^{-1} = 1 + M_B^{-1}$. After separation of the motion of the center of mass using the variable $\mathbf{R}_{c.m.}$, we find that the exact three-particle Hamiltonian has the following form in terms of these coordinates:

$$\mathcal{H} = -\frac{1}{4} \left[1 + (\mu_{A}\mu_{B})^{1/2} \right] \Delta_{\mathbf{q}} - \left[1 - (\mu_{A}\mu_{B})^{1/2} \right] \Delta_{\mathbf{Q}} - \frac{\mu_{A}^{1/2} Z_{A}}{|\mathbf{q} + (\mathbf{Q}/2)|} - \frac{\mu_{B}^{1/2} Z_{B}}{|\mathbf{q} - (\mathbf{Q}/2)|} + \frac{(\mu_{A}\mu_{B})^{1/2} Z_{A} Z_{B}}{|(\mu_{A}^{1/2} + \mu_{B}^{1/2})(\mathbf{Q}/2) + (\mu_{A}^{1/2} - \mu_{B}^{1/2})\mathbf{q} |}.$$
(6.12)

If we ignore temporarily the dependence of the internuclear interaction on q [represented by the last term in Eq. (6.12)], we can easily see that the Hamiltonian (6.12) is exactly the same as the Hamiltonian of an effective three-particle system composed of a "light particle" with a mass $m^* = (\mu_A \mu_B)^{-1} \approx 1$ and two "heavy particles" with identical masses $M^* = [1 - (\mu_A \mu_B)^{1/2}]^{-1} \ge 1$; then, **q** and **Q** are the Jacobean coordinates of such an effective system. Therefore, if $M_A \neq M_B$ and $Z_A = Z_B = Z$, the transformation of Eq. (6.11) converts the asymmetry of the masses of heavy particles into the asymmetry of charges: $Z_A^{\text{eff}} = \mu_A^{1/2} Z$ and $Z_{B}^{eff} = \mu_{B}^{1/2} Z$, so that after adiabatic separation of the motion of the "heavy particles" using the variable Q, we have the problem of two Coulomb centers with isotopically different charges. An allowance for the dependence of the internuclear interaction on **q** gives rise to an additional asymmetry in the effective "light particle" potential.

The transformation described by Eq. (6.11) greatly simplifies calculations of the isotope effects because it makes it possible to reduce the asymmetry of a quasimolecule to the asymmetry of modified adiabatic states which can then be allowed for within the framework of perturbation theory using a small parameter δ . The role of the isotope effects is particularly large in mesoatomic physics, because the parameter δ is in this case two orders of magnitude greater than for ordinary quasimolecules since the muon mass is large $(m_{\mu} = 206m_{\rm e})$. The transformation of Eq. (6.11) has been used⁷⁵ to calculate the cross section for the charge transfer process

 $d\mu (n) + t \rightarrow d + t\mu (n) \tag{6.13}$

from a state with the principal quantum number n = 2. This transfer reaction plays an important role in the problem of muon catalysis of nuclear fusion reactions and has been calculated earlier in the two-level quantum approximation for the motion of the nuclei⁷⁶ and also employing a semipheno-menological approach.⁷⁷ The difference between the masses of deuterium and tritium gives rise to an isotopic resonance defect between the initial and final states in Eq. (6.13). The transformation of Eq. (6.11) converts this defect into a resonance defect of adiabatic terms of the problem of two Coulomb centers with isotopically renormalized charges (in this case the dependence of the internuclear interaction on **q** is ignored, because charge transfer occurs at a large distance of the order of 30 mesoatomic units and the asymmetry of the internuclear interaction amounts to 10^{-3} of the asymmetry associated with renormalization of the charges). Consequently, calculation of the cross section of the reaction (6.13) reduces to calculation of the cross section of an ordinary quasiresonant charge transfer carried out using expressions given in subsections 3 in Secs. 3 and 5. The charge transfer cross section obtained in this way⁷⁵

$$\sigma = \frac{0.85}{E_{\star} (\text{eV})} \cdot 10^{-17} \text{ cm}^2$$

agrees for the energy of the incident tritium $E_1 > 1$ eV within 5% with the results of Refs. 76 and 77.

7. CONCLUSIONS

The progress in computer techniques has ensured that theoretical investigations of electron transitions due to collisions between atoms are carried out more and more frequently by numerical integration of the tight-binding equations tackled by development of files of special programs designed to automate the calculation of the relevant cross sections (see, for example, Ref. 78). However, in the slow collision range, where the transition probabilities are low, this approach becomes much more difficult to apply because of the occurrence of physically meaningless transitions associated with the incompleteness of the final state of the basis states. These transitions accumulate in the course of integration of the tight-binding equations along the internuclear distance and may distort greatly the true transition probability (as discussed at the beginning of the preceding section). On the other hand, in the asymptotic theory considered here there are no such problems and this theory can compete readily with direct numerical calculations in respect of its precision and particularly in respect of the time required for such calculations. Moreover, in problems of the kind encountered in calculation of the energy spectrum of electrons only the adiabatic approximation is at present capable of ensuring quantitative agreement with the experimental results (Fig. 11b). It also provides important information on the reasons for the process in question and on the internuclear distances at which it occurs. Extensive use of the adiabatic approximation has been greatly hindered by the absence of a general method for finding quasicrossings relating given initial and final states. In practice only the Landau-Zener and Rosen-Zener-Demkov transitions have been taken into account and these are due to a subbarrier resonant interaction of the states localized at different nuclei. This has given rise to a situation, mentioned already at the beginning of Sec. 5, when for example in the case of the H_2^+ molecule it has been found that there are no quasicrossings. However, the recent discovery of the S and T series of latent quasicrossings has made it possible to obtain a complete set of inelastic transitions in the adiabatic approximation framework applied to the simplest quasimolecule of the Z_1eZ_2 system. Our analysis of the system shows that a universal method may be possible to calculate latent quasicrossings. As shown in Ref. 58, in the $Z_1 e Z_2$ problem they appear every time when an adiabatic state corresponds to an unstable periodic path in the classical limit. An approach based on an investigation of unstable periodic paths and their monodromic matrices does not require separation of variables and is generally valid.

We can therefore, distinguish three types of one-electron transitions considered in the adiabatic approximation: the first are the transitions corresponding to large internuclear distances, which are due to a subbarrier resonant interaction of states and are characterized by small Massey parameters (Secs. 5.3 and 5.4); the second represents transitions in the range of intermediate values of the internuclear distance and a large Massey parameter, associated with the passage of the system through a state corresponding to an unstable periodic path (Secs. 5.1 and 5.2); the third is in the form of rotational transitions at short internuclear distances when the Massey parameter vanishes for head-on collisions and rises rapidly on increase in the impact parameter (Sec. 3.2). Only the transitions of the second type have not yet been investigated sufficiently thoroughly. However, at least for the $Z_1 e Z_2$ system, it is now possible to develop a file of programs for automated calculation of all the electron transitions in the adiabatic approximation, including those involved in ionization.

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⁴)We can draw here the formal analogy with an approximate calculation

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of the integral by the saddle-point method when deformation of the integration contour from the real axis to a complex plane yields an explicit expression for the integral in terms of the values of the integrand at complex saddle points.

- ⁵⁾The terms or energy levels have the obvious property $E_p^*(R^*) = E_p$ (R), so that all their singularities are distributed in pairs which are symmetric relative to the real axis in the R plane.
- ^(b) The functions $\varphi_{\rho}^{*}(\mathbf{r}, R)$ are modified by formal replacement of R with R * for real values of R so as to retain the analyticity in respect of R in the matrix elements.
- ⁷⁾We shall use the following terminology. All the states which correspond to poles of the S matrix in the lower half-plane of the complex wave number $k = (2E)^{1/2}$ will be called antibonding (since their wave functions rise exponentially in the limit $r \rightarrow \infty$) and, depending on whether a given level is "above" or "below" the boundary of a continuous spectrum, they can be divided into quasistationary [Re $E_{\rho}(R) > 0$] and virtual [Re $E_n(R) < 0$].
- ⁸⁾The general case in mathematics is a situation which occurs always with the exception of a set of measure zero in the space of the parameters of the problem. An example of a statement which is only generally true is the Neumann-Wigner theorem.
- ⁹⁾The exponential function is omitted, because its modulus is equal to unity.
- ¹⁰⁾The initial condition is associated also with the selection of the integration contour L and the final form of the solution will be given later
- ⁽¹⁾This circumstance has been noted some time ago in an analysis of the exactly soluble models.44
- ¹²⁾Since it is simpler, we quote here the expression for E(R) and not R(E)
- $^{(3)}$ A fuller account of the approximate expressions can be found in Ref. 58.
- ⁽⁴⁾Although the difference between the reduced mass and the electron mass is small, it nevertheless can result in such serious difficulties as the absence of a discrete level in the adiabatic basis in the limit $R \rightarrow \infty$, whereas the real atomic system in this limit in fact has a weakly bound state.
- ¹⁵⁾A similar equation was used in Ref. 64. However, the variable *R* was identified there erroneously with the distance internuclear R, and this prevented a correct discussion of the problem of the boundary conditions.
- ¹⁶) We can show that these coordinates are equivalent to those used in Ref. 72, but are more compact.
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¹⁾Originating from the Greek adiabatos, meaning impassable.

²⁾In this review we shall use the atomic system of units $e = m_e = \hbar = 1$. ³⁾The momentum transfer effect is associated with the existence of an additional translational momentum of electrons during the motion of atoms; in the case of slow collisions this effect is small and its role will be discussed in Sec. 6.2

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